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(54) Title: IMPROVEMENT IN METAL-LIGAND CATALYST FORMATION

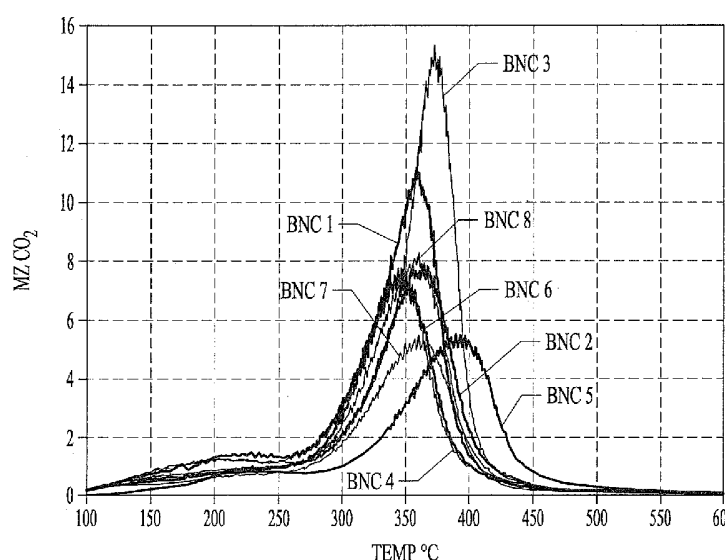


FIG. 1

(57) Abstract: As described herein, nickel treated with sulfur provides a surprisingly effective source of nickel atoms for generating nickel-phosphorus-containing ligand complexes useful as hydrocyanation catalysts.



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## IMPROVEMENT IN METAL-LIGAND CATALYST FORMATION

This application claims benefit of the filing date of U.S. Provisional Patent Application No. 61/495,784, filed June 10, 2011; U.S. Provisional Patent Application No. 61/496,142, filed June 13, 2011; U.S. Provisional Patent Application No. 61/503,917, filed July 1, 2011; U.S. Provisional Patent Application No. 61/507,159, filed July 13, 2011; and U.S. Provisional Patent Application No. 61/552,473, filed October 28, 2011, the contents of which applications are all specifically incorporated herein by reference in their entireties.

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### Background of the Invention

Some types of nickel metal catalyst systems are available in the art. For example, nickel-phosphorus ligand catalyst systems have been used for hydrocyanation of butadiene to form pentenenitrile (PN) and for hydrocyanation of pentenenitrile to form adiponitrile (ADN). Examples of catalyst compositions and processes for the hydrocyanation of monoethylenically unsaturated compounds using zero-valent nickel and bidentate phosphite ligands in the presence of Lewis acid promoters include those described, for example in U.S. patent numbers 5,512,696; 5,723,641; and 6,171,996.

Some nickel preparations and/or nickel complexes are also described, for example, in GB14607A, GB255884A, GB703826A, EP101733106A, EP0114704, EP0985448A1 and in U.S. Patent Nos. 4,416,825 3,903,1203; 496,217; 3,631,191; 3,816,098; 3,846,461; 3,847,959; 3,903,120; 4,118,342; 6,171,996; and 6,494,931.

Formation of hydrocyanation catalysts can involve formation of complexes between nickel atoms and phosphorus-containing ligands. However, commercially available sources of nickel often do not efficiently form these complexes. Moreover, different batches and lots of nickel from the same supplier often have different compositions and exhibit unpredictable activity for forming nickel-ligand complexes. For example, as illustrated herein, nickel starting materials from different batches and diverse commercial sources can exhibit up to 200% variability in their ability to form complexes with phosphorus-containing ligands. Different types of phosphorus-containing ligands also vary in their ability to form catalytic complexes with nickel. Such variability in

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complex formation by currently available nickel sources and ligands leads to low efficiency catalysts and manufacturing processes, as well as significant waste.

To solve the problems of inefficient nickel-ligand complex formation, manufacturers have previously employed activators such as phosphorus trichloride ( $\text{PCl}_3$ ) to promote the formation of catalytically active nickel complexes with monodentate phosphorus-containing ligands. *See, e.g.*, U.S. Patent No. 5,688,986 to Tam, Kreutzer & McKinney. However, such activators can react with some phosphorus-containing ligands and inactivate the ligands. Thus, the useful lifetime of catalysts can be shortened by use of activators. Therefore, improved nickel metal preparations and methods of making catalytically active nickel-ligand complexes are needed.

### Summary of the Invention

The invention solves the problem of short-lived, poorly forming nickel-ligand catalyst complexes by providing methods of making the complex without an activator that could destroy the ligand and by providing forms of nickel that readily complex with phosphorus-containing ligands. For example, particulate nickel forms with the physical properties described herein can readily form complexes with phosphorus-containing ligands without addition of activators that destroy the ligands. The invention also solves the problems of nickel metal particles with variable activity for forming nickel-ligand catalyst complexes by providing methods for making particulate nickel forms that are highly active for complex formation. For example, as illustrated herein, addition of a variety of sulfur sources surprisingly converts particulate nickel metal that inefficiently forms complexes with phosphorus-containing ligands into a nickel particulate form that exhibits excellent complex formation properties.

The inventive particulate nickel forms exhibit desirable physical properties such as a BET Specific Surface Area of at least about  $1 \text{ m}^2/\text{gm}$ , preferably at least about  $2 \text{ m}^2/\text{g}$ ; more preferably at least about  $4 \text{ m}^2/\text{g}$  and more preferably at least about  $10 \text{ m}^2/\text{g}$ . In addition, desirable nickel particulate forms can also include an average crystallite size of no greater than about 100 nm; preferably no greater than 70 nm, and more preferably no greater than 50 nm. In desirable nickel particulate forms at least 10% of the crystallites have a size ( $\text{C}_{10}$ ) that is less than about 20 nm. Desirable nickel particulate forms also

have on average have at least about  $10^{16}$  surface crystallites of size C10 or less per gram nickel. However, addition of a sulfur source can cure or offset the poor ligand complexation activity of nickel particles with inadequate physical properties. For example, compositions of particulate nickel metal with about 0.1 wt% to about 15 wt% sulfur efficiently complex with phosphorus-containing ligands. Thus, nickel particles with inadequate physical properties can be used as a source of particulate nickel for making nickel-ligand catalysts with excellent catalytic activity when a sulfur source is added either during manufacture of the particulate nickel or during formation of the nickel-ligand complex. A nickel particulate form with a high BET Specific Surface Area, low average crystallite size, low C10 value, 0.1-15 wt% sulfur content, or a combination thereof, optimally form complexes with phosphorus-containing ligands.

One aspect of the invention is a method of generating a complex between nickel atoms and one or more phosphorus-containing ligands comprising:

- (a) contacting:
  - (i) a nickel starting material with a sulfur source, and generating nickel metal from a mixture of the nickel starting material and the sulfur source to form a particulate sulfur-containing nickel metal; or
  - (ii) a nickel metal with a sulfur source to form a particulate sulfur-containing nickel metal; and
- (b) contacting the particulate sulfur-containing nickel metal with one or more phosphorus-containing ligand(s) to thereby form a complex between nickel atoms from the nickel metal and one or more phosphorus-containing ligands.

Such a method can further include determining a sulfur content of the nickel starting material or the nickel metal before contacting the nickel metal or the nickel starting material with the sulfur source. For example, the nickel metal or the nickel starting material can be contacted with the sulfur source if the sulfur content of the nickel metal or the nickel starting material is less than 0.4 wt% to 0.8 wt% relative to the weight of the nickel metal or the nickel starting material.

The method can involve contacting a weight percentage of about 0.1 wt% to about 50 wt% sulfur with the nickel metal or the nickel starting material, wherein the sulfur weight percentage is relative to the total weight of nickel in the nickel metal or the nickel

starting material. For example, the contacting step can generate a sulfur to nickel atomic ratio of about 0.003 to about 1.8.

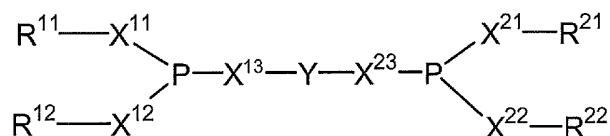
Examples of suitable sulfur sources are those selected from the group consisting of elemental sulfur, sulfur-containing gases, sulfur-containing salts, sulfur-containing ions and combinations thereof. Additional examples of sulfur sources include those selected from the group consisting of hydrogen sulfide, nickel sulfate, nickel sulfite, nickel sulfide, nickel hyposulfite, nickel thiosulfate, sulfur trioxide, sulfur dioxide, sulfur monoxide, disulfur dichloride, sulfur dichloride, sulfur tetrachloride, sulfur chloride pentafluoride, disulfur decafluoride, sulfur hexafluoride, sulfur tetrafluoride, sulfur trifluoride and combinations thereof. The sulfur source can be 95% to 99.9% free of silicon, sodium, potassium, calcium, magnesium, phosphorus, aluminium, copper, tungsten, mercury, iron, and combinations thereof.

The nickel starting material or nickel metal can also be 95% to 99.9% free of silicon, sodium, potassium, calcium, magnesium, phosphorus, aluminium, copper, tungsten, mercury, iron and combinations thereof. Examples of suitable nickel starting materials include basic nickel carbonate, nickel carbonate, nickel bicarbonate, nickel oxalate, nickel formate, nickel squarate, nickel hydroxide, nickel oxide, nickel salts or a combination thereof.

During such methods the nickel metal or the nickel starting material can be contacted with the sulfur source before or after reduction of the nickel starting material or the nickel metal to zero valent nickel. The nickel starting material can be reduced in hydrogen at 200 °C to 400 °C for about 3 to about 5 hours.

A complex can be formed between nickel atoms from the particulate sulfur-containing nickel metal and one or more phosphorus-containing ligands in the presence of a Lewis acid. When generating such a complex, the nickel metal in step (ii) can be simultaneously contacted with the sulfur source and one or more phosphorus-containing ligand(s). The methods generate particulate sulfur-containing nickel metal that efficiently complexes with phosphorus-containing ligands. For example, an equilibrium of complex formation between nickel atoms from the particulate sulfur-containing nickel metal and one or more phosphorus-containing ligands is reached by about 2 hours (or within about 1 hour, or even within 30 minutes) when about 4% nickel is mixed at about 60 °C to 80 °C

in an organonitrile solvent with about 0.5 to 2.5 moles Lewis acid per mole phosphorus-containing ligand. Such a complex can be at least partially dissolved in an organonitrile solvent, for example, a pentenenitrile solvent. One or more of the phosphorus ligands in such a complex can be a ligand of Formula (III):



Formula (III)

wherein:

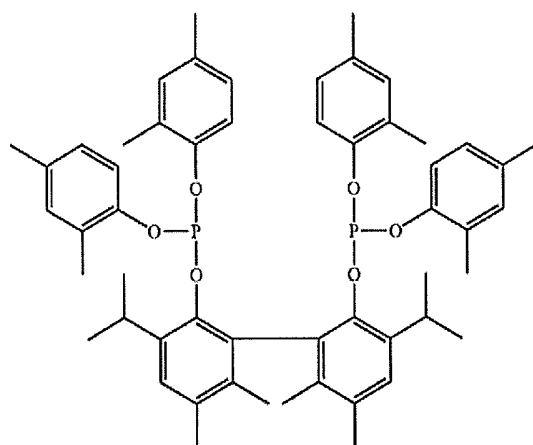
$\text{X}^{11}$ ,  $\text{X}^{12}$ ,  $\text{X}^{13}$ ,  $\text{X}^{21}$ ,  $\text{X}^{22}$  and  $\text{X}^{23}$  independently represent oxygen or a single direct bond;

$\text{R}^{11}$  and  $\text{R}^{12}$  independently represent identical or different, single or bridged organic radicals;

$\text{R}^{21}$  and  $\text{R}^{22}$  independently represent identical or different, single or bridged organic radicals; and

Y represents a bridging group.

In another example, one or more of the phosphorus ligands in the complex can be Ligand (V):



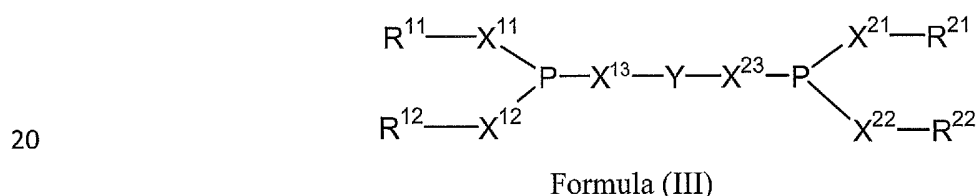
Ligand (V).

The methods described herein can form a complex between nickel atoms from the particulate sulfur-containing nickel metal and one or more phosphorus-containing ligands

where the complex can catalyze hydrocyanation of an olefin. For example, the olefin can be pentenenitrile.

The methods described herein can generate a particulate sulfur-containing nickel metal that includes nickel crystallites, wherein the sulfur-containing nickel metal has a  
 5 BET Specific Surface Area of at least about  $1 \text{ m}^2 / \text{gm}$ , and/or where on average there are at least about  $10^{15}$  surface crystallites present per gram nickel, as calculated for substantially cuboidal crystallites. The sulfur-containing nickel metal can have other properties and features, including any of those described herein.

Another aspect of the invention is a catalyst preparation mixture that includes a  
 10 particulate nickel metal, one or more phosphorus-containing ligands and about 0.001 wt% to about 15 wt% sulfur, wherein the sulfur weight percentage is relative to the total weight of nickel in the mixture. Such a catalyst preparation mixture can be in an organonitrile solvent. The catalyst preparation mixture can also include a Lewis acid, for example, a Lewis acid selected from the group consisting of zinc chloride, ferrous chloride, or a  
 15 combination thereof. For example, the catalyst preparation mixture can have a zinc to phosphorus containing ligand molar ratio of about 0.5 to about 2.5. One or more of the phosphorus ligands in the catalyst preparation mixture can be Ligand (V) or a ligand of Formula (III):



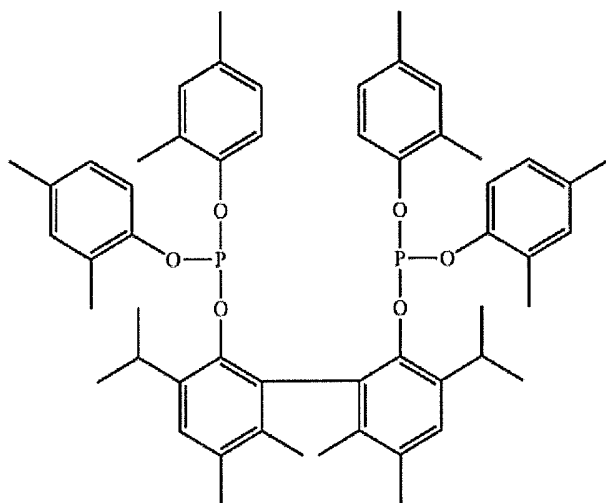
wherein,

- 25  $\text{X}^{11}$ ,  $\text{X}^{12}$ ,  $\text{X}^{13}$ ,  $\text{X}^{21}$ ,  $\text{X}^{22}$  and  $\text{X}^{23}$  independently represent oxygen or a single direct bond;  
 $\text{R}^{11}$  and  $\text{R}^{12}$  independently represent identical or different, single or bridged organic radicals;  
 $\text{R}^{21}$  and  $\text{R}^{22}$  independently represent identical or different, single or bridged organic radicals; and  
 $\text{Y}$  represents a bridging group.

The weight percent of the one or more phosphorus containing ligands within the catalyst preparation mixture can be about 2 to about 8 wt%. The nickel weight percent within the catalyst preparation mixture can be about 1 to about 7 wt%.

Another aspect of the invention is a complex formed between nickel atoms and one or more phosphorus-containing ligands that includes about 0.00001 wt% to about 15 wt% sulfur, wherein the sulfur weight percentage is relative to the total weight of nickel in the complex. For example, the complex can include about 0.0001 wt% to about 1 wt% sulfur. One or more of the phosphorus ligands can be present in the complex, for example, Ligand (V) or a ligand of Formula (III), described herein.

Another aspect of the invention is a nickel particulate form that includes nickel crystallites and about 0.2 wt% to about 12 wt% sulfur, wherein the nickel particulate form has a BET Specific Surface Area of at least about  $1 \text{ m}^2/\text{gm}$ ; at least 10% of the nickel crystallites have a size (C10) that is less than about 20 nm; and the nickel crystallite size distribution span is greater than about 1.0. For example, the nickel crystallites in the nickel particulate form can have an average crystallite size of no greater than about 100 nm. Such a nickel particulate form can have a BET Specific Surface Area / C50 ratio of not less than  $0.07 \times 10^9 \text{ m/gm}$ . Such a nickel particulate form can also have, on average, at least about  $10^{15}$  surface crystallites per gram of nickel. Such a nickel particulate form can also include particles, where at least 10% of the particles of the form have a size (D10) of no greater than about 6  $\mu\text{m}$ . The nickel particulate form can also have a large number of surface crystallites, for example, on average there can be at least about  $10^{16}$  surface crystallites per gram nickel that are smaller than or equal to size C10, where the C10 size can, for example, be less than about 20 nm. The nickel particulate form also efficiently forms a complex with one or more phosphorus-containing ligands. For example, the nickel particulate form reach an equilibrium of complex formation with Ligand (V) within about 2 hours (or about 1 hour, or even about 30 minutes) when about 4 to 5 wt% of the nickel particulate form is mixed with 3-pentenitrile containing approximately 5.25 wt% Ligand (V) and approximately 6300 ppm  $\text{ZnCl}_2$ ; wherein Ligand (V) has the following formula:



Another aspect of the invention is a mixture that includes a nickel particulate form with at least one ligand selected from monodentate phosphite ligands, bidentate phosphite ligands and mixtures thereof in the presence of pentenenitriles, wherein the nickel particulate form is characterized by:

- (a) 0.2 wt.% to 12 wt.% sulfur; and
- (b) BET Specific Surface Area of at least 1 m<sup>2</sup>/g.

The invention also relates to a product formed by mechanically agitating such a mixture. For example, the product can be a homogeneous product formed by mechanically agitating such a mixture.

It is surprising that sulfur treatment can improve the formation of nickel-ligand hydrocyanation catalysts because sulfur is reported to be a catalyst poison. See, e.g., Chen et al., IND. ENG. CHEM. RES. 27: 1391-96 (1988). Therefore, it is unexpectedly surprising that even sources of nickel metal that form nickel-ligand complexes poorly can be simply, effectively and efficiently converted into nickel metal preparations that form high levels of nickel-ligand complexes when the methods described herein are employed.

#### Brief Description of the Figures

FIG. 1 shows carbon dioxide (CO<sub>2</sub>) loss during calcination pre-treatment of the eight BNC samples #1-#8 listed in Table 2.

FIG. 2 is a thermal profile of hydrogen absorption during reduction of BNC samples #3, 4, and 6, which upon reduction provide inactive Ni that does not efficiently form complexes with phosphorus-containing ligands as described herein.

FIG. 3A is a thermal profile of hydrogen absorption during reduction of BNC samples #1, 2, 5, 7, and 8, which upon reduction provide active Ni that does efficiently complexes with phosphorus-containing ligands as described herein. FIG. 3B shows temperature-programmed desorption-reaction-mass spectroscopy (TPD-TPR MS) where the Test Conditions are Ar Balance ( $20 \text{ cm}^3 \text{ min}^{-1}$ , >99% Ar, BOC); Total Flow Rate =  $20 \text{ cm}^3 \text{ min}^{-1}$ ; Internal Standard = Ar ( $m/z=36$ ); Catalyst Mass = 50 – 60 mg; Rate =  $15 \text{ }^\circ\text{C min}^{-1}$ . FIG. 3C shows temperature-programmed reaction mass spectroscopy (TPR-MS) where the Test Conditions are 10%  $\text{H}_2$  ( $2 \text{ cm}^3 \text{ min}^{-1}$ , >99%  $\text{H}_2$ , BOC); Ar Balance ( $18 \text{ cm}^3 \text{ min}^{-1}$ , >99% Ar, BOC); Total Flow Rate =  $20 \text{ cm}^3 \text{ min}^{-1}$ ; Internal Standard = Ar ( $m/z=36$ ); Catalyst Mass = 50 – 60 mg; Rate =  $15 \text{ }^\circ\text{C min}^{-1}$ .

FIG. 4 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #1 listed in Table 2. The temperature axis shows the progression of increasing temperature applied during the hydrogenation process, the crystallite size axis shows crystallite sizes, as determined by XRD in these data, and the volume-% axis indicates the distribution by volume of the various crystallite size classes in each bulk sample. Sample numbering corresponds to that shown in Table 2. See also, Example 3.

FIG. 5 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #2 listed in Table 2. The graph was generated as described in Example 3 and for FIG. 4.

FIG. 6 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #3 listed in Table 2. The graph was generated as described in Example 3 and for FIG. 4.

FIG. 7 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #4 listed in Table 2. The graph was generated as described in Example 3 and for FIG. 4.

FIG. 8 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #5 listed in Table 2. The graph was generated as described in Example 3 and for FIG. 4.

FIG. 9 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #6 listed in Table 2. The graph was generated as described in Example 3 and for FIG. 4.

FIG. 10 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #7 listed in Table 2. The graph was generated as described in Example 3 and for FIG. 4.

FIG. 11 shows TP-XRD data for a Ni metal particulate form obtained by hydrogen reduction of BNC sample #8 listed in Table 2. The graph was generated as described in Example 3 and for FIG. 4.

FIG. 12 is a graph illustrating the cumulative fraction (%) of undersized Ni crystallites as a function of crystallite size for determination of the crystallite size distribution (i.e., the width of the crystallite size distribution CSD) of nickel metal powder prepared from BNC sample #8 by reduction at the indicated temperatures.

FIG. 13 shows that the crystallite size distribution (CSD) correlates with nickel activity. CSD data is shown for eight Ni powder samples prepared from the eight BNC samples listed in Table 2 after reduction at the indicated temperatures.

FIG. 14 graphically illustrates the relationship between nickel activity and the C10 value (the largest diameter in nanometers of the smallest 10% of crystallites) of various nickel samples generated from the eight BNC samples listed in Table 2 after reduction at the indicated temperatures.

FIGs. 15A – 15D are scanning electron photomicrographs of nickel particles.

FIG. 16A graphically illustrates surface crystallite number per gm versus nickel activity for Ni1-Ni3, Ni5-Ni6, and Ni9-Ni10 samples (Table 4) based on the assumption that the shape of the crystallite is roughly spherical. FIG. 16B graphically illustrates a correlation for the seven nickel active samples Ni1-Ni3, Ni5-Ni6, and Ni9-Ni10 between nickel activity and mean crystallite number per gram based on the assumption that the crystallite is of a substantially square cross section, i.e., is a cube or cuboidal shape. The properties of Ni1-Ni3, Ni5-Ni6, and Ni9-Ni10 are also described in Table 4.

FIGs. 17A-17C graphically illustrate correlations between nickel particle/crystallite surface area and the activity or of nickel preparations to form nickel-ligand complexes. FIG. 17A shows that BET SSA correlates with LD SSA for nickel

preparations Ni1, Ni3, Ni6, Ni7, Ni8 and Ni9 (see Table 4). FIG. 17B shows a correlation between BET SSA and D10 particle sizes of samples Ni1, Ni3, Ni6, Ni7, Ni8 and Ni9 (Table 4). FIG. 17C graphically illustrates BET SSA values versus nickel activity for nickel samples Ni1-Ni6 and Ni9-Ni10 with the properties described in Table 4.

5           FIG. 18 graphically illustrates nickel activity versus C10 and C50 values for samples Ni1-Ni6 and Ni8-Ni10 that have the properties listed in Table 4.

FIG. 19 graphically illustrates a correlation between the number of surface crystallites of a size not greater than the C10 value for a nickel sample and the nickel activity of that sample.

10           FIG. 20 graphically illustrates a correlation between nickel activity and BET SSA / C50 using the data presented in Table 4 for each of the nickel samples having activity of at least 1 as defined herein.

FIG. 21 graphically illustrates the a correlation between nickel activity and BET SSA for nickel samples with equivalent sulfur content (1%) that had been reduced under  
15           the same conditions (in hydrogen at 400 °C).

### Detailed Description of the Invention

Nickel metal (e.g., zero valent nickel metal) particles are used to form complexes with one or more phosphorus-containing ligands, and the complex between nickel atoms  
20           and the phosphorus-containing ligands can be an effective hydrocyanation catalyst. These nickel-ligand complexes can be soluble in organic media, such as a hydrocyanation reaction milieu. As illustrated herein, treatment with a sulfur source improves the ability of a particulate nickel metal preparation to form complexes with one or more phosphorus-containing ligands.

The physical form as well as the content of sulfur in a preparation of particulate nickel metal affects its ability to form catalytic complexes with phosphorus-containing ligands. For example, nickel particulate forms with a BET Specific Surface Area of at least about 1 m<sup>2</sup>/gm, and/or with a C10 value is less than about 20 nm after reduction at 300-400 °C, and/or with an average crystallite size of no greater than about 100 nm exhibit good activity for forming a complex with phosphorus-containing ligands. However, sulfur treatment of nickel particulate forms having a lower BET surface area and/or a higher

average crystallite size can dramatically improve the ability of those nickel particulate forms to complex with phosphorus-containing ligands. Combinations of desirable particulate nickel physical properties and sulfur concentrations provide optimal complex-formation activities.

Moreover, sulfur treatment of particulate nickel metal that poorly complexes with phosphorus-containing ligands can cure the defects in structurally inadequate nickel preparations to produce a nickel particulate form that readily complexes with phosphorus-containing ligands. To effect such treatment, sulfur sources can be added to a nickel  
5 starting material during manufacture of nickel metal particles, sulfur sources can be added directly to a mixture of particulate nickel metal and one or more phosphorus-containing ligands during nickel-ligand complex formation, or sulfur sources can be added directly to a hydrocyanation reaction mixture that contains a nickel-ligand catalyst.

Nickel particles treated with a sulfur source combine more effectively with one or  
10 more phosphorus-containing ligands and more efficiently generates an active hydrocyanation catalyst than does untreated nickel metal particles. The improvement in catalyst formation can be substantial. For example, after treatment of one commercially available source of nickel particles using the methods described herein the nickel exhibited a 14 – 15 fold improvement in complex formation with phosphorus containing  
15 ligands as measured, for example, by the solubility of the nickel-ligand complex in an organic medium. Prior to such treatment, that commercially available source of nickel was not useful for making nickel-ligand catalysts. Treatment with a sulfur source so dramatically improved complex formation by the nickel metal that a nickel source that otherwise may have been discarded could effectively be used to make excellent catalysts  
20 useful for manufacturing processes involving hydrocyanation.

The methods of generating active nickel hydrocyanation catalysts include contacting a nickel metal or a nickel starting material used to make nickel metal with a sulfur source. The nickel starting material can be contacted with the sulfur source during processing of the nickel starting material to generate nickel metal, or after nickel metal has  
25 been generated, or even during complex formation between the nickel metal and one or more phosphorus-containing ligand(s).

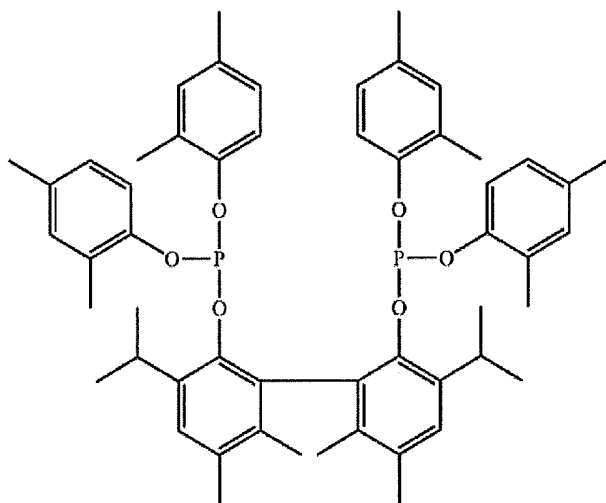
Desirable forms of nickel metal powder provided herein include particles of nickel metal composed of nickel crystallites having defined sizes, BET Specific Surface Areas and Laser Diffraction Specific Surface Areas, crystallite sizes, crystallite size distributions, surface crystallites per gram and combinations thereof. For example,

5 desirable surface areas include those with BET Specific Surface Areas of at least about 1  $\text{m}^2/\text{gm}$ , preferably at least about 2  $\text{m}^2/\text{g}$ , more preferably at least about 4  $\text{m}^2/\text{g}$ , and further preferably at least about 10  $\text{m}^2/\text{g}$ . A desirable nickel particulate form can have at least one property selected from the group consisting of: a BET Specific Surface Area of at least about 1  $\text{m}^2/\text{gm}$ ; a BET Specific Surface Area / C50 ratio of not less than  $0.07 \times 10^9 \text{ m/gm}$ ;

10 a C10 that is less than about 20 nm; an average crystallite size of no greater than about 30 nm; a crystallite size distribution span greater than about 1.0; on average at least about  $10^{15}$  surface crystallites per gram of nickel; at least 10% of the particles of the form have a size (D10) of no greater than about 6  $\mu\text{m}$ ; a Laser Diffraction Specific Surface Area of at least about 0.4  $\text{m}^2/\text{gm}$ ; a BET Specific Surface Area to D10 ratio of about  $0.3 \times 10^6 \text{ m/gm}$

15 to about  $10.0 \times 10^6 \text{ m/gm}$ ; on average at least about  $10^{16}$  surface crystallites per gram nickel that are smaller than or equal to size C10; and any combination thereof. Preferably the desirable nickel particulate form has at least two of these properties; more preferably, the desirable nickel particulate form has at least three of these properties; even more preferably, the desirable nickel particulate form has at least four of these properties.

Such desirable nickel particulate forms complex with Ligand (V) within about 2 hours when about 4 to 5 wt% of the nickel particulate form is mixed with 3-pentenitrile containing Ligand (V) and  $\text{ZnCl}_2$ ; wherein Ligand (V) has the following formula:



While such physical properties are desirable, treatment with a sulfur source can dramatically improve the ability of a particulate nickel form to complex with phosphorus-containing ligands. Thus, one or more desirable physical property can be lacking from a particulate nickel form if that particulate nickel form has been treated with a sulfur source during its preparation as a particulate metal or during complex formation of the particulate nickel metal form with one or more phosphorus-containing ligands.

### Sulfur Sources

As described herein, nickel starting materials and nickel metals contacted with sulfur sources exhibit improved complex formation with phosphorus-containing ligands.

The sulfur source employed can include elemental sulfur, polymeric sulfur, sulfur-containing gases, sulfur-containing salts, sulfur-containing ions and combinations thereof. The sulfur source can be in liquid, solid, gaseous or a combination of such physical forms.

The sulfur source can include, for example, sulfates, sulfites, sulfides, hyposulfites, thiosulfates, sulfur dioxide, sulfur monoxide, sulfur halides, and the like. Examples of sulfur sources that can be employed include hydrogen sulfide, nickel sulfate, nickel sulfite, nickel sulfide, nickel hyposulfite, nickel thiosulfate, sulfur trioxide, sulfur dioxide, sulfur monoxide, disulfur dichloride, sulfur dichloride, sulfur tetrachloride, sulfur chloride pentafluoride, disulfur decafluoride, sulfur hexafluoride, sulfur tetrafluoride, sulfur trifluoride and combinations thereof. Any of these and other sources of sulfur can be used to activate nickel for complex formation with phosphorus-containing ligands.

Elemental sulfur can be present in a number of forms, including solid elemental sulfur, gaseous sulfur, polymeric sulfur, mixtures of polymeric chains of sulfur, cyclic sulfur and combinations thereof. There are also a large number of allotropes of sulfur. The most common form found in nature is yellow orthorhombic  $\alpha$ -sulfur, which contains  
5 puckered rings of eight sulfur atoms ( $S_8$ ). In addition, other solid forms of sulfur contain sulfur rings of 6, 7, 9–15, 18 and 20 atoms. There are also sulfur gases, such as  $S_2$ ,  $S_3$ ,  $S_4$ , and  $S_5$ . Metallic-like sulfur forms can also be formed, for example, at high-pressures. Any and all of these forms of sulfur are sulfur sources for use in the methods described herein.

The sulfur source may be a sulfur-donor. Examples of sulfur donating compounds  
10 include thioethers, thioesters, disulfides and the like. For example, the disulfide can be selected from disulfides, thioacetic acid, thioacetate salts, polysulfides, bis-alkylamino disulfides, sulfenic sulfonic thioanhydrides, thiosulfonate salts, aminothiosulfonates, acylmethylmercapto azoles or azolium salts, thiazepines, thiopins, 1,4-dithiins, 1,2-, 1,3-, or 1,4-thiazines, 1,4,2-dithiazines, 1,3,4-, 1,2,6-, 1,3,5-thiadiazines, dihydro derivatives of  
15 dithiazines or thiadiazines, 1,2,3,4-thiatrazoles and combinations thereof. Vulcanizing agents such as those discussed by Porter, M. in *Vulcanization of Rubber*; Oae, S. Ed.; Organic Chemistry of Sulfur; Plenum: New York, 1977, Chapter 3, and by Hofmann, W. *Vulcanization and Vulcanizing Agents*; Palmerton: New York, 1967 may also be effective.

20 It may be preferable that the sources of sulfur not introduce organic compounds or organic moieties to the nickel preparations or the mixtures of nickel and phosphorus-containing ligands. For example, the sulfur source may not include carbon-containing or phosphate-containing compounds and moieties. Sources of sulfur may not include metal contaminants (other than nickel). For example, sources of sulfur may not include  
25 substantial amounts of alkali and alkaline earth ions or salts. In some instances such organic compounds or moieties can be removed during processing of a mixture of the sulfur source and a nickel starting material. For example, calcination and/or reduction processes used to generate nickel metal particles from nickel starting materials may remove some organic compounds or moieties.

30 Accordingly, a variety of sulfur sources can be employed to improve nickel activity. Sulfur sources with proven ability to transform nickel starting materials into

nickel particulate forms with good nickel-ligand complex formation properties include liquid or solid nickel sulfate, elemental sulfur (e.g., S<sub>8</sub>), and nickel sulfide (e.g., Ni<sub>3</sub>S<sub>2</sub>).

Such nickel sources can be added to a nickel starting material (e.g., basic nickel carbonate or nickel oxide) during manufacture of nickel metal particles, the sulfur source  
5 can be added directly to a mixture of particulate nickel metal and one or more phosphorus-containing ligands during nickel-ligand complex formation, or the sulfur source can be added directly to a hydrocyanation reaction mixture that contains a nickel-ligand catalyst.

### Nickel Starting Materials

10 Nickel metal (e.g., zero valent nickel metal) can be directly treated with a sulfur source before, during or after complex formation with phosphorus-containing ligands. However, a nickel starting material can also be contacted with a sulfur source, where the nickel starting material is processed to generate nickel metal. For example, the nickel starting material can include higher valent nickel in salt form. Thus, the sulfur source can  
15 be added to a nickel starting material prior to reduction of the nickel starting material to make nickel metal particles.

Many sources of nickel are available and can act as starting materials to prepare nickel metal. For example, the nickel starting material can be basic nickel carbonate, nickel carbonate, nickel bicarbonate, nickel oxalate, nickel formate, nickel squarate, nickel  
20 hydroxide, nickel oxide, nickel salts, or a combination thereof.

Different types of nickel starting materials may require different processes to generate nickel metal. Processes for generating nickel metal are available in the art and examples of such processes are described herein. Surprisingly, treatment of nickel starting materials with a sulfur source can occur at essentially any stage of the nickel metal  
25 preparation process. Typically, a process for generating nickel metal includes reduction of a higher valent form of nickel into zero valent nickel metal. Addition of a sulfur source prior to reduction of a nickel starting material is a good way to form nickel metal particles that effectively complex with phosphorus-containing ligands.

Nickel oxide is also a convenient nickel starting material. The nickel oxide is  
30 preferably in particulate form. To generate particulate nickel metal for making nickel-ligand complexes, the nickel oxide is reduced from valent state +2 to zero valent nickel

metal particles. Such reduction can be performed as described herein or by other available procedures.

As illustrated herein, even after reduction, many commercially available sources of nickel oxide do not form useful catalysts after reduction and combination with  
5 phosphorus-containing ligands. However, when such nickel oxide is treated with a sulfur source before, during or after reduction, the nickel formed can readily complex with phosphorus-containing ligands to a greater extent than does the nickel generated from nickel oxide prior to treatment with the sulfur source.

Basic nickel carbonate is another useful nickel starting material. Basic nickel  
10 carbonate is commercially available or it can be made as described herein. When basic nickel carbonate is employed as a starting material it is reduced to generate nickel metal. Optionally, the basic nickel carbonate can be calcined prior to reduction, thereby driving off carbon dioxide and providing a nickel oxide composition. Such a calcination step has been used to increase reactivity of the nickel sample with respect to formation of nickel-  
15 ligand complexes soluble in organonitrile solvents. However, when treated with a sulfur source as described herein, it may not be necessary to calcine the basic nickel carbonate to achieve satisfactory levels of nickel-ligand complex formation. However, if calcination is performed, the basic nickel carbonate can be contacted with a sulfur source during calcination to produce nickel oxide, during reduction to generate nickel metal or during  
20 complex formation of the nickel metal product with phosphorus-containing ligands.

As illustrated herein, even after calcination and reduction, many commercial sources of basic nickel carbonate do not readily form complexes with phosphorus-containing ligands. However, when such commercial sources of basic nickel carbonate are treated with a sulfur source before, during or after calcination and/or reduction, even  
25 these commercial sources of basic nickel carbonate can be transformed into nickel metal preparations that readily complex with phosphorus containing ligands.

Nickel formate can also be employed as a starting material useful for preparing nickel metal particles. As illustrated herein, nickel formate can be thermally treated to generate nickel metal particles useful for complex formation with phosphorus-containing  
30 ligands, especially when sulfur is present (e.g., more than about 500 ppm sulfur, preferably about 0.2 wt% to about 15 wt% sulfur). Thus, nickel formate can simply be

thermally treated in a non-oxygen containing gas such as nitrogen, and it may not be necessary to subject nickel formate to a reduction step.

When nickel formate is thermally treated to generate nickel metal particles, the nickel formate can be heated to 350 °C to 450 °C in a non-oxygen atmosphere for about 1  
5 to 4 hours. As illustrated herein, nickel formate can conveniently be thermally treated in a fluidized bed reactor where it is suspended in a nitrogen atmosphere and heated to about 400 °C for about 2 hours.

While reduction of nickel formate may not be necessary, such reduction can be performed using procedures described herein or available in the art. If calcination is  
10 desired, nickel formate can also be calcined using methods described herein. Thus, the nickel formate thermally treated in a non-oxygen atmosphere, the nickel formate can be reduced without calcination pre-treatment or it can be subjected to calcination pre-treatment followed by reduction to zero valent nickel metal particles. The sulfur source  
15 or complex formation) to generate a nickel-phosphorus ligand complex with catalytic activity.

Another nickel starting material useful for preparing nickel metal particles that can readily complex with phosphorus-containing ligands is a nickel salt. One example of a useful nickel salt for making nickel metal particles is nickel sulfate. When nickel sulfate is  
20 employed as a starting material for making nickel metal there may be no need for further sulfur treatment because the sulfate is an excellent source of sulfur. Therefore, nickel sulfate can be a useful starting material for generating nickel metal.

Nickel sulfate can be in solid (e.g., particulate) form or be in solution. When nickel sulfate is in solution, the solvent can be removed to generate a nickel(II)-containing  
25 powder. In general, the nickel sulfate is subjected to calcination to generate nickel oxide with sulfate ions, prior to reduction. Calcination of nickel sulfate reduces the probability that large amounts of  $\text{Ni}_3\text{S}_2$  will be formed during reduction, which may not complex well with phosphorus-containing ligands. The nickel (e.g.,  $\text{Ni}^{+2}$  and nickel oxide) in the solid and powdered materials formed by calcination of nickel sulfate are reduced to generate  
30 nickel metal (zero valent nickel) using the methods described herein or other available procedures.

Nickel metal can also be treated with a sulfur source. As illustrated herein, commercially available sources of nickel exhibit variable, unpredictable and typically poor activity for making nickel-ligand complexes as hydrocyanation catalysts. However, an active particulate nickel metal that readily reacts with phosphorus-containing ligands can readily be produced by adding the sulfur source to nickel metal particles. For example, a sulfur source can be added to a mixture of nickel particles and phosphorus-containing ligands in a convenient solvent (e.g., an organonitrile solvent) to generate nickel-ligand complexes that are effective hydrocyanation catalysts. The sulfur source can also be added to a hydrocyanation reaction mixture that contains a nickel-phosphorus ligand catalyst.

In general, untreated nickel metal from commercial sources exhibits poor complex formation with phosphorus containing ligands. While reduction of commercially available nickel metal may provide a slight improvement, addition of a sulfur source during nickel reduction, or simply during formation of the hydrocyanation catalyst, reliably transforms poor nickel metal sources into a form of nickel metal that efficiently combines with phosphorus-containing ligands to generate useful hydrocyanation catalysts.

When nickel metal is selected for treatment with a sulfur source, the nickel metal can be a particulate (powdered), zero valent nickel metal. If the nickel metal is partially oxidized it can be reduced by procedures available in the art, for example, by thermal hydrogen treatment as described herein.

### **Treatment with Sulfur Sources**

Nickel metal particles and nickel starting materials can be treated with varying amounts of a sulfur source at different stages of producing zero valent nickel metal, forming a nickel-ligand complex and maintaining an effective nickel-ligand catalyst during hydrocyanation reactions. For example, sulfur sources can be added to nickel starting materials before, during or after calcination. Sulfur sources can be added to nickel starting materials before, during or after reduction. A sulfur source can also be included during nickel- ligand complex formation and during hydrocyanation reactions that employ nickel-ligand catalysts.

The nickel starting materials or the nickel metal can be in solution, in suspension or in particulate form during treatment with a sulfur source. For example, the nickel can be in particulate form within a liquid medium or within a gas stream. Thus, the nickel starting materials or nickel metal can be in suspension. The solubility of nickel metal is generally quite low in many liquid solvents. However nickel metal can be suspended in a liquid or by a gas. Alternatively, the nickel starting materials or nickel metal in solid particulate form can simply be mixed with the sulfur source.

The sulfur source can be combined and/or mixed with the nickel starting materials or nickel metal for varying times. For example, the nickel starting materials or nickel metal and a sulfur source can be mixed together for about 1 minute to about 72 hours, or about 1 minute to 24 hours, or about 1 minute to 12 hours, or about 1 minute to 4 hours, or about 1 minute to 2 hours, or about 1 minute to 1 hour. Little mixing may initially be needed when the sulfur source is added to a nickel starting material that is subjected to further processes involving mixing, such as calcination, reduction or even catalyst complex formation.

During treatment of nickel starting materials or nickel metal with a sulfur source, the mixture can be maintained at about 4° C to about 450° C. Little or no additional heating or incubation may be needed to treat nickel metal or nickel starting materials with a sulfur source because various steps in the formation of nickel metal or the formation of a nickel-ligand catalyst complex provide sufficient heating and mixing for sulfur treatment of nickel. Thus, sulfur sources can be added to essentially any convenient step involved in the preparation of nickel metal or nickel-ligand complexes.

For example, a sulfur source can be added directly to a catalyst complex formation mixture that contains nickel metal particles and phosphorus-containing ligand(s) in an organic solvent (e.g., an organonitrile solvent) that is mixed and warmed to about 60°C - 80°C. A sulfur source can conveniently be added to any nickel starting material and the nickel starting material can be processed in the usual manner into particulate nickel metal, for example, by reduction (calcination is typically optional).

Nickel and nickel starting materials can effectively be treated with varying amounts of a sulfur source. For example, a molar ratio of sulfur to nickel can range from

about 0.003 to about 1.8; preferably the molar ratio is about 0.004 to about 0.2; and more preferably such a sulfur to nickel molar ratio is about 0.01 to about 0.05.

Effective amounts of sulfur in combination with nickel and nickel starting materials can vary from about 0.1 wt% sulfur to about 50 wt% sulfur relative to the total weight of the composition, or preferably from about 0.2% to about 4 wt% sulfur relative to the total weight of the composition, preferably from about 0.3% to about 2 wt% sulfur relative to the total weight of the composition.

For example, effective amounts of sulfur in a zero valent particulate nickel preparation can vary from about 0.1 wt% sulfur to about 50 wt% sulfur relative to the weight of nickel. The weight percentage of sulfur can vary from about 0.2 wt% sulfur to about 15 wt% sulfur, or about 0.2 wt% sulfur to about 10 wt% sulfur. Preferably, the amount of sulfur in a zero valent particulate nickel preparation can be about 0.5 wt% sulfur to about 5 wt% sulfur relative to the weight of nickel, or more preferably from about 0.6% to about 1% sulfur relative to the weight of nickel. As illustrated herein, an effective amount of sulfur in a particulate nickel metal preparation is about 0.8% sulfur relative to the weight of nickel.

Nickel starting materials such as basic nickel carbonate, nickel carbonate, nickel bicarbonate, nickel oxalate, nickel formate, nickel squarate or combinations thereof can be treated with about 0.1 wt% to about 25 wt% sulfur relative to the total weight of the composition, or about 0.2 wt% to about 10 wt% sulfur relative to the total weight of the composition, about 0.3 wt% to about 3 wt% sulfur relative to the total weight of the composition. Preferably, such nickel starting materials are treated with a source of sulfur ranging from about 0.3 wt% to about 1 wt% sulfur relative to the total weight of the composition, or about 0.3 wt% to about 0.5 wt% sulfur relative to the total weight of the composition. As is illustrated herein, an effective amount of sulfur in basic nickel carbonate is about 0.4 wt% sulfur relative to the total weight of the composition. Similar nickel starting materials can be treated with about 0.4 wt% sulfur relative to the total weight of the composition.

Nickel starting materials such as basic nickel carbonate (BNC), nickel carbonate, nickel bicarbonate, nickel formate, nickel oxalate or nickel squarate can be mixed with a sulfur source so that the sulfur content is at least 0.1% by weight on nickel basis, or at

least 0.2% by weight on nickel basis, or at least 0.3% by weight on nickel basis, or at least 0.4% by weight on nickel basis, or at least 0.5% by weight on nickel basis, or at least 0.6% by weight on nickel basis, or at least 0.7% by weight on nickel basis, or at least 0.8% by weight on nickel basis, or at least 0.9% by weight on nickel basis, or at least 1.0% by weight on nickel basis, or at least 2% by weight on nickel basis, or at least 3.0% by weight on nickel basis.

Somewhat more sulfur may be used to treat nickel oxide than basic nickel carbonate. For example, nickel oxide can be treated with about 0.2 wt% to about 30 wt% sulfur relative to the total weight of the composition, or about 0.3 wt% to about 10 wt% sulfur relative to the total weight of the composition, about 0.4 wt% to about 5 wt% sulfur relative to the total weight of the composition. Preferably, nickel oxide is treated with about 0.4 wt% to about 1 wt% sulfur relative to the total weight of the composition, or about 0.5 wt% to about 0.7 wt% sulfur relative to the total weight of the composition. As is illustrated herein, an effective amount of sulfur in a mixture with nickel oxide is about 0.6 wt% sulfur relative to the total weight of the composition. Similar nickel starting materials can be treated with about 0.6 wt% sulfur relative to the total weight of the composition.

Nickel oxide with a sulfur source so that the sulfur content is at least 0.2% by weight on nickel basis, or at least 0.3% by weight on nickel basis, or at least 0.4% by weight on nickel basis, or at least 0.5% by weight on nickel basis, or at least 0.6% by weight on nickel basis, or at least 0.7% by weight on nickel basis, or at least 0.8% by weight on nickel basis, or at least 0.9% by weight on nickel basis, or at least 1.0% by weight on nickel basis, or at least 2% by weight on nickel basis, or at least 3.0% by weight on nickel basis.

When sulfur containing salts are used a source of sulfur, the sulfur containing salts can be contacted with the nickel starting materials or nickel metal as a solid or as an aqueous solution. Where the salt is used as an aqueous solution, the concentration of the solution may be from about 0.01M to about 2 M, or from about 0.05 M to about 1.5 M, or from about 0.1 M to about 1.5 M, or the concentration may be 1M. For example,  $\text{NiSO}_4$  may be used as 1M aqueous solution. A weight ratio of about 1:2 to about 1:8 nickel starting material to 1M sulfur salt solution can be employed for effective treatment of the

nickel starting material. For example, as illustrated herein, a 1:5 weight ratio of basic nickel carbonate to a 0.05 to 1M nickel sulfate solution can be employed to generate a particulate nickel metal preparation (after drying and reduction) that efficiently forms a complex with one or more phosphorus-containing ligands. Testing demonstrates that a 1:5 weight ratio of nickel starting material 1M nickel sulfate solution can be employed for several types of nickel starting materials such as basic nickel carbonate, nickel oxide and passivated (NiO coated) nickel.

Also as illustrated herein, about 0.4% to 2% elemental sulfur or nickel sulfide (on a wt% sulfur basis relative to the total composition) can be added to basic nickel carbonate or nickel oxide to form particulate nickel metal preparations (after reduction) that effectively combine with phosphorus-containing ligands to form nickel-ligand complexes.

The nickel starting materials containing the sulfur can be reduced to make particulate zero valent nickel metal for use in a catalyst. Calcination is typically optional, however, if nickel sulfate is used as a nickel starting material, it may be desirable to calcine the nickel sulfate before reduction.

When the nickel to be contacted with sulfur is zero valent particulate nickel metal, the sulfur source can be added directly to a catalyst preparation mixture that contains the particulate nickel metal and phosphorus-containing ligand(s) in a solvent. A Lewis acid (e.g., zinc chloride) is generally also present in the catalyst preparation mixture. Such a Lewis acid can facilitate complex formation. The amount of sulfur source employed compared to nickel can vary so that about 0.1 wt% sulfur to about 50 wt% sulfur, or about 0.2 wt% sulfur to about 25 wt% sulfur, or from about 0.5 wt% sulfur to about 15 wt% sulfur is employed relative to the amount of nickel. As illustrated herein addition of as little as 150 ppm elemental sulfur or nickel sulfate to a catalyst preparation mixture improved nickel-ligand complex formation by about 3- to 5-fold. Addition of about 11% to 12% S<sub>8</sub> (relative to the nickel content) to a catalyst preparation mixture improved nickel-ligand complex formation by about 4- to about 12-fold.

Thus, methods of effective treatment of nickel with sulfur sources are simple, flexible and easily implemented.

### Preparing Nickel Starting Materials

Particulate nickel metal can be obtained from a higher valent nickel starting material such as a Ni(II) containing starting material. Examples of nickel starting materials include basic nickel carbonate, nickel carbonate, nickel bicarbonate, nickel oxalate, nickel formate, nickel squarate, nickel hydroxide, nickel oxide, nickel salts or a combination thereof. One frequently employed example of a higher valent nickel starting material is a nickel salt such as basic nickel carbonate, also referred to as BNC or BNC nickel. BNC can be used in the methods described below to produce an inventive Ni metal particulate form.

Basic nickel carbonate is available commercially. For example, basic nickel carbonate can be obtained by MetChem Corporation, an American distributor of this material. According to the vendor, the basic nickel carbonate provided is produced by precipitating the basic nickel carbonate from an aqueous solution comprising nickel, ammonia, ammonium carbonate, and water. According to the vendor, the basic nickel carbonate is produced from an ore comprising nickel and the basic nickel carbonate and may further comprise at least one element selected from the group consisting of aluminum, calcium, cobalt, copper, iron, magnesium, manganese, sodium, sulfur, and zinc. For example, analysis of MetChem basic nickel carbonate as received from the supplier indicates that it has composition shown in Table 1.

**Table 1: Analytical Results for MetChem Basic Nickel Carbonate Powder**

| Nickel 47% by weight |                |               |                |
|----------------------|----------------|---------------|----------------|
| Cobalt 65 ppm        | Copper 20 ppm  | Iron 55 ppm   | Zinc 12 ppm    |
| Magnesium 60 ppm     | Calcium 60 ppm | Sodium 60 ppm | Sulfur 175 ppm |

Without sulfur treatment, basic nickel carbonate obtained from MetChem typically does not form nickel metals that complex with phosphorus containing ligands at a commercially acceptable rate (e.g., within a few minutes to a few hours). However, when MetChem basic nickel carbonate is treated with a sulfur source during nickel metal preparation or during complex formation, the nickel metal derived from MetChem basic

nickel carbonate does form complexes with phosphorus containing ligands within a commercially acceptable time period (e.g., within about 15 minutes to about 3 hours).

It may be desirable to manufacture the basic nickel carbonate rather than obtaining it from a commercial source. For example, impurities may be avoided and the composition of the basic nickel carbonate can be controlled by manufacture of the basic nickel carbonate using selected reactants and manufacturing conditions.

BNC can be described with a chemical formula of



wherein  $x = z - (y/2)$ ;  $y = 2z - 2x$ ;  $z = 1$  to  $100$ ; and  $n = 0$  to  $400$ .

BNC can include nickel(II) ions, carbonate ions, hydroxide ions, and water molecules. BNC can be synthesized using available procedures.

The selected BNC nickel starting material can have low carbonate content. For example, a selected BNC nickel starting material can have a molar ratio of

$\text{NiCO}_3:\text{Ni}(\text{OH})_2$  less than approximately 1, with a mass ratio of Ni:C of at least about

10:1, or any combination thereof. Such BNC can produce Ni(0) with low levels of carbon impurities, including low levels of carbon impurities such as carbonate impurities.

Preparation of particulate nickel metal from BNC nickel that has a low carbonate content, such as a molar ratio of  $\text{NiCO}_3:\text{Ni}(\text{OH})_2$  less than approximately 1, a mass ratio of Ni:C of at least about 10:1, or any combination thereof, can more readily produce  $\text{CO}_2$  during calcination and thus can result in more complete conversion to NiO, with fewer carbon impurities in the NiO. By producing NiO with a lower carbon content, including a lower carbonate content, less carbon impurities can be present in the Ni(0) product, the Ni(0) product can be more "active" as defined herein, or both.

BNC can be made by (i) contacting a precipitant solution and a nickel solution in a precipitation reactor to form a reaction mixture; and (ii) precipitating the nickel salt from the reaction mixture, wherein the nickel solution comprises nickel(II) ions and water, and the precipitant solution is selected from the group consisting of: (a) bicarbonate ions and water, (b) carbonate ions and water, and (c) mixtures thereof.

The mole ratio of bicarbonate ions to nickel(II) ions in the reaction mixture at the conclusion of the feeding can range from 0:1 to 2:1, including from about 0:1 to about 1.6:1, from about 0:1 to about 1.2:1, from about 1.0:0 to about 1.9:1, from about 1.2:1 to

about 1.9:1, from about 0.8:1 to about 1.4:1, from about 1.0:1 to about 1.8:1, from about 1.0:1 to about 1.6:1, from about 1.0:1 to about 1.4:1, from about 0.8:1 to about 1.4:1, and from about 0.8:1 to about 1.2:1. The mole ratio of carbonate ions to nickel ions in the reaction mixture at the conclusion of the feeding can range from 0:1 to 1.6:1, including  
5 from about 0:1 to about 1.4:1, from about 1.0:0 to about 1.2:1, from about 0.8:1 to about 1.4:1, from about 1.0:1 to about 1.6:1, from about 1.0:1 to about 1.6:1, from about 1.0:1 to about 1.4:1, from about 0.8:1 to about 1.4:1, and from about 0.8:1 to about 1.2:1. Blends of bicarbonates and carbonates can also be used in the precipitant solution.

A precipitation reactor used for preparing precursor BNC samples can be any  
10 suitable containment vessel such as a tank, vessel or pipe. The precipitation of the BNC can be performed in a batch or continuous fashion. The reaction mixture can be agitated prior to and/or during the precipitation of the nickel composition. For example, agitation can be done by mechanical stirring, pumped circulation loop, flow-through static mixture, or ultrasound. The use of high sheer during precipitation can prevent particle  
15 agglomeration and can give smaller resulting BNC particles. Reactor designs, stirring designs, and the application of high amounts of power to stirring are examples of factors that can cause a high-sheer stirring of the reaction mixture during precipitation.

The BNC can be precipitated from the reaction mixture in the presence of added carbon dioxide. For example, the carbon dioxide can be added to the precipitation reactor, added to the nickel solution, added to the precipitant solution, added to the reaction  
20 mixture, and any combination thereof. While not to limit the invention by a recitation of theory, adding carbon dioxide may change the sulfur content of the BNC by indirectly influencing the neutralization stoichiometry. Also, the precipitant solution can be fed to the precipitation reactor over a period of time such as about 30 minutes to about 60  
25 minutes, and such addition can be performed in a semi-continuous or continuous manner. The precipitant solution can also be added to the nickel solution in the precipitation reactor in a semi-continuous or continuous manner, for example, by using gradual addition.

The BNC can be precipitated within a temperature range of from about 0°C to  
30 about 90°C, including from about 20°C to about 90°C, from about 20°C to about 70°C, from about 20°C to about 50°C, from about 50°C to about 90°C, from about 60°C to about

80°C, and from about 65°C to about 75°C. Increased temperature during precipitation may decrease the proportion of carbonate ions in the resulting BNC, which may be useful for generating useful hydrogenation catalysts.

5 The use of a higher pH during precipitation can decrease the proportion of carbonate ions in the resulting BNC precipitate. For example, a pH value of about 4, 5, 6, 7, 8, or about 9, or higher may be used. In one example, the pH increases from about 4.9 to about 5.8 during the precipitation.

10 The reaction mixture can also be digested after contacting the precipitant solution to the nickel solution by heating the reaction mixture from between about 50°C and about 90°C for a period of from about 0.25 hours to about 24 hours. Precipitation can occur before, during, or after digestion, or any combination thereof. Other suitable temperature ranges include from about 60°C to about 80°C, and/or from about 65°C to about 75°C. Other suitable digestion time periods can range from about 2 hours to about 24 hours, including from about 4 hours to about 20 hours, from about 6 hours to about 16 hours, and  
15 from about 8 hours to about 12 hours. Longer digestion times can cause larger BNC particles in the resulting precipitate.

The BNC preparation methods can also include, after the precipitation step, washing the precipitated BNC with water; and partially drying the precipitated BNC. For example, the precipitated BNC can be separated from the reaction mixture by filtration or  
20 decantation, the resulting precipitated BNC can be washed with water by filtration or decantation, and/or the resulting BNC can be dried by water evaporation between 60°C and 100°C. Drying can be performed under ambient pressure or under vacuum, and in the presence of an inert gas such as nitrogen.

A nickel solution used in preparation of the BNC, comprising nickel(II) ions and  
25 water, may be prepared by dissolving a nickel(II) salt in water. The nickel salt can be any salt that is soluble in water, for example  $\text{NiCl}_2$ ,  $\text{NiSO}_4$ , and  $\text{Ni}(\text{NO}_3)_2$ . Alternatively, a commercial BNC can be repurified, by first dissolving the crude BNC in an aqueous acid such as hydrochloric, sulfuric, or nitric acid, then using that solution for reprecipitation of purified BNC as described herein. Other water-insoluble Ni(II) sources can be converted  
30 to a soluble material in a similar manner and used as a source of BNC suitable for preparation of nickel active particulate forms of the invention.

The precipitant solution, comprising bicarbonate ions, can be prepared by dissolving a bicarbonate salt, for example,  $\text{NaHCO}_3$  and  $\text{NH}_4\text{HCO}_3$ , in water.

Alternatively, the precipitant solution can be prepared in-situ by dissolving  $\text{CO}_2$  and an alkali metal hydroxide or ammonia in water by known methods. Likewise, the precipitant

5 solution, comprising carbonate ions, can be prepared by dissolving a carbonate salt, for example  $\text{Na}_2\text{CO}_3$ . The precipitant solution can also be prepared in-situ by dissolving  $\text{CO}_2$  and an alkali metal hydroxide in water by known methods. The anion of the nickel salt and cation of the bicarbonate or carbonate salt may be selected such that a salt produced from the precipitation, comprising both the cation and anion from the reaction mixture (for  
10 example  $\text{NaCl}$ ), is soluble in the water of the reaction mixture. Such a selection provides a method for separating the anions and cations from the precipitated BNC.

As previously stated, the amount of bicarbonate or carbonate ions relative to the nickel(II) ions charged to make BNC, can affect the nickel reactivity of the resulting zero-valent nickel particles with the phosphorus-containing ligand, e.g., Ligand (V). Because of  
15 the high costs of nickel, producers of BNC-type nickel compositions would be led to add excess amounts of the precipitant solution so as to recover as much of the nickel as economically feasible. However, it has surprisingly been found that the use of excess precipitant produces nickel metal of low reactivity for the phosphorous-ligand complex reaction. Highly reactive nickel is produced when reduced levels of precipitant are used,  
20 where presumably more of the nickel(II) ions are allowed to remain dissolved in the water of the resulting reaction mixture and may not be precipitated.

It has also been found that the precipitated nickel composition made using bicarbonate ions filters and surprisingly washes much faster than the precipitated nickel composition made using carbonate ions. In addition, the filtered precipitated nickel  
25 composition made using bicarbonate ions dries to a soft powder with little shrinkage. For these reasons, producing the nickel-containing solid using bicarbonate ions provides further desirable properties for downstream processing and handling of the dried precipitated nickel BNC composition.

### Reduction of Nickel-Containing Materials

Generation of nickel metal can include direct reduction of certain nickel starting materials or reduction of nickel metal preparations. However, the extent of nickel reduction is typically not critical. Suitable nickel metal preparations include those that are  
5 fully reduced or partially reduced. The degree of reduction can readily be determined and selected by one of skill in the art using procedures described herein or available in the art.

A variety of nickel starting materials can be reduced such as BNC, nickel squarate, nickel oxalate, nickel sulfate, nickel oxide, nickel oxalate, and partially oxidized nickel metal, or nickel metal. In general, such nickel starting materials and/or nickel metals can  
10 be reduced with a reductant (e.g., hydrogen, methane, CO) at elevated temperatures.

The nickel starting materials can be calcined prior to reduction or they can be directly reduced with hydrogen or another reductant at elevated temperatures. Calcination can remove absorbed gases such as carbon dioxide, sulfur dioxide, and the like.

As described herein, a sulfur source can be mixed with the nickel metal or nickel  
15 starting materials during the reduction process.

Reduction can be performed in a convenient reduction or reactor vessel, such as a fluid bed reactor, an expanded fixed bed, a rotary kiln, a rotary pan or any such equipment known to the skilled person. To facilitate optimal exposure of nickel metal and/or nickel starting materials to the reductant, a fluidized bed reduction vessel can be employed.

For example, a fluidizing bed reactor can be employed to perform both calcination and reduction of the nickel starting materials and/or nickel metals to zero valent nickel metal powder. The nickel starting materials and/or nickel metal can be charged to a fluidizing bed reactor and the reactor can be closed. The reduction (and/or calcination) procedure can then be initiated. For the reduction process, the reactor can be flushed with  
20 an inert gas to remove oxygen from the reactor prior to introducing the reductant.

During reduction, steam can also be a component of the mixture of reductant. When steam is used such as during the reduction process, the nickel metal powder so generated can be free-flowing, which facilitates product removal from the reaction vessel and further processing of the nickel metal. Steam is not necessary under most conditions  
30 for producing a reactive nickel metal product but it does prevent agglomeration and clumping of the reduced nickel product.

For reduction to zero-valent nickel metal, the gas flowing through a bed of the nickel starting material or nickel metal contains a reductant, preferably in an inert carrier gas. The reductant can be any gaseous or particulate substance that can reduce nickel ions to nickel metal. Examples of reductants that can reduce nickel ions to nickel metal  
5 include, for example, hydrogen, methane, and carbon monoxide. A desirable reductant is hydrogen. For example, the fluidization gas can contain hydrogen in amounts sufficient to reduce at least a portion of the nickel in the fluidized nickel-containing material to nickel metal. Gas flow rate during the process can be determined by the type of equipment used for the reduction and is within the knowledge of the skilled person to choose.

10 The inert carrier gas is essentially free of oxygen. Examples of inert carrier gases that can be employed include nitrogen, argon and neon. Nitrogen is an inexpensive and convenient source of an inert carrier gas.

The gas or mixture of gases used for reduction can also contain steam, which can facilitate generation of a free-flowing nickel metal product. Steam is not necessary under  
15 most conditions for producing a reactive nickel metal product but it does prevent agglomeration and clumping of the reduced nickel product thereby facilitating product removal from the reduction vessel and further processing of the nickel metal. The percentage of steam in the reducing gas can be about 0.1% to 80% by volume, or about 0.1% to 70% by volume, or about 0.1% to 50% by volume, or from about 0.1% to 30% by  
20 volume. The fluidization gas can contain about 0.1% to 20% volume percent steam, or about 1% to about 20% volume percent steam. The presence of water vapor in the form of steam is effective in producing a free flowing nickel powder.

Conditions sufficient to reduce nickel starting materials and/or nickel metal to zero-valent nickel metal include an elevated temperature and both an amount of reducing  
25 agent (e.g., hydrogen gas) and a time sufficient to substantially reduce the nickel containing solids to form a third nickel-containing solid that comprises nickel metal.

The reducing step is advantageously performed at a temperature between 200°C and 500°C, for example, between 200°C and 450°C, or between 225°C and 425°C, or between 250°C and 400°C. Temperatures at the lower end of these ranges (e.g., 200°C and  
30 lower) require longer reduction times. Reductions at high temperatures (e.g., 500°C and

higher) can give nickel metal powders with reduced complex formation with phosphorus containing ligands.

The time for reduction can vary somewhat with temperature, with reduction proceeding somewhat faster at higher temperatures. In general, reduction is performed for  
5 about 30 minutes to 8 hours, preferably for about 1 to 6 hours, more preferably for about 2 to 5 hours and most preferably for about 4 hours.

It is observed that for temperatures of about 300°C and 475 °C or about 250°C and 400 °C the reduction step is substantially complete in about four hours, provided that at least one equivalent of hydrogen is reacted with nickel oxide. It can be desirable to add an  
10 excess of hydrogen (e.g., more than one equivalent), to ensure complete reduction. The range of temperatures that can be employed is therefore affected by the time of reduction and the amount of hydrogen provided. An acceptable temperature range includes any numerical range of integers representing a temperature range falling between 200°C and 500°C. However, preferred temperatures are about 250°C to 400 °C, or about 250°C and  
15 350 °C for about four hours.

When the hydrogen is used as the reducing agent, introduction of hydrogen to the fluidization reaction vessel can cause an immediate temperature increase in the bed of nickel-containing solids, for example, of about 10 – 50 °C depending on the concentration of hydrogen. Those of skill in the art are aware that such an increase can occur and can  
20 adjust the reduction conditions as desired.

In general, sufficient reducing agent (e.g., hydrogen) is passed through the reactor to convert the nickel containing solids to nickel metal powder. An effective steam concentration in the reducing gas can be from about 1% to about 80% by volume. For example, an effective hydrogen concentration can be from about 10% to about 95% by  
25 volume. A carrier gas can be present in concentrations of about 20% to about 85% by volume. An example of a gas composition effective for reduction comprises about 10-20% steam, about 10-20% hydrogen, and the remainder as nitrogen, by volume per cent (volumetric measurement).

Reactor pressure during the reduction step is not critical. Thus, reduction can be  
30 performed at a pressure of about 0.1 atmospheres to 20 atmospheres, or at about 0.5

atmospheres to 10 atmospheres, or at about 0.5 atmospheres to 2 atmospheres. The reduction can conveniently be performed at about one atmosphere pressure.

At the end of the reduction step, the reactor is filled with nitrogen, or another inert gas effective to remove residual hydrogen. The inert gas is selected to be nonreactive with the nickel metal powder. Oxygen contact with the nickel metal at this stage can oxidize at least the surface of a nickel particle to nickel oxide, potentially lowering reactivity in the catalyst formation step.

Prior to reduction, the fluidizing bed reactor containing the nickel-containing solids (e.g., the nickel starting materials and/or a nickel metal) can be flushed with an inert gas that is essentially free of oxygen to remove molecular oxygen from the apparatus and from the nickel-containing solids. The reductant or reducing agent (e.g., hydrogen gas) can then be introduced into the fluidizing gas so that a mixture of reducing agent and the inert carrier gas is used to fluidize and substantially support the solid. The gas flow rate during reduction is not critical and may be adjusted to support the nickel metal or nickel starting materials and/or be determined by the type of equipment used for the reduction.

Upon completion of the reaction, the bed temperature can drop by about 10 °C. The time period observed at the elevated bed temperature can correspond to the time required to add the stoichiometric amount of hydrogen which reduces the nickel starting materials and/or nickel metal to zero valent nickel metal. The zero valent nickel metal powder in the reactor can be cooled in an oxygen-free atmosphere and can exhibit ferromagnetism. The amount of nickel metal generated and its purity can be determined by a metal analysis using methods known to the skilled person. Similarly, the amount of nickel in any of the nickel-containing compositions used in the methods described herein can be determined by a metal analysis using methods known to the skilled person.

The suitability of a nickel metal powder preparation can be assessed by preparing zero-valent nickel-ligand complexes in a solvent or liquid substrate (e.g., 3-pentenitrile (3PN)). After warming the mixture for a selected time period, the level of solubilized nickel-ligand complex in solution is measured, for example, by liquid chromatography. Unreacted nickel metal can be removed from the milieu by filtration or centrifugation and, if desired evaluated. Nickel complexes with a phosphorus-containing ligand and remains

in solution in a solvent such as a 3PN (which also a hydrocyanation substrate) as it forms a suitable zero-valent nickel-ligand complex.

Suitable nickel metal powder preparations can be reacted with monodentate or bidentate phosphorous containing ligands in a nitrile solvent to efficiently produce nickel complexes that can be used as homogeneous catalysts for the hydrocyanation of conjugated dienes to mononitriles, and the hydrocyanation of unsaturated nitriles to dinitriles.

### Calcination

A reduction step can be carried out directly on nickel starting materials. Alternatively, a calcination step can be performed on nickel starting materials and then the reduction step can be carried out.

Prior to the reduction step, calcination step can be performed on nickel starting materials such as basic nickel carbonate, nickel carbonate, nickel bicarbonate, nickel oxalate, nickel formate, nickel squarate, nickel hydroxide, nickel oxide, nickel sulfate, nickel salts or combinations thereof. Calcination can remove volatile and gaseous substances from the nickel starting materials. For example, calcination converts BNC to nickel oxide, at least in part, by thermal decomposition of nickel carbonate (or nickel bicarbonate), with expulsion of carbon dioxide (CO<sub>2</sub>) gas and water. Calcination can also remove sulfur dioxide and/or sulfur trioxide from nickel sulfate to generate nickel oxide.

Calcination can be performed in a convenient vessel, such as a fluid bed reactor, an expanded fixed bed, a rotary kiln, a rotary pan or any such equipment known to the skilled person. To facilitate uniform exposure of nickel starting materials to heat and optimally remove volatile and gaseous substances that may be absorbed onto nickel starting materials, a fluidized bed reduction vessel can be employed.

In general, calcination can be performed in any gaseous atmosphere not reactive with the nickel composition, for example, in a gas that does not form undesirable nickel compounds. Suitable convenient gases for the calcination step include air and nitrogen; others may include argon and helium. Steam (water vapor) can be present during the calcination step.

Generally, calcination can be carried out for a time and under thermal conditions sufficient to calcine the nickel starting material.

To perform calcination the nickel starting material can be placed in a closed reactor a flowing gas such as air, nitrogen, argon or mixtures thereof can be employed to support the nickel starting material(s). Air is an inexpensive and convenient gas suitable for the calcination step.

The temperature can be raised to a desired calcination temperature, for example, about 200 °C to 600 °C. At the calcination temperature 300 °C- 450 °C, or higher, air with or without steam can be passed through the reactor for a period of about 1 to 2 hours, while volatile and gaseous substances are removed from the nickel starting material. For example, when BNC is used as a nickel starting material and the BNC is calcined, carbon dioxide can be removed and the BNC can be converted to nickel oxide. Similarly, calcination of nickel sulfate can release sulfur dioxide or sulfur trioxide to yield nickel oxide.

The calcination step can be performed at temperatures of about 200 °C to 600 °C. Below 200 °C, the calcination process may be slow or incomplete and thus unreacted nickel precursor may remain in the product. Above 600 °C, an excessive collapse of the nickel oxide can occur, consequentially reducing the reactivity of the nickel powder product. The time for the calcination step can range from tens of seconds at 600 °C to multiple hours at 200 °C. Suitable calcination temperatures can include, for example, temperatures of about 300 °C to about 475 °C. At temperatures of about 300 °C to about 475 °C or about 325 °C and 450 °C, calcination is substantially complete in a reasonable time period, such as about 1.25 to 2 hour.

After calcination, the nickel starting material (e.g., nickel oxide) can be reduced. For example, the reactor can be purged with a nitrogen atmosphere for a sufficient time to remove substantially all oxygen (e.g., 98% to 99.9% of oxygen) and the calcined nickel starting material can be reduced as described herein.

### **Particulate Nickel Preparations**

Novel nickel metal preparations are described herein that are highly reactive with ligands to form of zero-valent nickel-phosphorus ligands complexes. Such complexes are

used as catalysts, for example, as hydrocyanation catalysts. The nickel metal particulate forms of the invention are highly reactive with bidentate phosphite ligands in an organic liquid, such as an organonitrile liquid or an olefinic precursor for a hydrocyanation reaction. Upon contacting the nickel-ligand catalyst mixture with HCN, a hydrocyanation product of the olefin is produced in good yield.

A nickel particulate form of the invention embodies one or more of the characteristics described below and in the Figures. The invention provides a nickel particulate form for formation of a zero-valent nickel complex with a bidentate phosphorus-containing ligand, wherein the nickel particulate form has a large surface area as measured by the amount of gas molecules absorbed by the nickel particles (e.g., via BET Specific Surface Area measurements) and the nickel particulate form has a large number of small crystallites.

For example, the nickel particulate form can have a BET Specific Surface Area of at least about 1 m<sup>2</sup>/gm; more preferably, a BET Specific Surface Area of at least about 2 m<sup>2</sup>/gm; even more preferably, a BET Specific Surface Area of at least about 4 m<sup>2</sup>/gm; further more preferably, a BET Specific Surface Area of at least about 10 m<sup>2</sup>/gm.

Desirable nickel particulate forms can have a combination of physical characteristics. For example, preferred nickel particulate forms can have a combination of two or more of the following properties: a BET Specific Surface Area of at least about 1 m<sup>2</sup>/gm; nickel crystallites of average size of no greater than about 100 nm as determined by temperature programmed X-ray diffraction (TP-XRD); a C10 value that is less than about 20 nm after reduction at 300-400 °C; at least about 10<sup>16</sup> surface crystallites of size C10 or less per gram nickel; at least about 2 x10<sup>15</sup> surface crystallites per gram as calculated for cuboidal crystallites; a nickel crystallite size distribution span greater than 1.0.

In general, nickel particulate forms with two or more of these properties can effectively form complexes with phosphorus-containing ligands. More preferably, nickel particulate forms with three or more of these properties effectively form complexes with phosphorus-containing ligands.

The BET Specific Surface Area of a nickel particulate form can be a relevant physical property for nickel particulate forms. In general, nickel particulate forms with

higher BET Specific Surface Areas exhibit improved complex formation with phosphorus-containing ligands. Thus, when combined with other desirable features, the nickel particulate form can have a BET Specific Surface Area of at least about 1 m<sup>2</sup>/gm. However, the nickel particulate form preferably has a BET Specific Surface Area greater than 2 m<sup>2</sup>/gm, more preferably the nickel particulate form can have a BET Specific Surface Area greater than 4 m<sup>2</sup>/gm, even more preferably the nickel particulate form can have a BET Specific Surface Area of greater than about 10 m<sup>2</sup>/gm. Desirable nickel particulate forms can have a BET Specific Surface Area of 100 m<sup>2</sup>/gm or more. For example, the nickel particulate form can have a BET Specific Surface Area greater than 11 m<sup>2</sup>/gm, or greater than 12 m<sup>2</sup>/gm, or greater than 13 m<sup>2</sup>/gm, or greater than 14 m<sup>2</sup>/gm, or greater than 15 m<sup>2</sup>/gm, or greater than 16 m<sup>2</sup>/gm, or greater than 17 m<sup>2</sup>/gm, or greater than 18 m<sup>2</sup>/gm, or greater than 20 m<sup>2</sup>/gm. For example, the nickel particulate form can have a BET Specific Surface Area of about 1 m<sup>2</sup>/gm to about 100 m<sup>2</sup>/gm, or any numerical value between 1-100 m<sup>2</sup>/gm, or between 10-50 m<sup>2</sup>/gm.

While not wishing to be bound by theory, nickel atoms from nickel particulate forms having a large surface, for example, as measured by the BET Specific Surface Area, may more readily be released from the particulate nickel and combine with phosphorus-containing ligands. Alternatively, the phosphorus-containing ligands may have greater access to the larger surface area of nickel particulate forms with higher BET Specific Surface Areas.

BET surface area, or gas absorption, measurement techniques can be used to measure the surface area and porosity of the particles present in a sample. Molecules of an adsorbate gas are physically adsorbed onto the particle surfaces, including the surfaces of any pores or crystallites, under controlled conditions within a vacuum chamber. For example, BET Specific Surface Area (BET SSA) can be measured by observing nitrogen adsorption using the Tristar 3000 Nitrogen Adsorption Instrument after degassing the samples under vacuum at 105 °C overnight. Multi-point BET measurements can be made using a partial pressure range of 0.05-0.3 P/Po. An adsorption isotherm can be obtained by measuring the pressure of the gas above the sample as a function of the volume of gas introduced into the chamber. The linear region of the adsorption isotherm can then be used

to determine the volume of gas required to form a monolayer across the available particle surface area, using BET theory, as described by the following equation:

$$\frac{1}{v[(P/P_0)-1]} = \frac{c-1}{v_m} \left( \frac{P}{P_0} \right) + \frac{1}{v_m c}$$

- where v is the volume of gas, P is the pressure, P<sub>0</sub> is the saturation pressure, v<sub>m</sub> is the  
 5 volume of gas required to form a monolayer and c is the BET constant. Plotting relative pressure, φ (=P/P<sub>0</sub>), and volume allows the volume of a monolayer to be determined from the gradient and intercept of the line.

- The surface area of nickel particulate forms can also be measured by a Laser Diffraction Specific Surface Area technique. Nickel particulate forms can have a Laser  
 10 Diffraction Specific Surface Area of at least about 0.4 m<sup>2</sup>/gm. Also, at least 10% of the nickel particles (D<sub>10</sub>) can have a diameter of no greater than about 4 μm.

- Laser Diffraction Specific Surface Area (LD SSA) and particle size distribution (PSD) can be measured with a Mastersizer 2000 Particle Size Analyser (e.g., from Malvern Instruments Ltd using the Hydro 2000MU accessory and water as the dispersant).  
 15 Light having a certain wavelength measured in micrometers is diffracted by the smaller size particles. The angle of diffraction will depend on the range of sizes present. The following equation can be used to report the Specific Surface Area (SSA):

$$SSA = \frac{6 \sum \frac{V_i}{d_i}}{\rho \sum V_i} = \frac{6}{\rho D[3,2]}$$

- where V<sub>i</sub> is the relative volume in class i with a mean class diameter of d<sub>i</sub>, ρ is the density  
 20 of the material, and D[3,2] is the surface area weighted mean diameter. This calculation can be carried out automatically within the laser diffraction system software. LD SSA provides a means of rapidly estimating the particle surface area. In carrying out this calculation, it is often assumed that the particles are substantially spherical, solid spheres.

- The surface characteristics of the nickel particles composed of the crystallites can  
 25 be such that a ratio of BET Specific Surface Area to Laser Diffraction Specific Surface Area is between 15 and 25.

Nickel particulate forms can have on average per gram at least about  $10^{15}$  surface crystallites per gram nickel, preferably at least about  $5 \times 10^{15}$  surface crystallites per gram nickel, more preferably at least about  $10^{16}$  surface crystallites per gram nickel, even more preferably at least about  $5 \times 10^{16}$  surface crystallites per gram nickel, and more preferably at least about  $10^{17}$  surface crystallites per gram nickel. By a "surface crystallite" is meant a nickel crystallite on or within a nickel particle, where at least one side or edge of the crystallite is exposed to the surroundings. While not wishing to be bound by theory, the inventors herein believe that the suitability of nickel particulate forms having at least about  $10^{15}$  to  $10^{17}$  surface crystallites present is related to the presentation on the particle surface of numerous crystallite edges, which are believed to be more reactive than planar crystallite faces. The greater reactivity of the crystallite edges can be related to steric factors, electronic factors, or both in the interaction of the approaching ligand in solution to the surface of the solid nickel particulate form.

The desirable nickel particulate forms can have nickel crystallites of average size of no greater than about 70 nm (e.g., instead of 100 nm) as determined by temperature programmed X-ray diffraction (TP-XRD); or preferably the nickel crystallites have an average crystallite size of no greater than about 50 nm (instead of 100 nm or 70 nm); or more preferably the nickel crystallites have an average crystallite size of no greater than about 30 nm (instead of 100 nm, 70 nm or 50 nm). In general, nickel particulate forms with smaller nickel crystallites, particularly when combined with other desirable physical properties, are preferred.

The high degree of reactivity of the inventive nickel form is believed to arise, at least in part, from the properties of the nickel metal crystallites forming the particles. The inventive nickel particles can be composed of crystallites, regions of local crystalline order within the larger, disordered particle, wherein an average crystallite size (diameter) can be no greater than about 20-25 nm. More preferred nickel particulate forms can include nickel crystallite sizes with diameters in the range of 0.1 to 10 nm.

The nickel particulate forms can have combinations of even more desirable physical properties. For example, desirable nickel particulate forms can have on average have at least about  $5 \times 10^{16}$  surface crystallites (e.g., instead of  $10^{16}$  surface crystallites) of size C10 or less per gram nickel. More preferably, desirable nickel particulate forms can

have on average have at least about  $10^{17}$  surface crystallites (e.g., instead of  $10^{16}$  or  $5 \times 10^{16}$  surface crystallites) of size C10 or less per gram nickel.

In addition, the nickel crystallite size distribution span can be greater than 1.5. Crystallite size is typically measured as a diameter of the crystallite, for example, along  
5 the major dimension.

Other physical properties that the nickel particulate forms can have include those where at least 10% of the particles have a diameter (D10) of no greater than about 6  $\mu\text{m}$  or preferably no greater than about 4  $\mu\text{m}$ . The surface characteristics of the nickel particles composed of the crystallites can be such that the nickel particles have a ratio of BET  
10 Specific Surface Area to D10 of about  $0.3 \times 10^6$  m/gm to about  $10.0 \times 10^6$  m/gm, or about  $0.5 \times 10^6$  m/gm to about  $5 \times 10^6$  m/gm.

The nickel particulate form is zero-valent, i.e., metallic, nickel.

The nickel particulate form can be substantially dry, for example, a powder or particulate form. The nickel particulate form can be suspended, dissolved or partially  
15 dissolved in a solvent. The solvent is typically a non-aqueous solvent. The solvent can be an organic solvent. For example, the solvent for the nickel particulate form can be branched or unbranched C2-C20 hydrocarbon with one or more double bonds. The solvent for the nickel particulate form can be an organonitrile liquid such as a branched or unbranched C2-C20 alkyl or alkylene substituted by at least one nitrile (CN) group.  
20 Examples of solvent include pentenenitriles such as 2-pentenenitrile, 3-pentenenitrile, 4-pentenenitrile, 2-methyl-3-butenitrile, and 2-methyl-2-butenitrile.

The nickel particulate form can be substantially pure nickel in dry form or suspended or dissolved in a solvent. For example, the nickel particulate form can be isolated without, or be substantially free of, an associated ion (e.g., without an anion) or  
25 metal (e.g., without aluminum, copper, tungsten, zinc and/or iron). The nickel particular form can be free of impurities such as carbon-containing, silicon-containing and/or nitrogen-containing moieties and/or compounds. The nickel particulate form can be substantially free of impurities such as sodium, calcium, magnesium, potassium, and/or other alkali metals and/or alkaline earth metals. For example, the nickel particulate form  
30 can have less than 10% impurities, or less than 7% impurities, or less than 5% impurities, or less than 4% impurities, or less than 3% impurities, or less than 2% impurities, or less

than 1% impurities, or less than 0.7% impurities, or less than 0.6% impurities, or less than 0.5% impurities, or less than 0.4% impurities, or less than 0.3% impurities, or less than 0.2% impurities, or less than 0.1% impurities, or less than 0.07% impurities, or less than 0.05% impurities, or less than 0.03% impurities, or less than 0.01% impurities. Other than  
5 their sulfur content, the nickel particulate form can be 95% to 99.9% pure, or 98% to 99.99% pure.

Such nickel particulate forms can be combined with a phosphorus-containing ligand, for example, any of those described herein.

## 10 Phosphorus-Containing Ligands

A “phosphorus-containing ligand” as the term is used herein refers to a ligand containing at least one phosphorus atom, that is suitable for formation of a complex with a transition metal such as nickel, wherein the complex can possess catalytic activity for an organic reaction such as a hydrocyanation reaction of an olefin, such as the  
15 hydrocyanation of butadiene to yield pentenenitrile, or the hydrocyanation of pentenenitrile to yield adiponitrile.

The hydrocyanation catalysts provided herein are composed of nickel and at least one phosphorus-containing (P-containing) ligand. The P-containing ligand can, for example, be a phosphite, a phosphonite, a phosphinite, a phosphine, and a mixed P-  
20 containing ligand or a combination of such members. The P-containing ligands may be monodentate or multidentate, for example, bidentate or tridentate.

The P-containing ligands can chemically bond to a metal, e.g., nickel, as complexes comprising a metal, and one or more P-containing ligands.

The term “monodentate” is known in the art and means only one phosphorus atom  
25 of the ligand (which can contain one or more phosphorus atoms per molecule) may be bonded to a single metal (e.g., nickel) atom. Two monodentate ligands can separately be bonded to the metal atom, or one monodentate ligand and one multidentate ligand can each be bonded to the metal atom.

The term “bidentate” is known in the art and means two phosphorus atoms of the  
30 ligand (which can contain two or more phosphorus atoms per molecule) may be bonded to a single metal (e.g., nickel) atom. A bidentate P-containing ligand can, for example, be

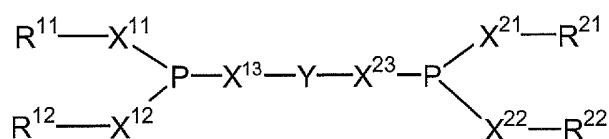
selected from the group consisting of a bidentate phosphite, a bidentate phosphonite, a bidentate phosphinite, a bidentate phosphine or a mixed bidentate ligand.

A mixed bidentate ligand can, for example, be selected from the group consisting of a phosphite-phosphonite, a phosphite-phosphinite, a phosphite-phosphine, a phosphonite-phosphinite, a phosphonite-phosphine, and a phosphinite-phosphine.

The term "tridentate" means three phosphorus atoms of the ligand (which can contain three or more phosphorus atoms per molecule) may be bonded to a single metal (e.g., nickel) atom. The terms "bidentate" and "tridentate" may also be called chelate ligands.

The phosphorous-containing ligand may be a monodentate phosphite, monodentate phosphonite, monodentate phosphinite, monodentate phosphine, bidentate phosphite, bidentate phosphonite, bidentate phosphinite, or bidentate phosphine, and any combination of these members. Further, the phosphorous-containing ligand may be a monodentate phosphite to form the nickel complex of the monodentate phosphite then the nickel complex of the monodentate phosphite may be combined with a bidentate phosphorous-containing ligand. Likewise, the phosphorous-containing ligand may be a bidentate phosphite further comprising a monodentate phosphite. For example, suitable phosphorus-containing ligands include mixtures of one or more members selected from monodentate phosphite ligands, bidentate phosphite ligands and mixtures of monodentate and bidentate phosphite ligands.

Suitable phosphorus-containing ligands for the catalyst include those selected from the group consisting of compounds of Formula (III), Formula (IV), Formula (IVa) or combinations thereof. Formula (III) has the structure:



Formula (III)

wherein,

$\text{X}^{11}$ ,  $\text{X}^{12}$ ,  $\text{X}^{13}$ ,  $\text{X}^{21}$ ,  $\text{X}^{22}$  and  $\text{X}^{23}$  independently represent oxygen or a single (direct) bond;

$R^{11}$  and  $R^{12}$  independently represent identical or different, single or bridged organic radicals;

$R^{21}$  and  $R^{22}$  independently represent identical or different, single or bridged organic radicals; and

5 Y represents a bridging group.

For example,  $X^{11}$ ,  $X^{12}$ ,  $X^{13}$ ,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen. In such a case, the bridging group Y is bonded to phosphite groups. Alternatively,  $X^{11}$  and  $X^{12}$  may each be oxygen and  $X^{13}$  a single bond, or  $X^{11}$  and  $X^{13}$  can each be oxygen and  $X^{12}$  a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphonite. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{21}$  and  $X^{22}$  may each be oxygen and  $X^{23}$  a single bond, or  $X^{21}$  and  $X^{23}$  may each be oxygen and  $X^{22}$  a single bond, or  $X^{23}$  may be oxygen and  $X^{21}$  and  $X^{22}$  each a single bond, or  $X^{21}$  may be oxygen and  $X^{22}$  and  $X^{23}$  each a single bond, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite, phosphonite, phosphinite or phosphine, preferably a phosphonite. Preferably,  $X^{13}$  may be oxygen and  $X^{11}$  and  $X^{12}$  each may be a single bond, or  $X^{11}$  may be oxygen and  $X^{12}$  and  $X^{13}$  each may be a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphonite. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{23}$  may be oxygen and  $X^{21}$  and  $X^{22}$  each a single bond, or  $X^{21}$  may be oxygen and  $X^{22}$  and  $X^{23}$  each a single bond, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite, phosphinite or phosphine, preferably a phosphinite. In some cases,  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphine. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite or phosphine, preferably a phosphine. The bridging group Y is particularly an arylene group which is substituted, for example by  $C_1$ - $C_4$ -alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, arylene, such as phenylene, or such an arylene is unsubstituted. The arylene can be a group having from 6 to 20 carbon atoms in the aromatic system, in particular pyrocatechol, bis(phenol) or bis(naphthol). The

$R^{11}$  and  $R^{12}$  radicals may each independently be identical or different organic radicals. Advantageous  $R^{11}$  and  $R^{12}$  radicals may be aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in particular by  $C_1$ - $C_4$ -alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups. The  $R^{21}$  and  $R^{22}$  radicals may each independently be identical or different organic radicals. Advantageous  $R^{21}$  and  $R^{22}$  radicals may be aryl radicals, particularly those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in particular by  $C_1$ - $C_4$ -alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups. The  $R^{11}$  and  $R^{12}$  radicals may each be separate or bridged. The  $R^{21}$  and  $R^{22}$  radicals may also each be separate or bridged. The  $R^{11}$ ,  $R^{12}$ ,  $R^{21}$  and  $R^{22}$  radicals may each be separate, two may be bridged and two separate, or all four may be bridged, in the manner described.

Formula (IV) has the structure,

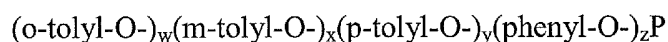


Formula (IV)

wherein,

$X^1$ ,  $X^2$  and  $X^3$  independently represent oxygen or a single direct bond; and  $R^1$ ,  $R^2$  and  $R^3$  are each independently identical or different organic radicals.

For example,  $R^1$ ,  $R^2$  and  $R^3$  can each independently be alkyl radicals preferably having from 1 to 10 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, or aryl groups such as phenyl, o-tolyl, m-tolyl, p-tolyl, 1-naphthyl, 2-naphthyl, or hydrocarbyl, preferably having from 1 to 20 carbon atoms, such as 1,1'-biphenol, 1,1'-binaphthol. The  $R^1$ ,  $R^2$  and  $R^3$  groups may be bonded together directly, i.e. not solely via the central phosphorus atom. Preference may be given to the  $R^1$ ,  $R^2$  and  $R^3$  groups not being bonded together directly.  $R^1$ ,  $R^2$  and  $R^3$  groups can also be radicals selected from the group consisting of phenyl, o-tolyl, m-tolyl and p-tolyl. In particular, a maximum of two of the  $R^1$ ,  $R^2$  and  $R^3$  groups should be phenyl groups. A maximum of two of the  $R^1$ ,  $R^2$  and  $R^3$  groups can be o-tolyl groups. Particular compounds that may be used are those of the formula (IVa) below:



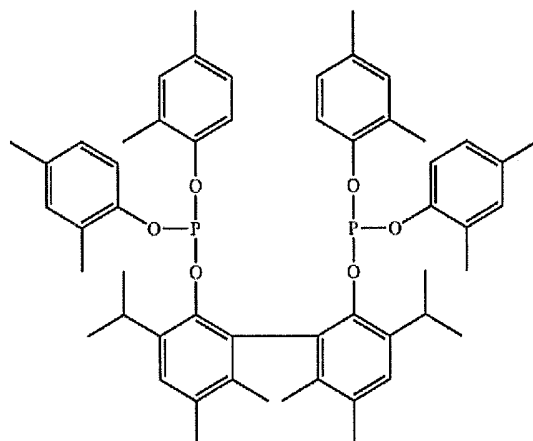
Formula (IVa)

where w, x, y, z are each a natural number and the following conditions apply:

$w+x+y+z=3$  and z is less than or equal to 2.

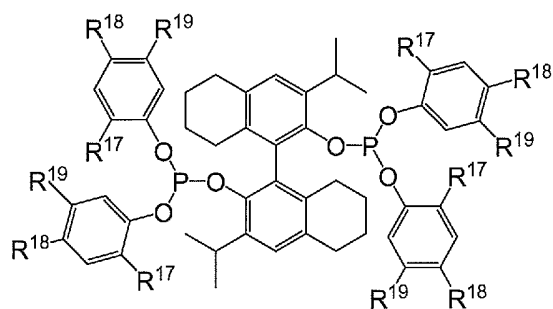
- 5 Examples of compounds of formula (IVa) are (o-tolyl-O)<sub>3</sub>P, (p-tolyl-O)(phenyl-O)<sub>2</sub>P, (m-tolyl-O)(phenyl-O)<sub>2</sub>P, (o-tolyl-O)(phenyl-O)<sub>2</sub>P, (p-tolyl-O)<sub>2</sub>(phenyl-O)<sub>2</sub>P, (m-tolyl-O)<sub>2</sub>(phenyl-O)<sub>2</sub>P, (o-tolyl-O)<sub>2</sub>(phenyl-O)<sub>2</sub>P, (m-tolyl-O)(p-tolyl-O)(phenyl-O)<sub>2</sub>P, (o-tolyl-O)(p-tolyl-O)(phenyl-O)<sub>2</sub>P, (o-tolyl-O)(m-tolyl-O)(phenyl-O)<sub>2</sub>P, (p-tolyl-O)<sub>3</sub>P, (m-tolyl-O)(p-tolyl-O)<sub>2</sub>P, (o-tolyl-O)(p-tolyl-O)<sub>2</sub>P, (m-tolyl-O)<sub>2</sub>(p-tolyl-O)<sub>2</sub>P, (o-tolyl-O)<sub>2</sub>(p-tolyl-O)<sub>2</sub>P, (o-tolyl-O)(m-tolyl-O)(p-tolyl-O)<sub>2</sub>P, (m-tolyl-O)<sub>3</sub>P, (o-tolyl-O)(m-tolyl-O)<sub>2</sub>P, (o-tolyl-O)<sub>2</sub>(m-tolyl-O)<sub>2</sub>P or mixtures of such compounds.

An example of a useful bidentate phosphite ligand is Ligand (V), shown below

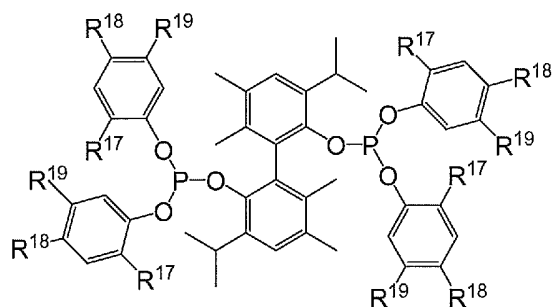


Ligand (V).

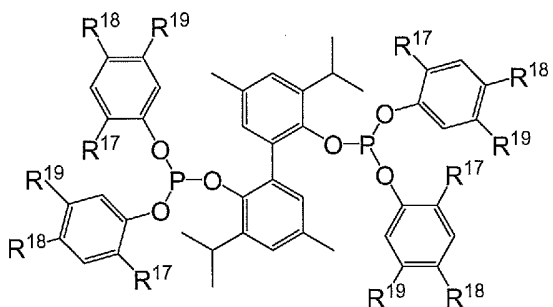
Further examples of bidentate phosphite ligands that are useful in the present process include those having the Formulae (VI) to (IX), shown below wherein for each formula, R<sup>17</sup> is selected from the group consisting of methyl, ethyl or isopropyl, and R<sup>18</sup> and R<sup>19</sup> are independently selected from H or methyl:



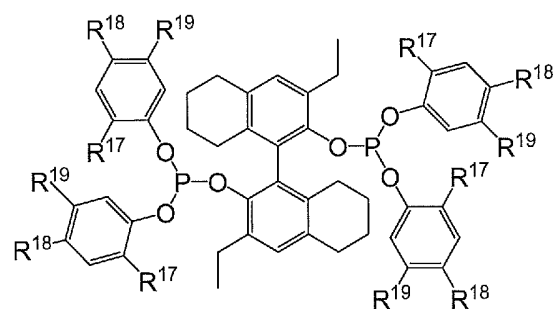
(VI)



(VII)



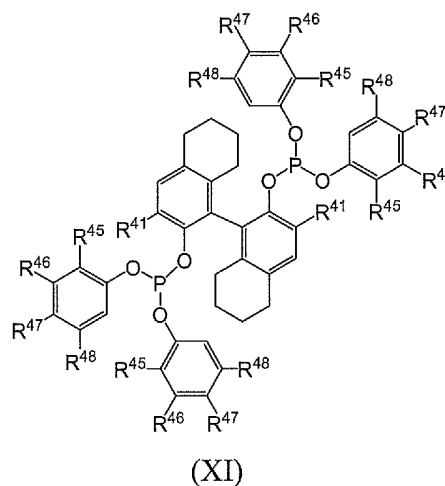
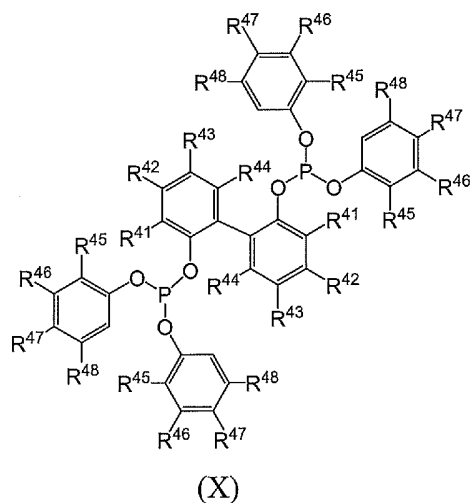
(VIII)



(IX)

Additional examples of bidentate phosphite ligands that are useful in the present  
 10 process include a ligand selected from a member of the group represented by Formulae

(X) and (XI), in which all like reference characters have the same meaning, except as further explicitly limited:



5

wherein,

$R^{41}$  and  $R^{45}$  are independently selected from the group consisting of  $C_1$  to  $C_5$  hydrocarbyl, and each of  $R^{42}$ ,  $R^{43}$ ,  $R^{44}$ ,  $R^{46}$ ,  $R^{47}$  and  $R^{48}$  is independently selected from the group consisting of H and  $C_1$  to  $C_4$  hydrocarbyl. As used herein, “hydrocarbyl” particularly is alkyl or cycloalkyl.

10

For example, the bidentate phosphite ligand can be selected from a member of the group represented by Formula (X) and Formula (XI), wherein

$R^{41}$  is methyl, ethyl, isopropyl or cyclopentyl;

$R^{42}$  is H or methyl;

15

$R^{43}$  is H or a  $C_1$  to  $C_4$  hydrocarbyl;

$R^{44}$  is H or methyl;

$R^{45}$  is methyl, ethyl or isopropyl; and

$R^{46}$ ,  $R^{47}$  and  $R^{48}$  are independently selected from the group consisting of H and  $C_1$  to  $C_4$  hydrocarbyl.

20

As additional examples, the bidentate phosphite ligand can be selected from a member of the group represented by Formula (X), wherein

$R^{41}$ ,  $R^{44}$ , and  $R^{45}$  are methyl;

$R^{42}$ ,  $R^{46}$ ,  $R^{47}$  and  $R^{48}$  are H; and

$R^{43}$  is a  $C_1$  to  $C_4$  hydrocarbyl;

or

R<sup>41</sup> is isopropyl;

R<sup>42</sup> is H;

R<sup>43</sup> is a C<sub>1</sub> to C<sub>4</sub> hydrocarbyl;

5 R<sup>44</sup> is H or methyl;

R<sup>45</sup> is methyl or ethyl;

R<sup>46</sup> and R<sup>48</sup> are H or methyl; and

R<sup>47</sup> is H, methyl or tertiary-butyl;

or the bidentate phosphite ligand can be selected from a member of the

10 group represented by Formula XI, wherein

R<sup>41</sup> is isopropyl or cyclopentyl;

R<sup>45</sup> is methyl or isopropyl; and

R<sup>46</sup>, R<sup>47</sup>, and R<sup>48</sup> are H.

As yet another example, the bidentate phosphite ligand can be represented by  
15 Formula (X), wherein R<sup>41</sup> is isopropyl; R<sup>42</sup>, R<sup>46</sup>, and R<sup>48</sup> are H; and R<sup>43</sup>, R<sup>44</sup>, R<sup>45</sup>, and R<sup>47</sup>  
are methyl.

It will be recognized that Formulae (V) to (XI) are two-dimensional  
representations of three-dimensional molecules and that rotation about chemical bonds can  
occur in the molecules to give configurations differing from those shown. For example,  
20 rotation about the carbon-carbon bond between the 2- and 2'- positions of the biphenyl,  
octahydrobinaphthyl, and or binaphthyl bridging groups of Formulae (V) to (XI),  
respectively, can bring the two phosphorus atoms of each Formula in closer proximity to  
one another and can allow the phosphite ligand to bind to nickel in a bidentate fashion.  
The term "bidentate" is well known in the art and means both phosphorus atoms of the  
25 ligand are bonded to a single nickel atom. In addition, use of an optically active moiety  
such as *sec*-butyl for R<sup>41</sup> can result in optically active catalysts.

### Bidentate Phosphorus-Containing Ligand Synthesis

Ligand (V) is an example of a bidentate phosphorus-containing ligand. Ligand (V)  
30 may be prepared by any suitable synthetic means known in the art. For example, 3,3'-  
diisopropyl-5,5',6,6'-tetramethyl-2,2'-biphenol can be prepared by the procedure

disclosed in U. S. Published Patent Application No. 2003/0100802 in which 4-methylthymol can undergo oxidative coupling to the substituted biphenol in the presence of a copper chlorohydroxide-TMEDA complex (TMEDA is N,N,N',N'-tetramethylethylenediamine) and air. The phosphorochloridite of 2,4-xylenol, [(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O]<sub>2</sub>PCl, can be prepared, for example, by the procedure disclosed in U.S. Published Patent Application No. 2004/0106815. To selectively form this phosphorochloridite, anhydrous triethylamine and 2,4-xylenol can be added separately and concurrently in a controlled manner to PCl<sub>3</sub> dissolved in an appropriate solvent under temperature-controlled conditions. The reaction of this phosphorochloridite with the 3,3'-diisopropyl-5,5',6,6'-tetramethyl-2,2'-biphenol to form the desired Ligand (V) can be performed, for example, according to the method disclosed in U.S. Patent No. 6,069,267. The phosphorochloridite can be reacted with 3,3'-diisopropyl-5,5',6,6'-tetramethyl-2,2'-biphenol in the presence of an organic base to form Ligand (V), which can be isolated according to techniques available in the art, for example as also described in U.S. Patent No. 6,069,267.

Additional bidendate ligands, ligand complexes, and methods of making the same, are disclosed in U.S. Patent No. 6,171,996, herein incorporated by reference in its entirety.

### Nickel-Phosphorus Ligand Complex Formation

Nickel-phosphorus ligand complexes can be effective hydrogenation catalysts. Such nickel-phosphorus ligand complexes can be formed by mixing nickel metal particles, and one or more phosphorus-containing ligands in an organonitrile solvent. A Lewis acid can also be included in the nickel metal – phosphorus ligand complex forming solution. As described herein sulfur sources can be added to the mixture of the nickel metal particles, and one or more phosphorus-containing ligands to improve complex formation between nickel atoms and the phosphorus-containing ligands.

The phosphorus-containing ligand(s) can be any of those described herein.

The nickel metal used for complex formation can be pre-treated with a sulfur source as described herein or it can be treated with a sulfur source while in the nickel metal – phosphorus ligand complex forming solution.

The nickel metal used for complex formation with one or more phosphorus-containing ligand(s) can be a particulate (powdered) nickel metal. Particulate nickel metals can have a range of particle sizes. A “nickel particle” is a discrete particle, typically visible in a scanning electron micrograph. For example, at least 10% of the nickel particles  
5 can have a diameter (D10) of less than about 6  $\mu\text{m}$ . The term “D10” refers to the largest particle diameter of the smallest 10% of the particles in a sample of particles. Useful particulate nickel starting materials can have surface crystallites. A “crystallite” is a region of local crystalline order within, or on, a nickel particle. A “surface crystallite” refers to a crystallite contained within a particle, but wherein a portion of the crystallite is exposed to  
10 the environment surrounding the particle, such as an organic liquid containing a ligand. Each nickel particle ideally has a large number of crystallites. For example, the nickel can have an average of at least about  $10^{15}$  surface crystallites per gram of nickel. The nickel metal particles can also have a BET Specific Surface Area of at least about  $1 \text{ m}^2/\text{gm}$  or the BET Specific Surface Area for the nickel metal particles can be at least about  $10 \text{ m}^2/\text{gm}$ .  
15 Such nickel metal particles can be treated with a sulfur source prior to complex formation with phosphorus-containing ligand(s), or during complex formation with phosphorus-containing ligand(s).

The organonitrile solvent can be selected from one or more members of the group consisting of 2-pentenitrile, 3-pentenitrile, 4-pentenitrile, 2-methyl-3-butenitrile,  
20 2-methyl-2-butenitrile, adiponitrile, 2-methylglutaronitrile, and ethylsuccinonitrile. For example, the organonitrile can be a pentenenitrile or a mixture of pentenenitriles.

The Lewis acid can be selected from the group consisting of inorganic or organometallic compounds in which the cation is selected from the group including scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron,  
25 aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium, lanthanum, europium, ytterbium, tantalum, samarium, tin and mixtures thereof. A Lewis acid can be selected from the group consisting of zinc chloride, ferrous chloride, or a combination of zinc chloride, ferrous chloride and mixtures thereof. For example, the Lewis acid can be zinc chloride.

30 The nickel metal, sulfur source, Lewis acid, phosphorus-containing ligands and/or organonitrile solvent can be substantially free of metals such as aluminum, copper,

tungsten, mercury and/or iron. For example, the nickel particles, sulfur source, Lewis acid, phosphorus-containing ligands and/or organonitrile solvent can be substantially free of silicon-containing moieties and/or compounds. The nickel particles, sulfur source, Lewis acid, phosphorus-containing ligands and/or organonitrile solvent can also be substantially free of sodium, calcium, magnesium, potassium, and/or other alkali metals and/or alkaline earth metals.

The nickel and/or sulfur source mixed with the phosphorus-containing ligands can be substantially free of hydrocarbons, carbon dioxide, and other carbon containing compounds. For example, the nickel and/or sulfur source mixed with the phosphorus-containing ligands can be substantially free of silicon, sodium, potassium, calcium, magnesium, phosphorus, aluminum, copper, tungsten, mercury, and/or iron impurities. The nickel and/or sulfur source mixed with the phosphorus-containing ligands can have less than 10% impurities, or less than 7% impurities, or less than 5% impurities, or less than 4% impurities, or less than 3% impurities, or less than 2% impurities, or less than 1% impurities, or less than 0.7% impurities, or less than 0.6% impurities, or less than 0.5% impurities, or less than 0.4% impurities, or less than 0.3% impurities, or less than 0.2% impurities, or less than 0.1% impurities, or less than 0.07% impurities, or less than 0.05% impurities, or less than 0.03% impurities, or less than 0.01% impurities.

The nickel particles, Lewis acid and one or more phosphorus-containing ligands can be mixed with the organonitrile solvent at a temperature and for a time sufficient for complex formation between nickel atoms and the phosphorus-containing ligands. For example, the nickel particles, Lewis acid and one or more phosphorus-containing ligands can be mixed with the organonitrile solvent at a temperature between 0°C and 150°C for about 15 minutes to about 24 hours. For example, a temperature sufficient for complex formation can be about 4°C to about 130°C, or about 10°C to about 110°C, or about 15°C to about 100°C, or about 20°C to about 100°C, or about 40°C to about 100°C, or about 60°C to about 80°C.

A time sufficient for complex formation is a time for reaching equilibrium in the formation of nickel – phosphorus containing ligands. For example, a time for reaching equilibrium can be about 5 minutes to about 24 hours, or about 10 minutes to about 12 hours, or about 15 minutes to about 8 hours, or about 20 minutes to about 4 hours, or

about 20 minutes to about 2 hours. A preferred time for reaching equilibrium can be about 20 minutes to about 40 minutes, or about 30 minutes.

The nickel-phosphorus ligand complexes can typically be formed under a non-oxygen atmosphere. For example, a nitrogen atmosphere can be employed.

5

### **Assay for Nickel-Phosphorus Ligand Complex Formation**

To evaluate the suitability of nickel preparations for preparation of hydrocyanation catalysts, a nickel preparation is evaluated to ascertain whether nickel metal in the nickel preparation forms a complex with one or more phosphorus-containing ligands at a rate  
10 sufficient for use in a manufacturing process.

An assay can be used to evaluate the suitability of nickel preparations for preparation of hydrocyanation catalysts. Such an assay involves mixing a nickel test sample (e.g., 1-7 wt% nickel relative to the total weight of the reaction mixture) with one or more phosphorus-containing ligands and a Lewis acid in an organonitrile solvent. The  
15 phosphorus-containing ligand can be any of the phosphorus-containing ligands described herein. Preferably, the phosphorus-containing ligand can be a bidentate phosphite ligand such as Ligand (V). The Lewis acid can be zinc chloride. The organonitrile solvent can be pentenenitrile.

A sample of known mass of the nickel powder (e.g., 4 wt% nickel) can be  
20 contacted with about 0.5 to 2.5 moles Lewis acid (such as zinc chloride) per mole bidentate phosphite ligand (e.g., Ligand (V)) in a 3-pentenenitrile (3PN) solution. The mixture can be warmed for a period of hours, during which time the level of solubilized nickel in solution is measured by liquid chromatography (LC). The amount of ligand and/or zinc chloride in the assay mixture can be in stoichiometric excess relative to the  
25 amount of nickel powder added. However, it may be desirable to limit the amount of ligand and/or zinc chloride in the assay mixture relative to the amount of nickel powder added. Thus, the concentration of ligand and/or zinc chloride in the assay mixture can be limiting relative to the amount of nickel powder present.

Nickel becomes soluble in the organonitrile solvent (e.g., a hydrocyanation  
30 substrate such as 3PN) when it forms a complex with the phosphorus-containing ligand. Unreacted nickel metal can be removed from the mixture by filtration or centrifugation.

To avoid contact with air, a reactor bottle, equipped with a magnetic stir bar, can be charged with the reactants inside a Vacuum Atmospheres dry box operating with a dry nitrogen atmosphere. The reactants added to this bottle can include the nickel preparation to be tested, one or more phosphorus-containing ligands (e.g. Ligand (V)), where the solvent is 3-pentenitrile. Zinc chloride can also be added to the assay mixture.

To standardize the test procedure, 4-5 wt% nickel is mixed at about 60 °C to 80 °C in a 3-pentenitrile (3PN) solution containing about 0.5 to 2.5 moles zinc chloride per mole bidentate phosphorus-containing ligand. For example, 4 wt% nickel preparation can be mixed with approximately 5.25 wt% Ligand (V) and 6300 ppm  $\text{ZnCl}_2$  in a solution of 3-pentenitrile. The zinc to Ligand (V) molar ratio employed is then about 0.75.

The reactor bottle can be sealed, removed from the dry box, and moved to a laboratory fume hood where it can be placed on a magnetic stir plate. The reaction mixture within the reaction bottle can then be heated to 60°C - 80°C (e.g., 60°C). Sufficient agitation can be used to suspend the nickel-containing solid in this reaction mixture.

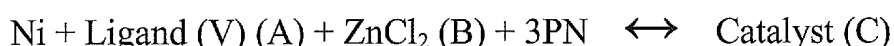
Filtered liquid samples from the reaction mixture can be removed from the reactor bottle at intervals of from 5 minutes to one hour. A final sample can be taken after 24 hours. The amount of soluble nickel in the samples is measured using liquid chromatography (LC). This limit of detection for this assay is about 20-50 ppm soluble nickel in the form of soluble nickel complexes of Ligand (V).

The activity of a nickel preparation is therefore measured by its propensity to form soluble zero-valent nickel metal phosphorus ligand complexes. The activity of a nickel preparation can be compared to a control nickel preparation in this assay for formation of soluble zero-valent nickel metal phosphorus ligand complexes. For example, the control nickel preparation can be a nickel preparation that is determined to have inadequate activity. An active nickel preparation is therefore a nickel form that has more activity than the inactive negative control nickel preparation. The control nickel preparation can be a nickel preparation that is determined to have good activity. An active nickel preparation is therefore a nickel form that has about the same or more activity than the active positive control nickel preparation.

One example of a control nickel preparation is a nickel powder obtained from MetChem BNC using a one-step hydrogenation process (i.e., not including calcination

pretreatment), where the hydrogenation is performed at 400 °C. Such a nickel preparation made from MetChem BNC is described in Table 1 and has nickel activity that is typically below that which enables the efficient preparation of the zero-valent nickel complexes suitable for use in a manufacturing process involving a hydrocyanation catalyst.

- 5           An empirical rate equation for Ni dissolution in catalyst-preparation assay is employed to provide a numerical value indicative of nickel ‘activity’ (ability to become a soluble catalyst complex with Ligand (V)) in the following reaction:



The following equation describes the rate of Nickel-Ligand (V) catalyst formation:

$$10 \quad r = a * k' * w_{\text{Ni}} * C_A^{a'} * C_B^b * [1 - C_c / (K_{\text{eq}} * C_A * C_B)] * 2 * (C_A / C_{A0}) / [1 + (C_A / C_{A0})]$$

where:

$a$  = activity of nickel

$w_{\text{Ni}}$  = weight loading of nickel (weight of nickel/weight of solution)

$k'$  = Arrhenius rate constant:

$$15 \quad [(\text{mmoles Ni/liter})^{0.5} / \text{hr}] = 1.539 \times 10^{10} \exp[-6832.1/T(\text{K})]$$

$C_A$  = concentration of Ligand (V) (mmol/L)

$C_{A0}$  = Initial concentration of Ligand (V) (mmol/L)

$C_B$  = concentration of  $\text{ZnCl}_2$  (mmol/L)

$$20 \quad a' = \text{order of reaction with respect to D80} = 0$$

$b$  = order of reaction with respect to  $\text{ZnCl}_2 = 0.5$

$K_{\text{eq}}$  = equilibrium constant for the chemical reaction  
[liters/mmol] =  $\exp [11555/T(\text{K}) - 35.231]$

$$25 \quad T = \text{temperature in degree Kelvin.}$$

It is assumed that the 3-pentenitrile is in far excess so its order of reaction with respect to the rate of 3-pentenitrile dissolution is considered zero. The order of reaction with nickel loading is considered to be 1.

The rate constant  $k'$  is defined for a standard MetChem BNC reduced at 400 °C under pure hydrogen to nickel. However, to account for other sources of nickel that can have different in properties, a factor is applied that is termed the activity of nickel dissolution. The 'activity' number was chosen to be 1 for the specific condition of  
5 MetChem BNC reduced at 400 °C to nickel, dissolved at 80 °C in the catalyst-preparation solution with  $\text{ZnCl}_2/\text{Ligand (V)}$  molar ratio of 0.8 and 4 wt% nickel loading where dissolution is at a rate of 980 ppm Ni/hr. In principle, a higher activity is essentially a higher rate constant specific to a given nickel. In order to move away from separately determining rate constant for each type of nickel, the activity term is defined to get around  
10 this issue.

Using such an equation, a nickel preparation is active if it has an activity of at least 2.0, preferably at least 3.0 and more preferably at least 4.0.

Nickel preparations are also active if they efficiently form zero-valent nickel phosphorus ligand complexes at a rate suitable for use in a manufacturing process  
15 involving a hydrocyanation catalyst. A suitable rate is a time for achieving equilibrium in the formation of a nickel metal phosphorus ligand complex of no more than 8 hours, no more than 6 hours, no more than 5 hours, no more than 4 hours, no more than 3 hours, no more than 2 hours, no more than 1 hour, or no more than 30 minutes. Nickel preparations that form complexes with phosphorus-containing ligands very slowly (e.g., by requiring  
20 several days or a week for formation) are not active nickel preparations useful for generating hydrocyanation catalysts.

### **Containers for Catalyst Storage and Shipment**

Containers such as barrels, drums, of various sizes and shapes may be used for the  
25 storage and transport of the nickel, phosphorus-containing ligand and/or catalyst. In particular, containers which allow ingress and egress of contents with minimal exposure to the atmosphere and other sources of oxygen may be used. Polymeric materials are particularly used for any contact with the nickel and/or ligand catalyst. Collapsible drums suitable for the nickel and/or catalyst ligand storage and transport are described in WO  
30 2011/094411 published 4 August 2011 and assigned to Pack-Gen of Auburn, Maine USA.

Materials used for such containers and coming into contact with the nickel and/or catalyst ligand include polymers such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polypropylene and polyethylene as well as metal containers that are resistant to leaching by the ligand catalyst.

5 Containers having an oxygen-scavenging core layer are described in U.S. Patent 7,056,565 issued to Chevron and various structural and chemical compositional aspects of the container may be used for storage and transport of ligand compounds.

Containers for oxygen-sensitive products are described in U.S. Patent 7,854,973 issued to Sonoco wherein an oxidation catalyst is provided in a first outer layer to  
10 consume oxygen which diffuses into the interior. Various structural and chemical compositional aspects of U.S. Patent 7,854,973 may be used as containers, provided that the mechanism for scavenging the oxygen does not oxidize the nickel and/or ligand. Wall layers are provided which may be an ethylene-vinyl alcohol copolymer, polyamide homo or copolymer, polyacrylonitrile copolymer, polyvinyl chloride (PVC) or other polymer  
15 with low oxygen permeability.

Catalyst container structures described in U.S. Patent 4,946,068 issued to Amoco and WO 2006/052677 issued to Exxon-Mobil for catalyst storage, transfer and dispensing may be used for storage and transport of the nickel and/or ligands.

Thermoplastic containers for the storage and transportation of dangerous liquid  
20 fillings are described in EP 0 673 841 issued to Mauser-Werke of Bruhl, Germany.

Inert atmospheric packaging (IAP) or modified atmosphere packaging (MAP) is generally useful for storage and transport of the ligands and/or nickel metal preparations described herein. Thus, charging of the ligand/solvent mixture for storage or shipment into an appropriate container is accompanied by, followed by or both, rendering the headspace  
25 above the liquid surface as an inert or very low reactivity atmosphere.

## Definitions

As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise.

30 In this document, the term "or" is used to refer to a nonexclusive or, such that "A or B" includes "A but not B," "B but not A," and "A and B," unless otherwise indicated.

The term "about" can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range. When a range or a list of sequential values is given, unless otherwise specified any value within the range or any value between the given sequential values is also disclosed.

5 BET surface area (BET SSA), or gas absorption, is a measure of the surface area and porosity of nickel metal particles. BET theory relates to the adsorption of gas molecules on a solid surface and provides methods for measurement of the specific surface area of a material. *See, e.g.*, Brunauer et al., J. Am. Chem. Soc. 60: 309 (1938). Molecules of an adsorbate gas are physically adsorbed onto the particle surfaces, including  
 10 the surfaces of any pores or crystallites, under controlled conditions within a vacuum chamber. For example, BET Specific Surface Area (BET SSA) can be measured by observing nitrogen adsorption using the Tristar 3000 Nitrogen Adsorption Instrument after degassing the samples under vacuum at 105 °C overnight. Multi-point BET measurements can be made using a partial pressure range of 0.05-0.3 P/P<sub>0</sub>. An adsorption isotherm is  
 15 obtained by measuring the pressure of the gas above the sample as a function of the volume of gas introduced into the chamber. The linear region of the adsorption isotherm can then be used to determine the volume of gas required to form a monolayer across the available particle surface area, using BET theory, as described by the following equation:

$$\frac{1}{v[(P/P_0)-1]} = \frac{c-1}{v_m} \left( \frac{P}{P_0} \right) + \frac{1}{v_m c}$$

20 where v is the volume of gas, P is the pressure, P<sub>0</sub> is the saturation pressure, v<sub>m</sub> is the volume of gas required to form a monolayer and c is the BET constant. Plotting relative pressure, φ (=P/P<sub>0</sub>), and volume allows the volume of a monolayer to be determined from the gradient and intercept of the line.

The ratio BET SSA/C50 provides a value that is independent of the crystallite's  
 25 geometry. The values obtained for a set of samples, can be correlated with "nickel activity" as defined here, and a reasonable linear correlation between activity and BET SSA/C50 has been found, as discussed herein.

A "crystallite" is a region within a particle of local crystalline order. Each active nickel particle comprises a large number of crystallites.

The term "crystallite size" as used herein refers to an average diameter for a possibly irregularly-shaped crystallite. Crystallite size can be measured as a diameter of the crystallite, for example, along the crystallite's major dimension, or as the cube root of the volume of the crystallite. The crystallite size can be determined by x-ray diffraction (XRD) analysis using procedures and equipment available in the art. An "average crystallite size" or "mean crystallite size" refers to an average (mean) value for a population of crystallite sizes as defined above. An average crystallite size can also be defined as the cube root of the average volume of a sample comprising multiple crystallites, and assumes that all crystallites have the same size and shape. For a distribution of sizes, the mean size can be defined as the mean value of the cube roots of the individual crystallite volumes or the cube root of the mean value of the volumes of the individual crystallites.

The term "C10" is a measure of crystallite sizes in the nickel particulate form, and refers to the largest diameter (e.g., in nanometers) that the smallest 10% of crystallites have in the nickel particulate form. The term "C50" is also a measure of crystallite sizes in the nickel particulate form, and refers to a diameter (size) wherein 50% of the Ni crystallites in a bulk sample have a size less than the stated value. The C50 value is also referred to herein as the mean crystallite size (MCS). The term "C90" is also a measure of crystallite sizes in the nickel particulate form, and refers to a diameter (size) wherein 90% of the nickel crystallites in a bulk sample have a size less than the stated value. C<sub>x</sub> is the size of the crystallite for which x% of the sample has a smaller size. Crystallite size can be measured using X-ray diffraction (XRD).

The term "crystallite size distribution span" as used herein refers to a statistical value denoting a spread in crystallite size defined as  $(C_{90}-C_{10})/C_{50}$ .

A "surface crystallite" as the term is used herein refers to a crystallite contained within a particle, but wherein a portion of the crystallite is exposed to the environment surrounding the particle, such as an organic liquid containing a ligand. To calculate BET SSA / crystallite size ratios, the equations  $BET\ SSA/4\pi(C_{50}/2)^2$  for spherical crystallites and  $BET\ SSA/C_{50}^2$  for cuboidal crystallites (cross section of cubes) can be used.

A surface crystallite "edge" as the term is used herein refers to those surface portions of a crystallite that are not planar surfaces.

Though the shape of crystallites is usually irregular, the shapes can often be described as being spherical, cuboidal, tetrahedral, octahedral, or parallelepipeds such as needles or plates, prisms or cylinders. Most applications of Scherrer analysis assume spherical crystallite shapes. If the average crystallite shape is known from another analysis, a proper value can be selected for the Scherrer constant  $K$ . Anisotropic peak shapes can be identified by anisotropic peak broadening if the dimensions of a crystallite are  $2x * 2y * 200z$ , then (h00) and (0k0) peaks will be more broadened than (00l) peaks. Also, see the discussion at this website: [clays.org/journal/archive/volume%2047/47-6-742.pdf](http://clays.org/journal/archive/volume%2047/47-6-742.pdf), published as M. Crosa, et al. (1999), "Determination of Mean Crystallite Dimensions from X-Ray Diffraction Peak Profiles: A Comparative Analysis of Synthetic Hematites", *Clays and Clay Materials*, 47(6), 742-747, and references contained therein, which reference and cited references are incorporated herein by reference in their entirety. The average number of crystallites per unit mass is expressed as the number of crystallites per gram of the nickel form, and any assumptions made about crystallite shape in carrying out the calculations are stated.

The term "D10" is a measure of particle sizes in a nickel particulate form, and refers to the largest diameter (e.g., in microns) that the smallest 10% of nickel particles have in the nickel particulate form.

A "Ni particle" is a discrete particle or agglomerated particle, typically visible in a scanning electron micrograph.

The term "particle size" as used herein refers to an average diameter of a possibly irregularly-shaped particle. Such a particle size can be determined by measurement with a Mastersizer 2000 Particle Size Analyser from Malvern Instruments Ltd using the Hydro 2000MU accessory and water as the dispersant, as is well known in the art. An "average particle size" or "mean particle size" refers to an average (mean) value for a population of particle sizes as defined above. For sizes below 100-200 microns the average particle size can be measured using a laser diffraction technique.

Standard abbreviations for chemical groups such as are well known in the art can be used herein, and are within ordinary knowledge; e.g., Me = methyl, Et = ethyl, i-Pr = isopropyl, Bu = butyl, t-Bu = tert-butyl, Ph = phenyl, Bn = benzyl, Ac = acetyl, Bz = benzoyl, and the like.

Provisos can apply to any of the disclosed categories or groups, wherein any one or more of the other above disclosed categories, groups or species can be excluded from such categories or groups.

5 The term "room temperature" as used herein refers to ambient temperature, which can be, for example, between about 16 °C and about 27 °C.

"Substantially spherical" refers to particles or crystallites that are substantially symmetrical around a center point. For example, while the distance (radius) from a center point to the surface of a substantially spherical particle or crystallite can vary, such variation is not so great or so predictable that the shape of the substantially spherical  
10 particle or crystallite would more accurately be defined as another geometric shape (e.g., as a cube instead of as a sphere). In some embodiments, the substantially spherical particle or crystallite can have a radius that varies by about up to about 25%, or up to about 20%, or up to about 15%, or up to about 10%, or up to about 5%. In some embodiments, the substantially spherical particle or crystallite can be partially spherical. For example, the  
15 substantially spherical particle or crystallite can be hemispherical, or be a quarter of a sphere. The substantially spherical crystallite can be fused to a particle or another crystallite such that the substantially spherical crystallite is a partial, substantially spherical projection from the particle or other crystallite. A partially substantially spherical crystallite that is fused to a particle or another crystallite can therefore be about  
20 25% to about 95% of a sphere, or any percentage of a sphere between 25% and 95%.

The Scherrer method (using full width at half maximum, FWHM, method) gives the ratio of the root-mean-fourth-power to the root-mean-square value of the thickness. The Stokes and Wilson method (using integral breadth) determines the volume average of the thickness of the crystallites measured perpendicular to the reflecting plane. The  
25 variance methods give the ratio of the total volume of the crystallites to the total area of their projection on a plane parallel to the reflecting planes

All values shown as % or ppm (parts per million) are intended to be by weight, unless otherwise specifically stated (e.g., as volume %). In other words, a numerical percentage or a numerical parts per million is that numerical percentage or parts per  
30 million by weight of the total composition (unless otherwise specified).

As used herein, "substantially" refers to a majority of, or mostly, as in at least about 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, 99.999%, or at least about 99.9999%.

The following Examples illustrate aspects of the invention.

5

**Example 1: Assays for Nickel-Ligand Complex Formation and Ni & S Content**

This Example describes assays employed to evaluate the activity of nickel metal samples for forming a complex with phosphorus-containing ligands, as well as assays to determine the content of nickel and sulfur in various basic nickel carbonate, nickel oxide,  
10 nickel metal etc. samples.

To evaluate the suitability of nickel preparations for generating hydrocyanation catalysts, the nickel is mixed with a phosphorus-containing ligand (e.g., Ligand (V)) in a 3-pentenitrile (3PN) solution and warmed for a period of hours and the level of solubilized nickel in solution is measured by liquid chromatography (LC) over time in the  
15 assay described below. In general, the goal is to identify nickel preparations that form complexes with phosphorus-containing ligands at a rate suitable for use in a manufacturing process involving a hydrocyanation catalyst. For example, a suitable nickel preparation forms sufficient nickel-ligand complex and/or reaches an equilibrium in nickel metal phosphorus ligand complex formation assay in no more than about 2 hours, no more  
20 than 1 hour, or no more than 30 minutes. Preferably, equilibrium is reached in no more than 30 minutes.

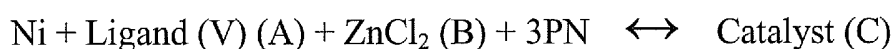
*Nickel-Ligand Complex Formation Assay procedure*

For assays of nickel metal complex formation with phosphorus-containing ligands,  
25 the nickel metal is handled in a dry, nitrogen atmosphere. The assay for complex formation is performed as follows: a reactor bottle is charged with 80 gram of a 5% by weight Ligand V solution in 3-pentenitrile (3PN) solvent, 3.2 gram of the nickel metal (Ni(0)), and 0.5 gram of anhydrous ZnCl<sub>2</sub>. The reactor bottle is sealed, removed from the dry box, and moved to a laboratory fume hood where it is placed on a magnetic stir plate.  
30 The reaction mixture within the reaction bottle is then heated to 60°C. In some tests the assay mixture is heated to 80°C. The reaction mixture is mixed to maintain the nickel-

containing solid in suspension. Filtered liquid samples are withdrawn as a function of time and analyzed for soluble nickel concentration by liquid chromatography.

In some tests, nickel prepared from MetChem BNC (described in Table 1) is used as a control, where the activity of the MetChem nickel is deemed to be 1.0 and nickel  
5 metal samples that form soluble complexes with Ligand V at a greater rate exhibit improved nickel activity. Nickel samples are also deemed to be minimally active if soluble nickel (in a complex with Ligand V) forms at a minimal rate of at least 317 ppm/hr at 60 °C or at a rate of at least 980 ppm/hr at 80°C.

An empirical rate equation for Ni dissolution in catalyst-preparation assay is  
10 employed to provide a numerical value indicative of nickel 'activity' (ability to become a soluble catalyst complex with Ligand (V)) in the following reaction:



The following equation describes the rate of Nickel-Ligand (V) catalyst formation:

$$r = a * k' * w_{\text{Ni}} * C_A^{a'} * C_B^b * [1 - C_c / (K_{\text{eq}} * C_A * C_B)] * 2 * (C_A / C_{A0}) / [1 + (C_A / C_{A0})]$$

15 where:

a = activity of nickel

$w_{\text{Ni}}$  = weight loading of nickel (weight of nickel/weight of solution)

$k'$  = Arrhenius rate constant:

$$[(\text{mmoles Ni/liter})^{0.5} / \text{hr}] = 1.539 \times 10^{10} \exp[-6832.1/T(\text{K})]$$

20

$C_A$  = concentration of Ligand (V) (mmol/L)

$C_{A0}$  = Initial concentration of Ligand (V) (mmol/L)

$C_B$  = concentration of  $\text{ZnCl}_2$  (mmol/L)

$a'$  = order of reaction with respect to Ligand (V) = 0

25

b = order of reaction with respect to  $\text{ZnCl}_2$  = 0.5

$K_{\text{eq}}$  = equilibrium constant for the chemical reaction  
[liters/mmol] =  $\exp [11555/T(\text{K}) - 35.231]$

T = temperature in degree Kelvin.

It is assumed that the 3-pentenitrile is in far excess so its order of reaction with respect to the rate of 3-pentenitrile dissolution is considered zero. The order of reaction with nickel loading is considered to be 1.

The rate constant  $k'$  is defined for a standard MetChem BNC reduced at 400 °C under pure hydrogen to nickel. However, to account for other sources of nickel that can have different in properties, a factor is applied that is termed the activity of nickel dissolution. The 'activity' number was chosen to be 1 for the specific condition of MetChem BNC reduced at 400 °C to nickel, dissolved at 80 °C in the catalyst-preparation solution with  $\text{ZnCl}_2/\text{Ligand (V)}$  molar ratio of 0.8 and 4 wt% nickel loading where dissolution is at a rate of 980 ppm Ni/hr. In principle, a higher activity is essentially a higher rate constant specific to a given nickel. In order to move away from separately determining rate constant for each type of nickel, the activity term is defined to get around this issue.

Note that if recrystallized Ligand (V) is employed in the assay, the measured nickel activity is higher than if an extracted (e.g., recycled) Ligand (V) preparation is employed. The difference in activity is about 2-fold.

#### *Sulfur Content Assay Procedures*

Sulfur content in basic nickel carbonate, nickel oxide, nickel metal and other nickel sources was measured by combustion with infrared (IR) spectroscopy analysis, microcoulometry, or inductively coupled plasma (ICP) mass spectrometry.

For combustion IR detection, 0.2 - 0.5g BNC/NiO/Ni etc. samples are weighed into boats, the boats are introduced into a furnace, the samples are heated (1350°C) in a stream of oxygen. The combustion gases are scrubbed to remove moisture and swept into the infrared detection cell. The amount of sulfur detected is converted to total sulfur in the sample using the stored calibration curve and the known sample weight. The samples are analyzed in duplicate with the mean value reported. The limit of detection is around 20ppm. Instrument uncertainty is 5% relative or better.

Microcoulometry is a more sensitive technique than combustion IR detection. Microcoulometry also uses combustion with the formation and measurement of  $\text{SO}_2$ . Sample weight for microcoulometry is normally around 20-50mg. Samples are introduced

into a furnace at 1100°C. Combustion gases are scrubbed to remove moisture and to cool the gases before the gases are introduced into an equilibrated coulometric titration cell. Sulfur is detected by reaction of the SO<sub>2</sub> formed with I<sup>3</sup> to form I<sup>-</sup> and SO<sub>4</sub>, and calculated from the charge needed to rebalance the cell. The limits of detection for microcoulometry  
5 can be less than 1 ppm although levels only as low as 1 ppm are quoted and the instrument uncertainty is 5% or less.

#### *Nickel Content Assay Procedures*

The nickel content of samples described in Examples 2-4 was determined by  
10 inductively coupled plasma optical emission spectrometry (ICP-OES), while the nickel content of the samples described in Examples 5 and 6 was determined by thermogravimetric analysis (TGA).

Samples (20-50 mg) are evaluated for nickel content in a Perkin Elmer TGA4000 thermogravimetric analyzer by heating the sample from 30 to 995 °C at a rate of 50 °C/min  
15 in a nitrogen atmosphere with a flow rate of 40 mL/min. The water content is characterized by the first thermal event (first weight loss) and the nickel content by the final total weight loss observed at 995 °C where all the material has been fully decomposed to NiO.

Unless specified, the analytical data provided below for the various nickel metal  
20 preparations (e.g., regarding sulfur content, BET, XRD data etc.) is for a reduced passivated nickel preparation that has a thin NiO coating. Such passivation occurs as the nickel becomes exposed to oxygen during performance of the analytical techniques employed. It is assumed that such passivation (i.e. the amount of NiO on the surface) has a negligible impact on the analytical results.

25

#### *Carbonate Content*

Carbonate content is determined using the method described by Donald L. Pile *et al.* in Journal of Chemical Education, LA-UR-97-1384, "A Precise Method for Determining the CO<sub>2</sub> Content of Carbonate Materials." The technique uses a simple  
30 apparatus designed to measure the volume change originating from CO<sub>2</sub> gas formed by a reaction of the BNC sample and a solution of hydrochloric acid.

**Example 2: Nickel Activity varies with BNC Sample Type**

Eight basic nickel carbonate (BNC) samples are evaluated for suitability in preparing Ni metals. All samples tested are commercial products with the exception of BNC #5, which is prepared according the BNC precipitation procedure described above. As described below different particulate nickel metal preparations made from different BNC sources exhibit variability in complex formation with phosphorus-containing ligands.

Table 1 (above) and Table 2 provide analytical data concerning trace impurities in the BNC samples. All percentage and parts per million (ppm) values are weight:weight (w/w), unless otherwise stated.

**Table 2: Samples of Basic Nickel Carbonate Evaluated for Preparation of Inventive Ni Form**

| BNC No. | C   | H   | N     | S     | Cl  | Nickel | CO <sub>3</sub> <sup>2-</sup> | Ni:C Wt Ratio | Ni:C Mole Ratio |
|---------|-----|-----|-------|-------|-----|--------|-------------------------------|---------------|-----------------|
|         | %   | %   | %     | ppm   | ppm | %      | %                             |               |                 |
| 1       | 3.9 | 3.3 | 0.09  | 212   | 13  | 42.08  | 19.5                          | 10.79         | 2.21            |
| 2       | 4.6 | 2   | 0.08  | 1902  | 3   | 50.71  | 23                            | 11.02         | 2.26            |
| 3       | 6.4 | 2.2 | 0.02  | 5     | 9   | 45.33  | 32                            | 7.08          | 1.45            |
| 4       | 4.8 | 2.4 | <0.02 | 7     | <1  | 46.19  | 24                            | 9.62          | 1.97            |
| 5       | 4.5 | 2.1 | <0.02 | 21000 | 7   | 51.57  | 22.5                          | 11.46         | 2.35            |
| 6       | 5.6 | 2.4 | <0.02 | 10    | 2   | 45.53  | 28                            | 8.13          | 1.66            |
| 7       | 3.3 | 3.3 | <0.02 | 9800  | 3   | 45.15  | 16.5                          | 13.68         | 2.80            |
| 8       | 4.5 | 2.7 | <0.02 | 4600  | 3   | 46.44  | 22.5                          | 10.32         | 2.11            |

**Exemplary Procedure for Production of Ni Powders**

For conversion of the above-listed BNC samples to Ni powders and evaluation of those Ni powders for activity in the reaction with the test phosphite ligand, Ligand (V), in the organic liquid 3PN, the following procedures can be used.

Calcination pretreatment can be employed, such as with air flow, optionally including steam, prior to the step of reduction. Fifteen grams of the dried solid BNC

sample are placed inside a reaction tube that can be heated within an electrical furnace located in a lab fume hood. Calcination can be carried out in the 300-400 °C temperature range. FIG. 1 shows CO<sub>2</sub> loss during calcination pre-treatment of the eight BNC samples numbers 1-8, whose properties are shown in Table 2.

5           Calcination pretreatment is not essential because the BNC can be simultaneously calcined while the nickel in the BNC is reduced. For example, a sample of BNC, listed as BNC #1 in Table 2 above that is supplied by MetChem (an American distributor of BNC), is reduced without calcination. Fifty grams of BNC#1 material is reduced in hydrogen at a flow rate of 0.5 liter H<sub>2</sub>/min at 400 °C for four hours. The reduction is done in a  
10       temperature controlled tube furnace. The reduction tube is taken into a dry box and the contents transferred to a bottle. The resulting powder is magnetic, indicating that nickel metal is produced by the reduction.

          BNC samples #2-8 in Table 2, above, are processed in a similar manner, except that a calcination pretreatment is also employed, to provide the Ni-containing powders for  
15       evaluation for zero-valent nickel phosphorus ligand preparation as described in Example 1.

### *Product Properties*

          It has been found that some BNC samples are more suitable for preparation of  
20       nickel particulate compositions of the invention than are other samples. Data presented herein and in the Figures illustrate the properties of BNC samples during and after processing to show when a particular sample will be a nickel active inventive particulate form of zero-valent nickel metal.

          As noted above, BNC samples 2-8 are subjected to calcination, but BNC sample 1  
25       is not. However, all eight samples are reduced via hydrogenation. The characteristics of nickel preparations generated from the eight reduced BNC samples are shown in Table 3. Nickel samples 1-8 in Table 3 are prepared from the corresponding BNC samples 1-8 listed in Table 2.

          In Table 3, "Ni active" means that the Ni metal prepared by reduction from the  
30       corresponding BNC is better than, BNC sample #1, the Ni powder obtained from the MetChem BNC via a one-step reduction process (i.e., not including calcination

pretreatment). Sample 1 has nickel activity barely sufficient to enable the efficient preparation of the zero-valent nickel phosphorus ligand complexes suitable for use as a hydrocyanation catalyst. By efficient preparation is meant that the nickel powder reacts with sufficient completeness and at a sufficient rate to be economically suitable for use in carrying out industrial-scale olefin hydrocyanation reactions, such as the hydrocyanation of 3PN to form adiponitrile (ADN), an important intermediate in the manufacture of various nylons such as Nylon 6 and Nylon 6,6.

**Table 3: Nickel Sample Properties**

| BNC No | Active Ni | Mean Ni Crystal Size (nm) |
|--------|-----------|---------------------------|
| 1      | Yes       | 31                        |
| 2      | Yes       | 21                        |
| 3      | No        | 80                        |
| 4      | No        | 40                        |
| 5      | Yes       | 28                        |
| 6      | No        | 47                        |
| 7      | Yes       | 27                        |
| 8      | Yes       | 21                        |

In Table 3, samples marked “yes” have active nickel while samples 3, 4 and 6 do not have active nickel as assessed by assays involving nickel-phosphorus ligand complex formation useful for catalysis of industrial-scale olefin hydrocyanation reactions. A relationship between mean (average) crystallite size and activity is also apparent from the data in Table 3. The three samples judged to be insufficiently active for zero-valent nickel bidentate ligand catalyst preparation, sample numbers 3, 4, and 6, have the three largest average crystallite sizes among the eight samples tested, as determined by XRD. All active samples have mean crystallite sizes of about 30 nm or less.

### 20 **Example 3: BNC Physical and Chemical Properties**

“Ni active” samples 2, 5, 7, and 8 described in Example 1 are further evaluated and compared to samples 3, 4 and 6 that do not have sufficient active nickel for efficient

formation of nickel phosphorus ligand complexes, and that have larger crystallite mean size than the active samples.

#### *Analytical Procedures--Methodology*

##### 5 *TP-XRD Measurements*

A Siemens Bruker D5000 diffractometer with Anton Paar HTK heating stage is used. The BNC specimens are mounted as a dry compacted layer on a platinum (Pt) foil, itself attached to an electrically heated Pt bar. A gas flow of 4% H<sub>2</sub>/N<sub>2</sub> is used.

10 A pre-heating scan at room temperature is obtained from the starting material; this also allows the system to flush fully with H<sub>2</sub>/N<sub>2</sub>. Following the heating profile a room temperature scan of the product is obtained for reference.

The following measurement conditions are used.

| <b>Diffractometer</b>    | <b>Siemens/Bruker D5000 D7</b> |
|--------------------------|--------------------------------|
| X-ray Tube               | Cu LFF                         |
| Radiation                | Cu K $\alpha$                  |
| Generator Voltage        | 40 kV                          |
| Generator Current        | 40 mA                          |
| Diffraction Geometry     | Reflection Bragg Brentano      |
| Variable Divergence Slit | 6 mm irradiated length         |
| Antiscatter Slit         | 2mm irradiated length          |
| Receiving Slit           | 0.6 mm                         |
| Primary soller slit      | 2.3°                           |
| Secondary soller slit    | -                              |
| Detector                 | Scint                          |
| Monochromator            | Graphite Monochromator         |
| Filter                   | -                              |
| <b>Pre-Heating</b>       |                                |
| Step Size                | 0.05°                          |
| Time per step            | 2s                             |

|                        |                                                          |
|------------------------|----------------------------------------------------------|
| Scan start angle       | 5°                                                       |
| Scan finish angle      | 90°                                                      |
| Specimen format        | Compressed Dry powder                                    |
| Specimen loading       | Top compression                                          |
| Temperature            | Room temperature 5                                       |
| Temperature Ramp rate  | -                                                        |
| Atmosphere             | 40cm <sup>3</sup> /min 4% H <sub>2</sub> /N <sub>2</sub> |
| <b>Heating Profile</b> |                                                          |
| Step Size              | 0.02° 10                                                 |
| Time per step          | 3s                                                       |
| Scan start angle       | 38°                                                      |
| Scan finish angle      | 106°                                                     |
| Specimen format        | Compressed Dry powder                                    |
| Specimen loading       | Top compression 15                                       |
| Temperature            | 100°C then 160-420°C in 20C intervals                    |
| Temperature Ramp rate  | 0.5C/s                                                   |
| Atmosphere             | 40cm <sup>3</sup> /min 4% H <sub>2</sub> /N <sub>2</sub> |
| <b>Post Heating</b>    |                                                          |
| Step Size              | 0.02° 20                                                 |
| Time per step          | 2s                                                       |
| Scan start angle       | 30°                                                      |
| Scan finish angle      | 108°                                                     |
| Specimen format        | Compressed Dry powder                                    |
| Specimen loading       | Top compression 25                                       |
| Temperature            | Room temperature                                         |
| Temperature Ramp rate  | -                                                        |
| Atmosphere             | 40cm <sup>3</sup> /min 4% H <sub>2</sub> /N <sub>2</sub> |

Instrument profile parameters can be determined from a NIST lanthanum hexaboride diffraction pattern. Line profile analysis can determine the additional broadening present in each diffraction peak.

#### 5 *Reduction and Microstructure Monitoring*

Diffraction patterns are analysed using the Wilton “LOSS” software, which optimises the fit of a simulated diffraction pattern comprising a set of peak profiles calculated for a series of crystallite sizes. The crystallite size values obtained are volume-weighted means. The data is further analysed using a “Williamson Hall” plot to separate  
10 crystallite size broadening from lattice distortion broadening, if present. The presence of faulting in the cubic metal structure can be examined by comparison of the width of the line profiles of the 111 and 200 reflections.

Reaction progress can be calculated from the areas associated with the Ni metal peaks and from a pattern of the unreduced BNC material as observed in lower temperature  
15 diffraction patterns. This BNC pattern can be fitted by the LOSS program together with the simulated Ni peaks and simulated peaks corresponding to the Pt specimen carrier.

#### *TPR-MS & TPD-MS Measurement*

Temperature-programmed reaction mass spectroscopy (TPR-MS) and/or  
20 temperature-programmed desorption-reaction-mass spectrometric (TPD-TPR MS) studies are performed using where the test conditions can be as follows:

*Test Conditions TPD-MS (see FIG. 3B):*

Ar Balance ( $20 \text{ cm}^3 \text{ min}^{-1}$ , >99% Ar, BOC)

Total Flow Rate =  $20 \text{ cm}^3 \text{ min}^{-1}$

25 Internal Standard = Ar ( $m/z=36$ )

Catalyst Mass = 50 – 60 mg

Rate =  $15 \text{ }^\circ\text{C min}^{-1}$

*Test Conditions TPR-MS (see FIG. 3C):*

30 10%  $\text{H}_2$  ( $2 \text{ cm}^3 \text{ min}^{-1}$ , >99%  $\text{H}_2$ , BOC)

Ar Balance ( $18 \text{ cm}^3 \text{ min}^{-1}$ , >99% Ar, BOC)

Total Flow Rate =  $20 \text{ cm}^3 \text{ min}^{-1}$

Internal Standard = Ar ( $m/z=36$ )

Catalyst Mass = 50 – 60 mg

Rate =  $15 \text{ }^\circ\text{C min}^{-1}$

5

### *Analytical Results and Discussion*

Data are collected during the conversion of the eight BNC samples shown in Table 2 to the nickel metal powders to evaluate which BNC samples have suitable or unsuitable, properties for efficient conversion to zero-valent nickel / bidentate phosphite ligand  
10 complexes. For example, such data can provide additional information as to how variables such as crystallite mean size and SSA (BET and LD) affect the ability of the nickel preparations to form soluble zero-valent nickel-ligand complexes.

In the process of conversion of BNC to Ni powders, reduction must be employed but calcination is optional prior to the reduction step. Calcination can be carried out by the  
15 usual means known in the art, such as in a fluidized bed reactor, a rotary furnace, or the like, as discussed above.

Data is collected during the calcination of each of the eight BNC samples (see Tables 1, 2, and 3) and after conversion to particulate Ni samples to assess the suitability of the product as an active Ni composition. Samples 2, 5, 7, and 8 are found to be active  
20 Ni (Table 3), defined herein as being suitable for complex formation with ligands, such as with bidentate phosphite ligands, while samples 3, 4, and 6 are found to be unsuitable, as well as not meeting the structural/functional criteria defined herein for Ni powders of the invention with respect to SSA and crystallite mean size.

FIG. 1 shows a Thermal Programmed Desorption scan of each of the eight BNC  
25 samples listed in Table 2 at calcining temperatures in an argon atmosphere over the temperature range indicated, with detection of  $\text{CO}_2$  by mass spectroscopy. TPD (also known as TDS) involves heating a sample while it is contained in a vacuum and simultaneously detecting the residual gas in the vacuum by means of a mass analyzer. As the temperature rises, certain absorbed species will have enough energy to escape and will  
30 be detected as a rise in pressure for a certain mass.

FIG. 1 shows that inactive BNC #3 releases the largest amount of CO<sub>2</sub> during calcining while active BNC samples 5 and 7 release the least amount of CO<sub>2</sub> during calcining. Active Ni samples prepared from BNC # 2, 5, 7, and 8 also tend to have smaller crystallite mean size (e.g., less than about 30 nm) than the inactive nickel samples made from inactive BNC samples #3, 4 and 6. These data suggest that BNC samples that are more readily calcined can, at least in some instances, produce a Ni particulate form with good activity and the desirable structural features.

Further processing via hydrogenation illuminates additional characteristics of active Ni versus inactive Ni. Such hydrogenation reduces the BNC (or NiO if a calcination pre-treatment is applied) to Ni metal.

FIGs. 2 and 3 show the disparate hydrogen absorption profiles observed in the processing of the precursors yielding inactive Ni and in the processing of the precursors that yield active Ni, respectively.

As can be seen in FIG. 2, the BNC samples #3, 4, and 6 of Table 2, which yield inactive Ni samples upon reduction, exhibit a distinct pattern of two maxima of hydrogen absorption of unequal size, a smaller absorption maximum around 300° and a larger one around 400° C.

In contrast, FIG. 3A shows a pattern of hydrogen uptake versus increasing temperature for BNC samples #2, 5, 7, and 8 of Table 2, which yield active Ni samples upon reduction. The pattern of hydrogen uptake by calcined BNC samples #2, 5, 7, and 8 exhibit a single broadened hydrogen absorption maximum at around 400-450° C. This pattern is distinct from the pattern of hydrogen absorption exhibited for calcined BNC samples #3, 4, and 6 in FIG. 3A, where two peaks of absorption are observed. Thus, there is a correlation between the response of BNC to processing conditions and the activity of particulate form of Ni produced.

The outlier, BNC sample #1, is a minimally active sample that also is used to produce Ni1 with the properties shown in Table 4 below. As shown in FIG. 3A, a double maximum of hydrogen absorption is observed when BNC sample #1 is reduced, and such reduction occurs at a somewhat lower temperature than the temperature maxima observed for BNC samples #2, 5, 7, and 8. The two maxima observed for BNC #1 are also of approximately the same height.

Following the reduction step, analyses are performed on the resulting Ni metal-containing products, to examine crystallite size distributions for the various samples. For example, temperature programmed X-ray diffraction (TP-XRD) provides data showing Ni(111) based Ni crystallite size distribution for each of the eight BNC products.

5        FIGs. 4-11 show TP-XRD data for Ni metal particulate forms obtained by hydrogen reduction of BNC samples #1-8, respectively, as described above in Table 2. The temperature axis shows the progression of increasing temperature applied during the hydrogenation process, the crystallite size axis shows crystallite sizes, as determined by XRD in these data, and the volume-% axis indicates the distribution by volume of the  
10        various crystallite size classes in each bulk sample. Sample numbering corresponds to that shown in Table 2.

As illustrated, active samples #2, 5, 7, and 8 consistently show the presence of smaller crystallites throughout processing than do inactive samples #3, 4, and 6. Sample #1, considered to be marginally active at best, exhibits the larger crystallites, centered at  
15        about 30 nm, than the active nickel samples #2, 5, 7, and 8. Samples #2, 5, 7, and 8 all consistently exhibit a population of smaller crystallites, centered around about 20-25 nm, with a significant fraction of 10 nm or less. In contrast, inactive samples #3, 4, and 6 all are composed of significantly largely crystallites, averaging about 40-50 nm, with very little material present having a size of less than about 20 nm. It should be remembered that  
20        these data refer to crystallite size, not to the size of the actual Ni particles, which are of the order of microns to tens of microns in size. Each discrete Ni particle is composed of many crystallites. As used herein, "size" is an average diameter. A crystallite is a region of local crystalline order wherein neighboring crystallites do not extend that order, but have an internal order of their own.

25        FIG. 12 shows the crystallite size distribution (CSD) in a nickel sample prepared from BNC #8. CSD span is the width of the crystallite size distribution (CSD) where the crystallite size is obtained by TP-XRD and CSD is calculated as  $(C_{90}-C_{10})/C_{50}$ , where  $C_x$  is the size of the crystallite for which x% of the sample has a smaller size (e.g., the  $C_{90}$  size is the length (in nanometers) of the average diameter of Ni crystallites wherein  
30        90% of the Ni crystallites in a bulk sample have a size less than the stated value).

FIG. 13 shows crystallite size distribution (CSD) span data for the entire set of eight Ni powder samples prepared from the eight BNC samples of Table 2. As is apparent, these samples again fall into two groupings of “active” and “inactive”, i.e., “nickel active” and “not nickel active,” based on the numerical value of crystallite size distribution span. A CSD span of greater than 1, or greater than 1.5, is generally an indication of an active nickel. As the temperature of reduction increases, the CSD becomes narrower. Reduction temperatures of about 300-400 °C yield reduced nickel preparations with a good CSD span. In this study, it is found that BNC pre-calcination does not have a major impact on the CSD span.

FIG. 14 shows the relationship between C10 (the dimension in microns at which 10% of the crystallites have a size less than the stated value) and the nickel activity of the sample. Note that these data refer to crystallite size, not to the size of the discrete particles of nickel. It is apparent again that the grouping of active Ni samples versus inactive samples shown in FIG. 14 is reflected in the grouping of C10 values. A Ni particulate form of the invention can have a C10 value of less than about 10 nm. Nickel samples having a C10 value of greater than about 10 nm may not be active nickel materials as the term is used herein. As discussed herein, the reduction temperature can affect the distribution of crystallite sizes. In general, a reduction temperature range of about 300-400 °C can yield nickel samples with desirable C10 values.

FIGs. 15A - D show SEM photographs of various samples of the nickel particulate form of the invention. No outstanding features are noted in the physical structure of the particles, indicating that the highly nickel active properties of the compositions are provided by molecular or macromolecular features of the substances. Not wishing to be bound by theory, the inventors herein believe that this feature relates to the availability of crystallite edges on the surface of a nickel particle, inasmuch as edges are believed to be more reactive, e.g., with a ligand in solution, than are planar crystallite faces. A higher number of surface crystallites can correlate with a higher proportional abundance of crystallite edges available to approaching ligand molecules in solution.

**Example 4: Further Analysis of BNC Samples and Ni Derived Therefrom**

Selected BNC samples are further evaluated as discussed below.

*General Procedure for Production of Ni Powders*

Various BNC samples are tested as starting materials for nickel preparations. BNC  
5 samples, except the BNC used to generate the Ni1 in Table 4, are subjected to a  
calcination pretreatment followed by reduction at the indicated temperatures, with steam.  
Hydrogen gas flow to the reaction tube is set at 0.2 liters/minute (about one atmosphere)  
with any hydrogen off-gas from the reaction tube flowing through a bubbler. The  
temperature of the tube furnace is then increased at a rate of 10 °C/minute to a final  
10 temperature of 400 °C, and then held for one hour at 400 °C, after which the reaction tube  
is allowed to cool under hydrogen flow. After the reaction tube temperature falls below 50  
°C the flow to the reaction tube is switched to nitrogen gas to purge the hydrogen from the  
reaction tube. Valves on the reaction tube are then closed to prevent exposure of the  
resulting nickel-containing solid to air, and the entire reaction tube is transferred to a  
15 nitrogen-filled dry box where the nickel-containing solid is emptied into a bottle. This  
nickel-containing solid contains nickel metal as evidenced by the observation that it is  
attracted to a magnet. Exposing these nickel-containing solids to air can reduce rates for  
the reaction of the nickel with Ligand (V) in 3PN, and/or cause the nickel-containing  
solids to ignite.

20 Note that most of the Ni1-Ni10 nickel preparations in Table 4 are obtained from  
BNC samples from the same suppliers as those listed in Tables 2 and 3, however  
significant lot to lot, and batch to batch variation in the compositions of BNC from these  
suppliers is observed. Hence, although the BNC numbers in Table 4 correspond with the  
BNC numbers in Tables 2 and 3, and indicate that a BNC of the same number is obtained  
25 from the same supplier, different BNC batches obtained from the same supplier often have  
different compositions.

Analytical procedures similar to those described above are used to evaluate the  
nickel preparations. The D10 values for these nickel samples are determined by Particle  
Size Distribution analysis. Specific Surface Areas (SSA), i.e., surface area per unit mass,  
30 of the various samples is determined by two methods available in the art, BET SSA, and  
Laser Diffraction (LD) SSA, for each of the BNC reduction products. Laser Diffraction

Specific Surface Area (LD SSA) and particle size distribution (PSD) are measured with a Mastersizer 2000 Particle Size Analyser from Malvern Instruments Ltd using the Hydro 2000MU accessory and water as the dispersant. Nitrogen adsorption BET Specific Surface Area (BET SSA) is measured using the Tristar 3000 Nitrogen Adsorption Instrument after  
5 degassing the samples under vacuum at 105 °C overnight. Multi-point BET measurements are made using a partial pressure range of 0.05-0.3 P/Po.

Samples of basic nickel carbonate are processed according to the procedures described above, and evaluated for C50, C10, CSD span (crystallite size distribution span= (C90-C10)/C50), LD and BET SSA values, and number of surface crystallites per  
10 gram at C50 and C10 dimensions, as well as nickel activity with respect to soluble catalyst formation as described above. The processed nickel samples are designated Ni1-Ni10.

#### *Analytical Results and Discussion*

Table 4 summarizes data for the prepared Ni samples Ni1-Ni10. As can be seen in Table 4, a strong correlation exists between BET SSA and activity. Sample Ni1 with a  
15 BET SSA of more than 1 m<sup>2</sup>/gm but less than 10 m<sup>2</sup>/gm, is comparable in activity to sample Ni5, assigned a control activity of 1, and the seven nickel samples Ni2, Ni3, Ni6, Ni7-Ni9 and N10), prepared from BNC samples as described above and selected based on activity, show a close correlation of BET SSA with reactivity of the nickel with the bidentate phosphite Ligand (V) ("nickel activity," see FIG. 17C).

20 Another factor that strongly correlates with Ni activity in reaction with Ligand (V) in 3PN is crystallite size, number or surface area. Each particle of nickel metal from the hydrogen-reduced BNC, or calcined and reduced BNC, is of the order of several microns or more. Each nickel particle can also be formed as an agglomeration of nickel metal crystallites, that is, domains of local crystalline order, of the sizes as described and  
25 discussed below.

FIG. 16A shows a correlation for seven nickel active samples (Ni1-Ni3, Ni6, and Ni8-Ni10) between nickel activity and mean crystallite number per gram, based on the assumption that the shape of the crystallite is roughly spherical, using the following equation for calculation of the number of spherical crystallites:

30 # surface spherical crystallite=BET/4π(Cx/2)<sup>2</sup>.

FIG. 16B shows a correlation for the seven nickel active samples (Ni1-Ni3, Ni6, and Ni8-Ni10) between nickel activity and mean crystallite number per gram, based on the assumption that the crystallite is of a substantially square cross section, i.e., is a cube or cuboidal. The following equation is used for calculation of the number of cuboidal

5 crystallites:

$$\# \text{ surface cuboidal crystallites} = \text{BET}/(\text{Cx})^2.$$

As nickel is known to generally assume a face-centered cubic close-packing array in the elemental state, as assumption that the crystallites are cuboidal may be more accurate.

FIG. 16A thus presents results according to a standard Scherrer analysis as described  
10 above, and FIG. 16B recalculates the results based on a crystallite shape believed to be that taken by the cubic-packing Ni atoms.

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**Table 4: Nickel Samples with Crystallite Sizes, SSA Values, Number of Surface Crystallites, and Ratio BET SSA / C50**

| Nickel From BNC               | C50 nm | C10 nm | crystallite span | C50 SA, m <sup>2</sup> | C10 SA, m <sup>2</sup> | LD SSA m <sup>2</sup> /g | BET SSA m <sup>2</sup> /g | number of surface cuboidal C50/gm Ni | number of surface cuboidal C10/gm Ni | BET SSA / C50 x 10 <sup>9</sup> m/gm | activity |
|-------------------------------|--------|--------|------------------|------------------------|------------------------|--------------------------|---------------------------|--------------------------------------|--------------------------------------|--------------------------------------|----------|
| Ni1 (BNC #1) 400C, one step   | 28     | 19     | 0.6              | 7.84E-16               | 3.61E-16               | 0.123                    | 1.90                      | 2.42E+15                             | 5.26E+15                             | 0.07                                 | 1.09     |
| Ni2 (BNC #1) 300C, one step   | 19     | 11     | 1.14             | 3.61E-16               | 1.21E-16               | 0.123                    | 1.90                      | 5.26E+15                             | 1.57E+16                             | 0.10                                 | 2.00     |
| Ni3 (BNC #2) proc run 13      | 26.5   | 9      | 2.02             | 7.02E-16               | 8.10E-17               | 1.320                    | 30.20                     | 4.30E+16                             | 3.73E+17                             | 1.14                                 | 10.20    |
| Ni4 (BNC #3) 400C, one step   | 44.5   | 40.5   | 0.37             | 1.98E-15               | 1.64E-15               | NA                       | NA                        | NA                                   | NA                                   | NA                                   | 0.06     |
| Ni5 (BNC #3) 300C, two steps  | 30     | 16     | 0.9              | 9.00E-16               | 2.56E-16               | NA                       | NA                        | NA                                   | NA                                   | NA                                   | 1        |
| Ni6 (BNC #7) chem proc run 14 | 31     | 12     | 2.06             | 9.61E-16               | 1.44E-16               | 0.607                    | 12.90                     | 1.34E+16                             | 8.96E+16                             | 0.42                                 | 3.00     |
| Ni7                           | NA     | NA     | NA               | NA                     | NA                     | 0.469                    | 15                        | NA                                   | NA                                   | NA                                   | 6.29     |
| Ni8 (BNC #8) proc run 12      | 35.5   | 12.5   | 1.75             | 1.26E-15               | 1.56E-16               | 0.832                    | 18.10                     | 1.44E+16                             | 1.16E+17                             | 0.51                                 | 3.35     |
| Ni9 (BNC #8) proc run 16      | 32.5   | 12     | 2.06             | 1.06E-15               | 1.44E-16               | 0.808                    | 20.50                     | 1.94E+16                             | 1.42E+17                             | 0.63                                 | 5.24     |
| Ni10 (BNC #8) 400C two steps  | 29     | 10     | 1.63             | 8.41E-16               | 1.00E-16               | 0.707                    | 16.59                     | 1.97E+16                             | 1.66E+17                             | 0.57                                 | 5.40     |

A calculation of BET SSA / C50 (Table 4) is provided for comparison with nickel activity. It can be seen that a ratio of BET SSA / C50 of at least about  $0.07 \times 10^9$  or at least about  $0.1 \times 10^9$  m/gm provides a minimal nickel activity of 1. Higher values for the ratio correlate with greater nickel activities, with the greatest nickel activities correlating with a BET SSA / C50 ratio in the  $0.5 - 1.0 \times 10^9$  m/gm range.

FIG. 17A is a graph showing the correlation of BET SSA and LD SSA, while FIG. 17B is a graph of BET SSA versus D10 for nickel samples Ni1, Ni3, Ni6-Ni8 and Ni9. FIG. 17C illustrates a close correlation of BET SSA with the activity of the nickel to efficiently complex with the bidentate phosphite Ligand (V).

FIG. 18 graphically illustrates mean crystallite size (MCS = C50) versus nickel activity as defined herein as well as C10 versus nickel activity as defined herein. For these calculations, it is assumed that the geometry of crystallites is of a substantially square cross section, i.e. is a cube or cuboidal shape. It is also noted that BET SSA linearly correlates with Laser Diffraction SSA for Ni, see FIG. 17A.

As FIG. 18 illustrates, a mean crystallite size (C50) of less than about 30 nm and a C10 value of less than about 20 nm generally correlate with a nickel activity of 1 or greater. For higher nickel activity values to be achieved, small mean crystallite size and especially small C10 values are highly correlated. As can be seen in Table 4, C10 values approaching about 10 nm provide specimens with greater nickel activity. FIG. 19 shows a correlation between the number of surface crystallites of a size not greater than the C10 value for a nickel sample and the nickel activity of that sample.

The correlation of raw C50 values and nickel activity appears to be less strong. Ni7 and Ni8, control samples, having C50 values of 44.5 and 30 nm respectively, and C10 values of 40.5 and 16 nm, respectively, show the lowest nickel activities. Sample Ni1, having a C50 of 28 nm and a C10 of 19 nm has a slightly higher nickel activity. At nickel activities of greater magnitude, the C10 values grow steadily smaller, but the C50 values are relatively constant. FIG. 17C shows a correlation of BET SSA with nickel activity for the same nickel samples. A correlation is observed between increasing BET SSA and nickel activity for the seven samples Ni1-Ni3, Ni6, Ni8, Ni9, and Ni10.

These data indicate that nickel activity is increased by lower C10 values, greater BET SSA values, larger numbers of surface crystallites per gram, and larger numbers of particles having a size of D10 or less.

In Table 4, a ratio is calculated for BET SSA divided by C50, for each of the seven active samples, Ni1-Ni3, Ni5-Ni6, and Ni9-Ni10. This ratio can be viewed as normalizing the SSA for crystallite size within the range studied. It is apparent that a strong correlation exists between the SSA/C50 ratio and nickel activity, such that a nickel metal particulate composition with a BET SSA / C50 ratio of not less than about  $0.07 \times 10^9$  m/gm, or at least  $0.1 \times 10^9$  m/gm, or at least about  $0.4 \times 10^9$  m/gm, is an indicator of a nickel particulate form with good activity. Nickel particulate forms with very good activity can have BET SSA / C50 ratios of up to about  $1.0 \times 10^9$  m/gm. Samples having a higher BET SSA/C50 value, should they be prepared, are expected to have yet higher nickel activity as the term is used herein, i.e., with respect to formation of soluble zero-valent nickel catalyst complexes with phosphorus-containing ligands in an organic milieu.

FIG. 20 graphically illustrates the strong correlation between nickel activity and BET SSA / C50 using the data shown in Table 4 for each of the nickel samples having activity of at least 1 as defined herein.

Also, SSA values as determined by BET and LD methods are found to have a substantially constant ratio of about 23.46. Accordingly a ratio of LD SSA / C50 of greater than about  $(0.1 / 23.46) \times 10^9$  m/gm =  $.0043 \times 10^9 = 4.3 \times 10^6$  can be used to be an indication of a nickel composition of the invention, having a nickel activity suitable for efficient catalyst preparation with bidentate nickel-phosphite zero-valent complexes.

#### **Example 5: Unsuitable nickel precursors for making active nickel**

Nickel and nickel oxide samples as received from various commercial sources are analyzed to determine their sulfur content, and their activity for complex formation with Ligand (V) as described in Example 1.

After such analysis, 10 grams of these commercial sources of nickel metal and nickel oxide are loaded into a fluidized bed reactor, heated to 400°C under a nitrogen flow for 1h and reduced at 400°C with 20% H<sub>2</sub> in N<sub>2</sub> for 2h. The resulting reduced nickel powder is then transferred into a N<sub>2</sub> purged glovebox and analyzed again for complex formation with Ligand (V), mean crystallite size (MSD) and BET surface area using the assays described in Example 1.

The results are shown in Tables 5 and 6.

**Table 5: Commercial NiO (sample C) and  
Ni powders (samples A, B and D)**

| Supplier Code | Composition*                | ppm S in Ni <sup>a</sup> | BET SSA <sup>b</sup> of Ni, m <sup>2</sup> /g | Ni MCS <sup>c</sup> , nm | Activity Reduced Ni | Activity Unreduced Ni <sup>a</sup> |
|---------------|-----------------------------|--------------------------|-----------------------------------------------|--------------------------|---------------------|------------------------------------|
| A (Ni)        | 99% Ni                      | 1                        | 0.33 <sup>a</sup>                             | 102                      | 0.01                | 0                                  |
| B (Ni)        | 98-99% Ni                   | 1                        | 1.63 <sup>a</sup>                             | -                        | 0.51                | 0.01                               |
| C (NiO)       |                             | 110                      | 10.2                                          | 35.6                     | 0.48                | 0.48                               |
| D (Ni / NiO)  | 30-90% Ni;<br>remainder NiO | 200                      | 53.60 <sup>a</sup>                            | -                        | 0.24                | 0.03                               |

\* Composition is from Material Safety Data Sheets from the supplier;

<sup>a</sup> Data is for the nickel materials as received from the supplier;

<sup>b</sup> BET SSA is a measure of nickel particle surface area, described in more detail above;

<sup>c</sup> MCS is the mean crystallite size (C50), described in more detail above.

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Table 6: Commercial Basic Nickel Carbonate,  $\text{Ni}(\text{CO}_3)_x(\text{OH})_y(\text{H}_2\text{O})_z$ 

| BNC Supplier <sup>a</sup> | BNC Composition <sup>b</sup> |       |                   |                 |                             | Reduced Ni Properties |                            |                        |          |
|---------------------------|------------------------------|-------|-------------------|-----------------|-----------------------------|-----------------------|----------------------------|------------------------|----------|
|                           | %CO <sub>3</sub>             | %Ni   | %H <sub>2</sub> O | ppm S           | S/Ni Ratio $\times 10^{-4}$ | ppm S in Ni           | BET SSA, m <sup>2</sup> /g | Ni MCS <sup>c</sup> nm | activity |
| BNC #1                    | 19.50                        | 42.08 | 30.27             | 212             | 9.22                        | -                     | 2.50                       | 28                     | 1.00     |
| BNC #2                    | 21.89                        | 43.83 | 21.29             | 400             | 16.7                        | 400                   | 11.00                      | 25                     | 0.22     |
| BNC #2                    | 20.78                        | 41.64 | 25.23             | 300             | 13.2                        | 200                   | 12.70                      | 15                     | 1.98     |
| BNC #2                    | 22.70                        | 50.01 | 11.18             | 400             | 14.6                        | 500                   | 11.40                      | 19                     | 0.91     |
| BNC #2                    | 26.06                        | 40.17 | 25.27             | 300             | 13.7                        | 700                   | 11.80                      | 31                     | 0.23     |
| BNC #2                    | 33.75                        | 49.1  | 10.90             | 400             | 14.9                        | 700                   | 10.00                      | 82                     | 0.39     |
| BNC #3                    | 32.00                        | 45.33 | 19.49             | 5               | 0.20                        | -                     | -                          | 34                     | 0.07     |
| BNC #4                    | 24.51                        | 46.16 | 21.91             | 7               | 0.28                        | -                     | 0.80                       | 32                     | 0.05     |
| BNC #6                    | 28.00                        | 45.53 | 21.45             | 10              | 0.40                        | -                     | -                          | 41                     | 0.50     |
| BNC# 11                   | 26.28                        | 47.26 | 13.97             | nd <sup>d</sup> | -                           | -                     | -                          | -                      | 0.50     |

<sup>a</sup> The BNC Supplier numbers correspond to the same BNC suppliers listed in Tables 2-4; BNC #11 is a new supplier of BNC;<sup>b</sup> data is for the samples as received from the supplier;<sup>c</sup> MCS is the mean crystallite size (C50), described in more detail above;<sup>d</sup> nd: not detected.

Note that BNC sample #1 is MetChem BNC. After reduction at 400 °C, this MetChem BNC yields a nickel metal preparation with a relative activity of 1.00. Nickel metal generated from MetChem BNC has an initial rate of dissolution of 317 ppm/hr at 60 °C and 980 ppm/hr at 80 °C (4% Nickel loading).

**Example 6: Suitable precursors and methods for making active Nickel**

**A. Making active nickel from various commercial nickel starting materials containing sulfur impurities**

The properties of various commercially available nickel starting materials such as basic nickel carbonate and nickel formate are examined to evaluate which properties correlate with good nickel-ligand complex formation.

**a) Basic Nickel Carbonate (BNC):  $\text{Ni}(\text{CO}_3)_x(\text{OH})_y(\text{H}_2\text{O})_z(\text{SO}_4)_q$ .**

Basic Nickel Carbonate (BNC;  $\text{Ni}(\text{CO}_3)_x(\text{OH})_y(\text{H}_2\text{O})_z(\text{SO}_4)_q$ ) BNC from various commercial sources is analyzed by loading ten grams of the BNC samples into a fluidized bed reactor, heating the reactor to 400°C under a nitrogen flow for 1h and reducing the samples at 400°C with 20% H<sub>2</sub> in N<sub>2</sub> for 2h. The resulting reduced nickel powder is then transferred into a N<sub>2</sub> purged glovebox and evaluated using the nickel-ligand complex formation and other assays described in Examples 1-4. The results are shown in Table 7a.

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Table 7a: Properties of BNC Sources for Making Active Nickel-Ligand Catalysts

| BNC Supplier | BNC Composition <sup>a</sup> |       |                    |       |                              | Ni composition |                                        | reduced Ni properties      |            |          |
|--------------|------------------------------|-------|--------------------|-------|------------------------------|----------------|----------------------------------------|----------------------------|------------|----------|
|              | % CO <sub>3</sub>            | % Ni  | % H <sub>2</sub> O | ppm S | S/Ni Ratio x10 <sup>-4</sup> | ppm S          | %Ni <sub>3</sub> S <sub>2</sub> by XRD | BET SSA, m <sup>2</sup> /g | Ni MCS, nm | Activity |
| BNC #8       | 22.39                        | 47.74 | 17.18              | 2505  | 96                           | 5500           | 0.90                                   | 4.70                       | 50         | 7.96     |
| BNC #8       | 24.57                        | 46.25 | 17.90              | 3162  | 125                          | 5300           | 0.80                                   | 4.30                       | 38         | 8.66     |
| BNC #8       | 23.44                        | 47.3  | 17.52              | 3797  | 147                          | 8200           | 2.30                                   | 4.60                       | 48         | 10.11    |
| BNC #8       | 22.19                        | 47.15 | 18.24              | 4674  | 181                          | 8600           | 3.10                                   | 3.45                       | 51         | 6.31     |
| BNC #7       | 16.75                        | 40.97 | 27.31              | 18760 | 838                          | 26800          | 13.50                                  | 12.90                      | 31         | 9.00     |
| BNC #2       | 16.66                        | 44.49 | 18.15              | 23930 | 985                          | 33700          | 12.50                                  | 9.20                       | 42         | 16.34    |

<sup>a</sup> Data is for the samples as received from the supplier.

Table 7a illustrates that the ability of nickel metal to form nickel-phosphorus ligand complexes relates to the content of sulfur in the nickel (or BNC used to make the nickel metal).

5                   **b) Nickel formate, dihydrate (NF) :  $\text{Ni}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$**

The composition of nickel formate, dihydrate ( $\text{Ni}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ , referred to as 'NF') from two commercial sources is analyzed by loading ten grams of these NF samples into a fluidized bed reactor and heating the samples to 400°C under a nitrogen flow for 2h in the absence of hydrogen. The resulting nickel powder is then  
10 transferred into a  $\text{N}_2$  purged glovebox and evaluated using the nickel-ligand complex formation and other assays described in Examples 1-4. Table 7b provides the results.

**Table 7b: Composition of NF sources for making Active Nickel-Ligand Catalysts**

| NF Supplier | NF Composition <sup>a</sup> |                   |       |                             | activity |
|-------------|-----------------------------|-------------------|-------|-----------------------------|----------|
|             | %Ni                         | %H <sub>2</sub> O | ppm S | S/Ni Ratio $\times 10^{-4}$ |          |
| NF #1       | 32.12                       | 21.88             | 575   | 32.8                        | 1.97     |
| NF #2       | 31.33                       | 20.15             | 1300  | 75.9                        | 6.86     |

<sup>a</sup> Data is for the samples as received from the supplier.

15                   The results presented in Table 7b indicate that it is also possible to directly prepare active nickel from thermal decomposition of commercial nickel formate dihydrate containing a sulfur impurity (as sulfate ion) without reduction of the nickel metal (e.g., without hydrogen reduction). For a method of removing sulfate ion impurities, see N. Minkova, M. Krusteva, V. Valiseva, D. Trendafelov,  
20 Communications of The Department of Chemistry, p. 222-228, Volume 13, Number 12, 1980.

Thus, use of nickel formate contrasts with the use of commercial BNC or NiO powders that do require a reduction step with hydrogen to obtain a nickel material suitable for ligand catalyst preparation.

25

**c) Method for making a Ni inactive by removing sulfur from a BNC containing a sulphate impurity**

Removal of sulfur (sulfate ions) from a BNC that was initially suitable for making active nickel yields a BNC that is unsuitable for preparing active nickel.

Sulfur removal is accomplished by washing the BNC containing traces of sulfate ions with 2.5% sodium carbonate solution (10 parts carbonate solution/1 part BNC) at 90°C for 2h. After cooling the mixture to ambient temperature, the resulting desulfurized BNC is filtered onto paper using vacuum suction and dried for 20h in air at 80°C in an oven. The content of sulfur, CO<sub>3</sub>, nickel and water in the sample is then analyzed using methods described in Example 1.

Ten grams of the “desulfurized” BNC sample are loaded into a fluidized bed reactor, heated to 400°C under a nitrogen flow for 1h and reduced at 400°C with 20% H<sub>2</sub> in N<sub>2</sub> for 2h. The resulting reduced nickel powder is then transferred into a N<sub>2</sub> purged glovebox and evaluated using the nickel-ligand complex formation and other assays described in Examples 1-4.

Table 7c shows the composition of BNC#8, before and after sulfur removal. As shown, the activity of the Ni significantly decreases when the sulfur content in BNC is reduced.

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Table 7c: Composition of BNC#8 and its corresponding Ni activity before and after S removal

| BNC Supplier           | BNC Composition <sup>a</sup> |       |                    |       | Ni composition               |       | reduced Ni properties                  |                            |                     |
|------------------------|------------------------------|-------|--------------------|-------|------------------------------|-------|----------------------------------------|----------------------------|---------------------|
|                        | % CO <sub>3</sub>            | % Ni  | % H <sub>2</sub> O | ppm S | S/Ni Ratio x10 <sup>-4</sup> | ppm S | %Ni <sub>3</sub> S <sub>2</sub> by XRD | BET SSA, m <sup>2</sup> /g | Ni MCS, nm activity |
| BNC #8 as received     | 24.57                        | 46.25 | 17.90              | 3162  | 125                          | 5300  | 0.80                                   | 4.30                       | 38 8.66             |
| BNC #8 after S removal | 20.17                        | 53.90 | 10.10              | 698   | 23.7                         | 1100  | 0.36                                   | 2.20                       | 43 0.03             |

<sup>a</sup> Data is for the sample as received from the supplier.

**B. Method for making active nickel with a nickel sulfate solution - doping of a commercial Basic Nickel Carbonate (BNC)**

Commercial BNC is treated with various aqueous 1M salt solutions of  $\text{NiSO}_4$  by mixing the BNC with the salt at a ratio of 1:5 by weight and stirring the mixture for 15 min. at room temperature in air. The metal powder is then filtered onto paper using vacuum suction and dried for 20h in air at  $80^\circ\text{C}$  in an oven. The content of sulfur,  $\text{CO}_3$ , nickel and water in the samples is then analyzed using methods described in Example 1.

Ten gram samples of the dried powder are gently ground with a mortar and pestle to disperse the solids, the samples are loaded into a fluidized bed reactor, then heated to  $400^\circ\text{C}$  under nitrogen flow for 1h and reduced at  $400^\circ\text{C}$  with 20%  $\text{H}_2$  in  $\text{N}_2$  gas for 2h. The resulting reduced nickel powder is then transferred into a  $\text{N}_2$  purged glovebox and evaluated for nickel-ligand catalyst preparation activity as well as composition, BET SSA, and MCS using the assays described in Examples 1-4.

The results shown in the following Table 8 indicate that treatment of BNC with nickel sulfate improves the formation of nickel that actively complexes with phosphorus-containing ligands.

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Table 8: Treatment of BNC Samples with 1M Nickel Sulfate Solution

| BNC sample                        | BNC Composition   |       |                    |       |                              | Reduced Ni Composition |                                        | Reduced Ni properties      |            |          |
|-----------------------------------|-------------------|-------|--------------------|-------|------------------------------|------------------------|----------------------------------------|----------------------------|------------|----------|
|                                   | % CO <sub>3</sub> | %Ni   | % H <sub>2</sub> O | ppm S | S/Ni Ratio x10 <sup>-4</sup> | ppm S                  | %Ni <sub>3</sub> S <sub>2</sub> by XRD | BET SSA, m <sup>2</sup> /g | Ni MCS, nm | Activity |
| BNC #2<br>+ 1M NiSO <sub>4</sub>  | 15.97             | 47.83 | 14.79              | 34000 | 1301                         | 53000                  | 18.00                                  | 10.9                       | 42         | 17.03    |
| BNC #2<br>+ 1M NiSO <sub>4</sub>  | 18.30             | 46.08 | 15.87              | 32000 | 1271                         | 66000                  | 21.50                                  | 12.9                       | 92         | 19.53    |
| BNC #11<br>+ 1M NiSO <sub>4</sub> | 19.32             | 48.4  | 14.02              | 9880  | 373.6                        | 33000                  | 8.60                                   | 16.6                       | 31         | 10.42    |
| BNC #4<br>+ 1M NiSO <sub>4</sub>  | 20.66             | 46.6  | 18.49              | 12775 | 501.8                        | 31200                  | 13.10                                  | 2.6                        | 66.5       | 6.36     |

Additional experiments are performed to optimize sulfate incorporation into BNC samples. Commercially available basic nickel carbonate (BNC #11) is added to a series of 0.01 – 1 M nickel sulfate solutions. The BNC to NiSO<sub>4</sub> ratio is about 5. The BNC solids are slurried in the nickel sulfate solution and stirred for about 15 – 30 minutes. A further example is carried out in which water is used instead of the nickel sulfate solution. The resulting solids are then filtered from the solution and dried under vacuum at 80 °C overnight. The solids are then calcined at 400 °C in a muffle furnace under air to produce nickel oxide.

The nickel oxides are then reduced with 30% hydrogen under flow reactor conditions as previously described to give reduced nickel. The nickel is transferred to a nickel catalyst preparation setup without any exposure to air. The activity of nickel dissolution is determined by measuring nickel dissolved vs. time in the nickel-ligand complex formation assay described in Example 1. As indicated in the following table, as the nickel sulfate concentration is raised from 0.01 M to 0.05 M, the nickel activity jumps from 1.4 to greater than 8.

**Table 9: Treatment of BNC with Nickel Sulfate**

| BNC Sample                         | % S (wt %) in Ni | Ni Activity |
|------------------------------------|------------------|-------------|
| BNC #11                            | 0.0%             | 0.5         |
| BNC #11 water washed               | 0.12%            | 0.5         |
| BNC #11 + 0.01 M NiSO <sub>4</sub> | 0.30%            | 1.4         |
| BNC #11 + 0.05 M NiSO <sub>4</sub> | 0.88%            | 8.2         |
| BNC #11 + 0.10 M NiSO <sub>4</sub> | 1.37%            | 7.5         |
| BNC #11 + 1.00 M NiSO <sub>4</sub> | 2.60%            | 8.7         |

**C. Active nickel made by nickel sulfate doping of BNC remains active over time and through several cycles of ligand formation**

Commercially available BNC (BNC#11) is doped with sulfur by using nickel sulfate. The BNC – nickel sulfate mixture is calcined and reduced at 400 °C with 10 – 30% hydrogen in nitrogen. The resulting nickel is tested for its dissolution and complex formation using the nickel-catalyst preparation assay described in Example 1. After the first dissolution of nickel with ligand, the dissolved nickel-ligand catalyst is decanted leaving the undissolved/unreacted nickel behind. The undissolved nickel is again tested for its activity for to dissolve and complex with ligand. This is repeated in total of 4 times to check for the variability of activity and determine if there is a

reduction in the activity after one or more dissolutions. The amount of sulfur in starting material is 2.6% by weight on nickel basis.

**Table 10: The Presence of Sulfur Improves Nickel Complex Formation**

| BNC #11 Sample                                 | Nickel at start of dissolution (g) | Activity |
|------------------------------------------------|------------------------------------|----------|
| BNC #11                                        | 3.20                               | 0.5      |
| BNC #11 + 2.6% S                               | 3.22                               | 8.71     |
| BNC #11 + 2.6% S<br>– First complex formation  | 3.01                               | 8.55     |
| BNC #11 + 2.6% S<br>– Second refresh           | 2.81                               | 7.00     |
| BNC #11 + 2.6% S<br>– Third complex formation  | 2.60                               | 8.57     |
| BNC #11 + 2.6% S<br>– Fourth complex formation | 2.40                               | 7.10     |

5

**D. Method for making active nickel from NiSO<sub>4</sub> solution by doping of commercial NiO (sample C) or NiO-coated (passivated) nickel (sample D)**

Commercially available NiO or NiO-coated nickel samples that are previously assessed to be inactive (see Example 5) are mixed with 1M NiSO<sub>4</sub> aqueous solution at a ratio of 1:5 by weight and stirred for 15 min at room temperature in air. The powder is then filtered onto paper using vacuum suction and dried for 20h in air at 80°C in an oven. The resulting powder (~10g) is gently ground with a mortar and pestle to disperse the solids. The ground powder is then loaded into a fluidized bed reactor, heated to 400°C under nitrogen flow and directly reduced with 20% H<sub>2</sub> in N<sub>2</sub> for 2h at 400°C. The resulting reduced nickel powder is then transferred into a N<sub>2</sub> purged glovebox and evaluated for nickel-ligand catalyst preparation activity as described in Example 1.

**Table 11: Low Activity Nickel Sources are Improved by NiSO<sub>4</sub> Treatment**

| NiO sample               | Ni composition |                                        | Reduced Ni properties      |            | activity |
|--------------------------|----------------|----------------------------------------|----------------------------|------------|----------|
|                          | ppm S          | %Ni <sub>3</sub> S <sub>2</sub> by XRD | BET SSA, m <sup>2</sup> /g | Ni MCS, nm |          |
| C + 1M NiSO <sub>4</sub> | 7155           | 2.90                                   | 11.20                      | 31         | 6.74     |
| D + 1M NiSO <sub>4</sub> | 25000          | 7.4                                    | 24.70                      | 39.0       | 11.32    |

20

**E. Method for making active nickel by elemental sulfur doping of basic nickel carbonate and its subsequent nickel oxide**

Commercially available BNC #1 is tested to evaluate whether sulfur (e.g., rather than sulfate) can activate the nickel therein to improve complex formation with phosphorus-containing ligands.

Three aliquots of BNC #1 are tested (#1A, #1B and #1C). About 35 g of BNC #1A is mixed with 0.16 g of elemental sulfur (1 wt % on nickel basis). The mixture is calcined at 400 °C in a muffle furnace under air to nickel oxide. The nickel oxide/sulfur powder is reduced at 400 °C with 30% hydrogen in nitrogen gas mixture for 2 hours. The reduced nickel is evaluated for activity under standard catalyst preparation conditions described in Example 1.

Another BNC sample (BNC #1B) is first calcined to form nickel oxide. The nickel oxide is then doped with 1% elemental sulfur (on nickel basis) and further reduced at 400 °C with 30% hydrogen in nitrogen gas mixture for 2 hours.

Finally, a third BNC #1C sample is calcined and reduced at 400 °C using the aforementioned conditions without any sulfur addition. The activity of all reduced nickel samples is measured under the nickel-ligand complex formation assay described in Example 1.

The activity of MetChem nickel with sulfur is 6X higher than nickel not doped with elemental sulfur.

**Table 12: Use of Elemental Sulfur to Activate Nickel**

| BNC #1 Sample                                 | % S in final nickel (wt %) | Activity |
|-----------------------------------------------|----------------------------|----------|
| BNC #1A + 1% elemental S                      | Tbd                        | 5.8      |
| BNC #1B → nickel oxide, then + 1% elemental S | 0.95%                      | 6.1      |
| BNC #1C (no sulfur added)                     | 0.12%                      | 1.3      |

**F. Method for activating nickel by doping a commercial source of nickel oxide with elemental sulfur: Comparative operative and inoperative examples of product Nickel**

Twenty gram samples of various commercial nickel oxides are mixed with about 0.16 g of elemental sulfur (1% by weight on nickel basis) and reduced at 400 °C under flow of 10 – 30% H<sub>2</sub>/N<sub>2</sub> for few hours until the material is completely reduced.

The reduced nickel is then dissolved the nickel-ligand complex formation assay mixture described in Example 1, and the activity of dissolution is determined.

A 20 g sample of nickel oxide is separately reduced with 10 – 30% H<sub>2</sub>/N<sub>2</sub> at 400 °C for few hours to obtain reduced nickel untreated with sulfur.

- 5           The activity of the nickel products is determined using the catalyst preparation assay.

**Table 13: Treatment of Nickel Oxide with Sulfur Improves Reduced Nickel Activity**

| Nickel Oxide Sample   | % S (wt %) | Surface area (m <sup>2</sup> /g) |        | Activity |
|-----------------------|------------|----------------------------------|--------|----------|
|                       |            | Nickel oxide                     | Nickel |          |
| NiO sample E          | 0.12%      | 4.8                              | tbd    | 1.31     |
| NiO sample E + 1% S   | 0.95%      | 4.8                              | 2.8    | 6.07     |
| NiO sample F          | 0.17%      | 52.7                             | tbd    | 1.27     |
| NiO sample F + 1% S   | tbd        | 52.7                             | 5.14   | 8.04     |
| NiO sample F + 1.6% S | 1.62%      | 52.7                             | 5.14   | 9.01     |
| NiO sample G          | 0.05%      | 0.77                             | tbd    | 0.10     |
| NiO sample G + 1% S   | 0.5%       | 0.77                             | 1.47   | 2.96     |
| NiO sample H          | 0.05%      | 81.2                             | tbd    | 0.54     |
| NiO sample H + 1% S   | 1.04%      | 81.2                             | 1.4    | 4.63     |
| NiO sample I          | 0.22%      | 7.6                              | tbd    | 3.35     |
| NiO sample I + 1% S   | 0.74%      | 7.6                              | 4.0    | 6.96     |
| NiO sample J          | 0.16%      | 99.2                             | tbd    | 2.57     |
| NiO sample J + 1% S   | 1.05%      | 99.2                             | 3.4    | 5.23     |

10

#### **G. Relating activity of nickel with the BET surface area of reduced nickel**

- Example 6F shows that addition of approximately 1% elemental sulfur to nickel oxide samples followed by reduction resulted in improved nickel activity for these samples in the catalyst-preparation dissolution assay compared to its baseline activity without any sulfur addition. However, a plot of all the data in Table 13 relating to BET surface area vs. activity did not provide a meaningful correlation for these nickel oxide samples, possibly because the samples had different sulfur contents and reduction conditions.

- However, if the reduction conditions and the sulfur concentration of the nickel are held approximately constant there is a meaningful correlation between the activity of the nickel and the nickel BET surface area. Thus, nickel oxide samples with similar sulfur content (in this instance ~1%) are reduced under similar conditions (in this case reduction was carried out at 400 °C and 2 hours). FIG. 21 shows that the BET surface area of these nickel samples is correlated with nickel complex formation activity. The

extent of sulfur loading somewhat depends on the initial surface area of the nickel oxide. If the sulfur loading is not constant, the activity will not correlate very well with the BET surface area because sulfur content plays a dominant role in promoting the activity of nickel while BET SSA plays a secondary role.

5

#### H. Reduction temperature affects activity of elemental sulfur doped nickel

Nickel oxide sample F is doped with ~1% elemental sulfur (on nickel basis) and reduced at temperatures varying from 200 to 500 °C. The reduction time is 4 hours. The amount of hydrogen used is approximately 20 times the stoichiometric amount required for complete reduction of nickel oxides. Even though the amount of sulfur should be same in all these cases, the activity observed is a function of the temperature used. The activity went through an optimum value with highest observed for reduction temperature of 300 °C. The table below shows the effect of temperature.

**Table 14: Reduction Temperature Affects the Nickel Metal Activity**

| Sample                    | Temperature (°C) | % S (wt% of nickel) | Activity |
|---------------------------|------------------|---------------------|----------|
| NiO Sample F (no S added) | 400              | 0.17%               | 1.3      |
| NiO Sample F + 1% S       | 200              | 0.808               | 5.5      |
| NiO Sample F + 1% S       | 250              | 0.954               | 8.7      |
| NiO Sample F + 1% S       | 300              | 1.039               | 11.3     |
| NiO Sample F + 1% S       | 350              | 0.968               | 9.0      |
| NiO Sample F + 1% S       | 400              | 1.035               | 7.0      |
| NiO Sample F + 1% S       | 450              | 0.941               | 5.5      |
| NiO Sample F + 1% S       | 500              | 1.005               | 3.2      |

15

#### I. Method for making nickel with addition of solid nickel sulfate, or nickel sulfide to a commercial Basic Nickel Carbonate (BNC)

A commercial BNC sample (BNC #2) is mixed with  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  or  $\text{Ni}_3\text{S}_2$  using a mortar and pestle in air. The resulting powder (~10g) is then loaded into a fluidized bed reactor, heated to 400°C under nitrogen flow for 1h (no hold-up time for NiO) and reduced at 400°C with 20%  $\text{H}_2$  in  $\text{N}_2$  for 2h. The resulting reduced nickel

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powder is then transferred into a N<sub>2</sub> purged glovebox and evaluated in the nickel-ligand complex formation assay described in Example 1.

**Table 15: Active Nickel can be made by adding sulfur in various forms (sulfate, sulfide) to BNC in solid form**

5

| sample                                                | BNC/NiO Composition |       |                   | Ni properties |          |
|-------------------------------------------------------|---------------------|-------|-------------------|---------------|----------|
|                                                       | %CO <sub>3</sub>    | %Ni   | %H <sub>2</sub> O | ppm S         | activity |
| BNC #2<br>+ 8.7% NiSO <sub>4</sub> ·6H <sub>2</sub> O | 27.68               | 46.77 | 13.52             | 15413         | 15.76    |
| BNC #2<br>+ 3.5%Ni <sub>3</sub> S <sub>2</sub>        | 32.25               | 48.01 | 12.19             | 18755         | 20.91    |

**J. Method for making active nickel by Sulfur doping of reduced nickel without thermal treatment**

About 20 g of nickel oxide (sample E) is reduced at 400 °C with 30% H<sub>2</sub>/N<sub>2</sub> for a couple of hours until the oxide is fully reduced to nickel. About 2.5 wt% (on nickel basis) of elemental sulfur is added to the reduced nickel. The product is then tested for activity by dissolution in the nickel catalyst preparation assay. A similar nickel oxide is reduced and tested for the activity of the metal in the absence of sulfur.

A second source of nickel oxide is mixed with sulfur and evaluated in the nickel-ligand complex formation assay described in Example 1.

**Table 16: Sulfur Activation of Reduced Nickel**

| Sample                        | % S (wt %) | Surface area | Activity |
|-------------------------------|------------|--------------|----------|
| NiO (sample E)                | 0.12%      | tbd          | 1.3      |
| NiO (sample E) + 3.7% S       | tbd        | tbd          | 1.9      |
| NiO (sample F) => Ni          | 0.17%      | 52.7         | 1.3      |
| NiO (sample F) => Ni + 2.5% S | tbd        | 52.7         | 4.3      |

In another experiment, about 3.2 g of nickel is prepared by reduction of NiO (sample F) at 400 °C. The reduced nickel metal powder is tested in the catalyst preparation assay where about 150 – 500 ppm of elemental sulfur (on total weight basis of the catalyst preparation assay) is directly added to the catalyst preparation assay mixture using the procedures described in Example 1.

**Table 17: Direct Addition of Sulfur to Nickel Catalyst Preparation Mixture**

| Sample                           | S amount (ppm) in cat-prep | Activity |
|----------------------------------|----------------------------|----------|
| NiO (sample F) => Ni             | 0                          | 0.5      |
| NiO (sample F) => Ni<br>+ 0.4% S | 150                        | 2.8      |
| NiO (sample F) => Ni<br>+ 0.6% S | 250                        | 3.1      |
| NiO (sample F) => Ni<br>+ 1.2% S | 500                        | 4.0      |

In another experiment, BNC #11 and NiO (sample F) are reduced at 400 °C. About 3.2 g of reduced nickel is tested in the nickel catalyst preparation assay. About  
 5 10 – 150 ppm of equivalent sulfur in the form of nickel sulfate is added to the catalyst preparation assay mixture described in Example 1.

**Table 18: Addition of Nickel Sulfate to Nickel Catalyst Preparation Mixture**

| Sample                              | Equivalent S (ppm) from NiSO <sub>4</sub> | Activity |
|-------------------------------------|-------------------------------------------|----------|
| NiO (sample F) => Ni                | 0                                         | 0.5      |
| NiO (sample F) => Ni<br>+ 10 ppm S  | 10                                        | 0.7      |
| NiO (sample F) => Ni<br>+ 50 ppm S  | 50                                        | 1.3      |
| NiO (sample F) => Ni<br>+ 150 ppm S | 150                                       | 1.5      |
| BNC #11 → Ni                        | 0                                         | 0.5      |
| BNC #11 → Ni<br>+ 150 ppm S         | 150                                       | 2.0      |

In another experiment, elemental sulfur is added directly to a nickel catalyst  
 10 preparation mixture containing nickel metal. The mixture is then heated to 60°C and the assay procedure is conducted as described in Example 1.

**Table 19: Elemental Sulfur Addition to Nickel-Ligand catalyst preparation reaction mixture**

| sample                                         | activity |
|------------------------------------------------|----------|
| Ni D<br>+ 12% S <sub>8</sub> based on Ni       | 1.1      |
| Reuse Ni D<br>+ 12% S <sub>8</sub> based on Ni | 3        |

Note that in Table 5, Ni D had an activity of only about 0.24 when no sulfur source was added.

**5 K. Method for improving nickel activity by pre-mixing and heating elemental sulfur S<sub>8</sub> with unreduced NiO-coated Ni prior to the Nickel-ligand catalyst prep**

Elemental sulfur is mixed with a commercial NiO-coated Ni or a passivated Ni in a flask either in pentenenitrile solution or neat as a solid mixture. The mixture is  
 10 agitated while heated at 110°C for 24h. The resulting powder/slurry is then evaluated in the nickel-ligand complex formation assay described in Example 1.

**Table 20: Elemental Sulfur Addition to Nickel-Ligand catalyst preparation reaction mixture**

| sample                                                                       | activity |
|------------------------------------------------------------------------------|----------|
| Unreduced Ni B<br>+ 11%S <sub>8</sub> based on Ni in 3PN                     | 0.92     |
| Unreduced Ni B<br>+ 11%S <sub>8</sub> based on Ni (solid mix)                | 1.73     |
| BNC #12 derived passivated Ni<br>+ 12%S <sub>8</sub> based on Ni (solid mix) | 0.84     |

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Note also that, as shown in Table 5 above, unreduced nickel sample B had an activity of 0.01.

**L. Making active nickel by S doping of carbonyl based nickel**

20 Carbonyl based nickel sample is treated with sulfur either by directly doping them with nickel sulfate and thermal treatment or by forced sulfidation with elemental sulfur.

In the former case, sample nickel A is treated with 1 M NiSO<sub>4</sub> for about 15 – 30 minutes with stirring. The solution is filtered to retain nickel loaded with nickel  
 25 sulfate. These solids are then dried under vacuum at 80 °C and then further calcined and reduced at 400 °C. In reduced form, the nickel A sample has a BET surface area of 0.49 m<sup>2</sup>/g.

After the first dissolution/complexation, four additional dissolution/complexations are performed successively using undissolved nickel in the same nickel catalyst preparation mixture.

**Table 21: NiSO<sub>4</sub> Treatment Improves Nickel Complex Formation**

| Nickel Sample A                                           | % S (wt %) | Activity |
|-----------------------------------------------------------|------------|----------|
| Ni A                                                      | 0.006      | 0.15     |
| Ni A + 1 M. NiSO <sub>4</sub>                             | 0.354      | 0.78     |
| Ni A + 1 M. NiSO <sub>4</sub><br>First complex formation  | 0.354      | 2.23     |
| Ni A + 1 M. NiSO <sub>4</sub><br>Second complex formation | 0.354      | 1.04     |
| Ni A + 1 M. NiSO <sub>4</sub><br>Third complex formation  | 0.354      | 0.95     |
| Ni A + 1 M. NiSO <sub>4</sub><br>Fourth complex formation | 0.354      | 1.02     |

5

Samples of commercial nickel K and L (as received) are stirred in an Adiponitrile (ADN) solution containing a selected amount of sulfur for 24 – 48 hours at 110 – 120 °C. The activity of these nickel samples is shown in Table 21.

10

**Table 22: Sulfur Treatment Improves Nickel Catalyst Activity**

| Ni Sample       | S content | Activity |
|-----------------|-----------|----------|
| K               | 0         | 0        |
| K + 1.25% S/ADN | tbd       | 0.14     |
| K + 31.3% S/ADN | tbd       | 0.58     |
| L               | 0         | 0        |
| L + 1.25% S/ADN | tbd       | 0.12     |
| L + 31.3% S/ADN | tbd       | 0.78     |

The following statements are intended to describe some aspects of the invention.

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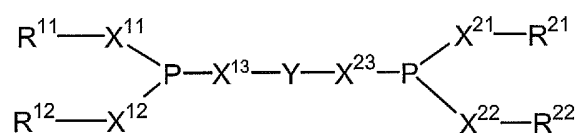
Statements Describing Features of the Invention

1. A method of generating a nickel hydrocyanation catalyst comprising:
  - (a) contacting a nickel metal with a sulfur source before or during complex formation between nickel atoms from the nickel metal and one or more phosphorus-containing ligand(s) to thereby form the nickel hydrocyanation catalyst; or
  - (b) contacting a nickel starting material with a sulfur source, generating nickel metal from the mixture of the nickel starting material and the sulfur source, and contacting the nickel metal with one or more phosphorus-containing ligand(s) to thereby form a complex between nickel atoms from the nickel metal and one or more phosphorus-containing ligands.
2. The method of statement 1, further comprising determining a sulfur content of the nickel metal or the nickel starting material before contacting the nickel metal or the nickel starting material with the sulfur source.
3. The method of statement 2, wherein the sulfur content of the nickel metal or the nickel starting material is determined using infrared (IR) spectroscopy analysis, microcoulometry, inductively coupled plasma (ICP) mass spectrometry or a combination thereof.
4. The method of statement 2 or 3, wherein the nickel metal or the nickel starting material is contacted with the sulfur source if the sulfur content of the nickel metal or the nickel starting material is less than 0.2 wt% to 0.8 wt% relative to the weight of the nickel metal or the nickel starting material.
5. The method of any of statements 2-4, wherein the nickel metal or the nickel starting material is contacted with the sulfur source if the sulfur content of the nickel metal or the nickel starting material is less than 0.4 wt% relative to the weight of the nickel metal or the nickel starting material.
6. The method of any of statements 1-5, wherein the sulfur source is selected from the group consisting of elemental sulfur, sulfur-containing gases, sulfur-containing salts, sulfur-containing ions and combinations thereof.
7. The method of any of statements 1-6, wherein the sulfur source is in liquid, solid, gaseous or a combination of such physical forms.
8. The method of any of statements 1-7, wherein the sulfur source comprises a sulfate, sulfite, sulfide, hyposulfite, thiosulfate, sulfur trioxide, sulfur dioxide, sulfur monoxide, sulfur halide, and a combination thereof.

9. The method of any of statements 1-8, wherein the sulfur source is selected from the group consisting of a polymer of sulfur, a mixture of polymeric chains of sulfur, cyclic sulfur, one or more allotropes of sulfur, and a combination thereof.
10. The method of any of statements 1-9, wherein the sulfur source is selected from  
5 the group consisting of hydrogen sulfide, nickel sulfate, nickel sulfite, nickel sulfide, nickel hyposulfite, nickel thiosulfate, sulfur trioxide, sulfur dioxide, sulfur monoxide, disulfur dichloride, sulfur dichloride, sulfur tetrachloride, sulfur chloride pentafluoride, disulfur decafluoride, sulfur hexafluoride, sulfur tetrafluoride, sulfur trifluoride and combinations thereof.
- 10 11. The method of any of statements 1-10, wherein the sulfur source is a sulfur-containing nickel salt.
12. The method of any of statements 1-11, wherein the sulfur source is at least 95% to 99.9% free of silicon, sodium, potassium, calcium, magnesium, phosphorus, aluminium, copper, tungsten, mercury, iron and combinations thereof.
- 15 13. The method of any of statements 1-12, wherein the sulfur source is contacted with the nickel metal or the nickel starting material when the nickel metal or the nickel starting material is in solution or in solid particulate form.
14. The method of any of statements 1-13, wherein the sulfur source is contacted with the nickel metal or the nickel starting material, before or during suspension of the  
20 nickel metal or the nickel starting material in a liquid organic medium or in a gas flow.
15. The method of any of statements 1-14, wherein the nickel metal and/or the nickel starting material is at least 95% to 99.9% free of silicon, sodium, potassium, calcium, magnesium, phosphorus, aluminium, copper, tungsten, mercury, iron and  
25 combinations thereof.
16. The method of any of statements 1-15, wherein the nickel starting material is basic nickel carbonate, nickel carbonate, nickel bicarbonate, nickel oxalate, nickel formate, nickel squarate, nickel hydroxide, nickel oxide, nickel salts or a combination thereof.
- 30 17. The method of any or statements 1-16, wherein the nickel starting material is contacted with the sulfur source before or after calcining the nickel starting material.

18. The method of any of statements 1-17, wherein the nickel starting material or the nickel metal is contacted with the sulfur source before reduction to zero valent particulate nickel.
19. The method of any of statements 1-18, wherein reduction is at 200 °C to 400 °C  
5 for about 3 to about 5 hours.
20. The method of any of statements 1-19, wherein the nickel metal or the nickel starting material is contacted with the sulfur source after reduction of the nickel metal or after reduction of the nickel starting material to zero valent nickel.
21. The method of any of statements 1-20, wherein a weight percentage of about 0.1  
10 wt% to about 50 wt% sulfur is contacted with the nickel metal or the nickel starting material, wherein the sulfur weight percentage is relative to the total weight of nickel in the nickel metal or the nickel starting material.
22. The method of any of statements 1-21, wherein a weight percentage of about 0.2 wt% to about 15 wt% sulfur is contacted with the nickel metal or the nickel  
15 starting material, where the sulfur weight percentage is relative to the total weight of nickel in the nickel metal or the nickel starting material.
23. The method of any of statements 1-22, wherein a weight percentage of about 0.4 wt% to about 12 wt% sulfur is contacted with the nickel metal or the nickel starting material, where the sulfur weight percentage is relative to the total weight  
20 of nickel in the nickel metal or the nickel starting material.
24. The method of any of statements 1-23, wherein the method generates a particulate nickel metal with a sulfur to nickel atomic ratio of about 0.003 to about 1.8.
25. The method of any of statements 1-24, wherein the method generates a particulate nickel metal with a sulfur to nickel atomic ratio of about 0.01 to about 0.2.
- 25 26. The method of any of statements 1-25, wherein the method generates a particulate nickel metal with a sulfur to nickel atomic ratio of about 0.003 to about 0.05.
27. The method of any of statements 1-26, wherein an equilibrium of complex formation is reached by about 2 hours when about 4 wt% nickel is mixed at about 60 °C to 80 °C in an organonitrile solvent with about 0.5 to 2.5 moles Lewis acid  
30 per mole phosphorus-containing ligand.
28. The method of any of statements 1-27, wherein an equilibrium of complex formation is reached by about 30 minutes when about 4% nickel is mixed at about 60 °C to 80 °C in an organonitrile solvent with about 0.5 to 2.5 moles Lewis acid per mole phosphorus-containing ligand.

29. The method of any of statements 1-28, wherein a Lewis acid is present during complex formation.
30. The method of statement 29, wherein the Lewis acid is selected from the group consisting of zinc chloride, ferrous chloride, or a combination thereof.
31. The method of any of statements 1-30, wherein complex formation occurs in an organonitrile solvent.
32. The method of statement 31, wherein the organonitrile solvent is a pentenenitrile.
33. The method of any of statements 1-32, wherein one or more of the phosphorus ligands is a ligand of Formula (III):



Formula (III)

wherein:

$\text{X}^{11}$ ,  $\text{X}^{12}$ ,  $\text{X}^{13}$ ,  $\text{X}^{21}$ ,  $\text{X}^{22}$  and  $\text{X}^{23}$  independently represent oxygen or a single direct

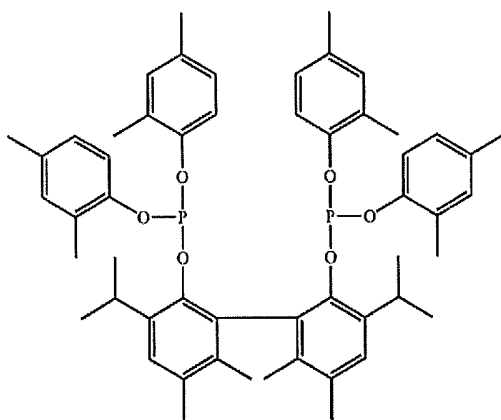
bond;

$\text{R}^{11}$  and  $\text{R}^{12}$  independently represent identical or different, single or bridged organic radicals;

$\text{R}^{21}$  and  $\text{R}^{22}$  independently represent identical or different, single or bridged organic radicals; and

Y represents a bridging group.

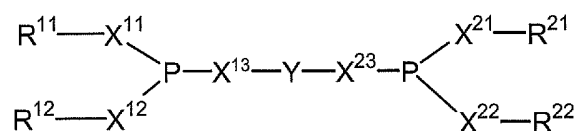
34. The method of any of statements 1-33, wherein one or more of the phosphorus ligands is Ligand (V):



Ligand (V).

35. The method of any of statements 1-34, wherein a complex forms between nickel atoms from the nickel metal and one or more phosphorus-containing ligands mixed under a non-oxygen containing atmosphere.
- 5 36. The method of any of statements 1-35, wherein a complex formed between nickel atoms from the nickel metal and one or more phosphorus-containing ligands catalyses hydrocyanation of an olefin.
37. The method of statement 36, wherein the olefin is pentenenitrile.
38. A catalyst preparation mixture comprising nickel metal, one or more phosphorus-containing ligands and about 0.001 wt% to about 15 wt% sulfur, wherein the sulfur weight percentage is relative to the total weight of nickel in the mixture.
- 10 39. The catalyst preparation mixture of statement 37, wherein the mixture is in an organonitrile solvent.
40. The catalyst preparation mixture of statement 39, wherein the solvent is a pentenenitrile.
- 15 41. The catalyst preparation mixture of any of statements 38 - 40, further comprising a Lewis acid.
42. The catalyst preparation mixture of statement 41, wherein the Lewis acid is selected from the group consisting of zinc chloride, ferrous chloride, or a combination thereof.
- 20 43. The catalyst preparation mixture of statement 42, wherein the Lewis acid is zinc chloride.
44. The catalyst preparation mixture of any of statements 38-43, wherein one or more of the phosphorus ligands is a ligand of Formula (III):

25



Formula (III)

wherein,

$\text{X}^{11}$ ,  $\text{X}^{12}$ ,  $\text{X}^{13}$ ,  $\text{X}^{21}$ ,  $\text{X}^{22}$  and  $\text{X}^{23}$  independently represent oxygen or a single direct

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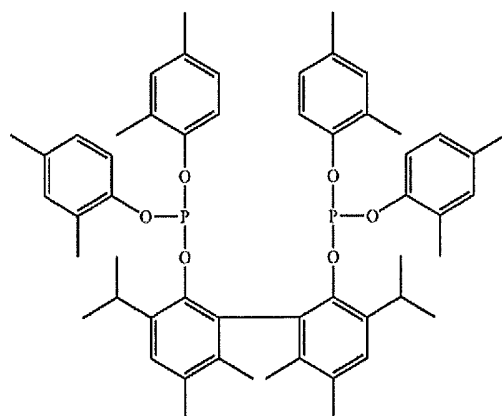
bond;

$\text{R}^{11}$  and  $\text{R}^{12}$  independently represent identical or different, single or bridged organic radicals;

$R^{21}$  and  $R^{22}$  independently represent identical or different, single or bridged organic radicals; and

Y represents a bridging group.

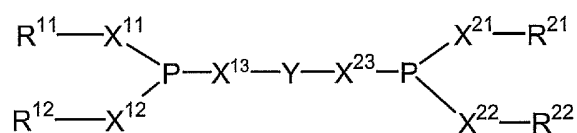
45. The catalyst preparation mixture of any of statements 38-44, wherein one or more  
5 of the phosphorus ligands is Ligand (V):



Ligand (V).

- 10 46. The catalyst preparation mixture of any of statements 38-45, comprising a weight percent of the one or more phosphorus containing ligands of about 2 to about 8 wt%.
47. The catalyst preparation mixture of any of statements 38-46, comprising a weight percent of the one or more phosphorus containing ligands of about 4.75 to about  
15 5.75 wt%,
48. The catalyst preparation mixture of any of statements 38-47, comprising a weight percent of the one or more phosphorus containing ligands of about 5.25 wt%.
49. The catalyst preparation mixture of any of statements 38-48, comprising a nickel weight percent of about 1 to about 7 wt%.
- 20 50. The catalyst preparation mixture of any of statements 38-49, comprising a nickel weight percent of about 4 to about 5 wt%.
51. The catalyst preparation mixture of any of statements 42-50, comprising a zinc to phosphorus containing ligand molar ratio of about 0.5 to about 2.5
52. The catalyst preparation mixture of any of statements 42-51, comprising a zinc to  
25 phosphorus containing ligand molar ratio of about 0.70 to about 0.80.

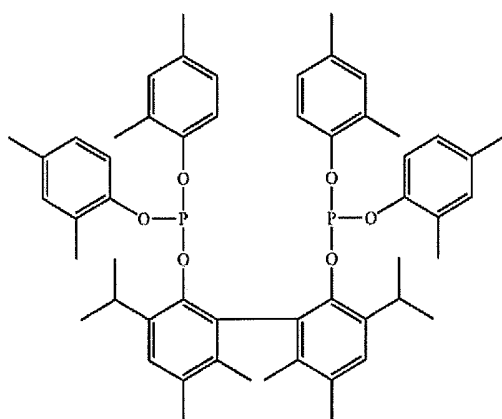
53. The catalyst preparation mixture of any of statements 38-52, comprising about 0.01 wt% to about 12 wt% sulfur, relative to the total weight of nickel in the mixture.
54. A complex formed between nickel atoms and one or more phosphorus-containing ligands comprising about 0.00001 wt% to about 15 wt% sulfur, wherein the sulfur weight percentage is relative to the total weight of nickel in the complex.
55. The complex of statement 54, comprising about 0.0001 wt% to about 2 wt% sulfur.
56. The complex of statement 54 or 55, wherein one or more of the phosphorus ligands is a ligand of Formula (III):



Formula (III)

wherein,

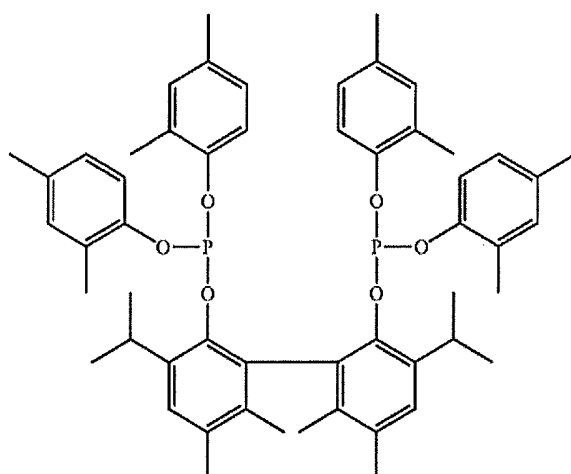
- 15  $\text{X}^{11}$ ,  $\text{X}^{12}$ ,  $\text{X}^{13}$ ,  $\text{X}^{21}$ ,  $\text{X}^{22}$  and  $\text{X}^{23}$  independently represent oxygen or a single direct bond;
- $\text{R}^{11}$  and  $\text{R}^{12}$  independently represent identical or different, single or bridged organic radicals;
- $\text{R}^{21}$  and  $\text{R}^{22}$  independently represent identical or different, single or bridged organic radicals; and
- 20 Y represents a bridging group.
57. The complex of any of statements 54-56, wherein one or more of the phosphorus ligands is Ligand (V):



Ligand (V).

58. The complex of any of statements 54-57, wherein the complex is in an organonitrile solvent.
59. The complex of any of statements 54-58, wherein the complex is in a pentenenitrile solvent.
60. A nickel particulate form comprising nickel crystallites, wherein the nickel particulate form has at least two properties selected from the group consisting of:
- the nickel particulate form has a BET Specific Surface Area of at least about 1 m<sup>2</sup>/gm;
  - at least 10% of the nickel crystallites have a size (C10) that is less than about 20 nm;
  - the nickel crystallites have an average crystallite size of no greater than about 100 nm;
  - the nickel particulate form has a BET Specific Surface Area / C50 ratio of not less than 0.07 x 10<sup>9</sup> m/gm;
  - the nickel crystallite size distribution span is greater than about 1.0;
  - the nickel particulate form on average has at least about 10<sup>15</sup> surface crystallites per gram of nickel;
  - at least 10% of the particles of the form have a size (D10) of no greater than about 6 μm;
  - the nickel particulate form has a Laser Diffraction Specific Surface Area of at least about 0.4 m<sup>2</sup>/gm;
  - the nickel particulate form has a BET Specific Surface Area to D10 ratio of about 0.3 x 10<sup>6</sup> m/gm to about 10.0 x 10<sup>6</sup> m/gm;

on average there are at least about  $10^{16}$  surface crystallites per gram nickel that are smaller than or equal to size C10; and  
 the nickel particulate form complexes with Ligand (V) within about 2 hours when about 4 to 5 wt% of the nickel particulate form is mixed with 3-pentenitrile containing approximately 5.25 wt% Ligand (V) and approximately 6300 ppm  $\text{ZnCl}_2$ ; wherein Ligand (V) has the following formula:



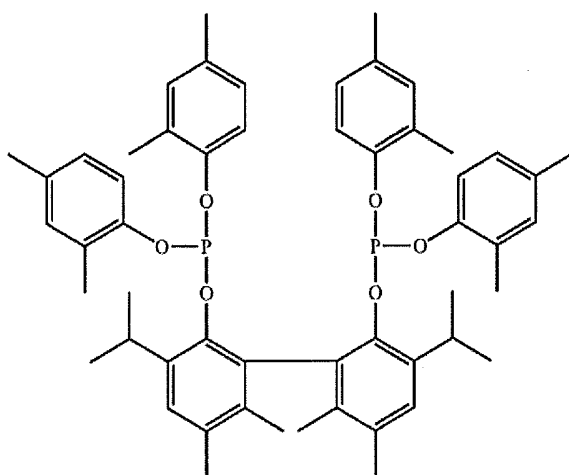
61. The nickel particulate form of statement 60, having at least three of the properties in the group.
- 5 62. The nickel particulate form of statement 60 or 61, having at least four of the properties in the group.
63. The nickel particulate form of any of statements 60-62, wherein the nickel particulate form has a BET Specific Surface Area of at least about  $2 \text{ m}^2/\text{g}$ .
64. The nickel particulate form of any of statements 60-63, wherein the nickel
- 10 particulate form has a BET Specific Surface Area of at least about  $4 \text{ m}^2/\text{g}$ .
65. The nickel particulate form of any of statements 60-64, wherein the nickel particulate form has a BET Specific Surface Area of at least  $10 \text{ m}^2/\text{g}$ .
66. The nickel particulate form of any of statements 60-65, wherein the BET SSA / C50 ratio is at least about  $0.1 \times 10^9 \text{ m/gm}$ .
- 15 67. The nickel particulate form of any of statements 60-66, wherein the average crystallite size of no greater than about 70 nm.
68. The nickel particulate form of any of statements 60-67, wherein the average crystallite size of no greater than about 50 nm.

69. The nickel particulate form of any of statements 60-68, wherein the average crystallite size of no greater than about 30 nm.
70. The nickel particulate form of any of statements 60-69, wherein the BET SSA / C50 ratio is at least about  $0.4 \times 10^9$  m/gm.
- 5 71. The nickel particulate form of any of statements 60-70, wherein the nickel particulate form has a Laser Diffraction SSA / C50 ratio of at least about  $4.3 \times 10^6$ .
72. The nickel particulate form of any of statements 60-71, wherein the Laser Diffraction SSA / C50 ratio is at least about  $10^7$ .
- 10 73. The nickel particulate form of any of statements 60-72, wherein at least 10% of the crystallites have a size (C10) that is less than about 10 nm.
74. The nickel particulate form of any of statements 60-73, having an average crystallite size of no greater than about 20-25 nm.
75. The nickel particulate form of any of statements 60-74, with a nickel crystallite size distribution span greater than 1.5.
76. The nickel particulate form of any of statements 60-75, wherein the nickel particulate form on average has at least about  $2 \times 10^{15}$  surface crystallites per gram nickel.
77. The nickel particulate form of any of statements 60-76, wherein the nickel particulate form on average has at least about  $5 \times 10^{15}$  surface crystallites per gram nickel.
78. The nickel particulate form of any of statements 60-77, wherein the nickel  
15 particulate form on average has at least about  $1 \times 10^{16}$  surface crystallites per gram nickel.
79. The nickel particulate form of any of statements 60-78, wherein the surface crystallites per gram nickel are calculated for substantially spherical crystallites or substantially cuboidal crystallites.
80. The nickel particulate form of any of statements 60-79, wherein on average per gram there are at least about  $2 \times 10^{15}$  surface crystallites per gram nickel as calculated for cuboidal crystallites, or at least about  $10^{15}$  surface crystallites per gram nickel as calculated for substantially spherical crystallites, or both.
81. The nickel particulate form of any of statements 60-80, wherein the at least 10% of the particles have a diameter (D10) of no greater than about 4  $\mu$ m.

82. The nickel particulate form of any of statements 60-81, wherein a ratio of BET Specific Surface Area to Laser Diffraction Specific Surface Area is between 20 and 30.
83. The nickel particulate form of any of statements 60-82, wherein a ratio of BET Specific Surface Area to D10 is from 3 to 5 m<sup>2</sup>/gm/μm or about 0.5 x 10<sup>6</sup> m/gm to about 5 x 10<sup>6</sup> m/g.
84. The nickel particulate form of any of statements 60-83, wherein on average there are at least about 10<sup>16</sup> surface crystallites of size C10 or less per gram nickel.
85. The nickel particulate form of any of statements 60-84, wherein on average there are at least about 5x10<sup>16</sup> surface crystallites of size C10 or less per gram nickel; or wherein on average there are at least about 10<sup>17</sup> surface crystallites of size C10 or less per gram nickel
86. The nickel particulate form of any of statements 60-85, wherein the nickel particulate form is substantially zero-valent nickel.
87. The nickel particulate form of any of statements 60-86, wherein the nickel particulate form is generated by reduction of basic nickel carbonate.
88. The nickel particulate form of any of statements 60-87, wherein the nickel particulate form is generated by reduction of basic nickel carbonate, where the basic nickel carbonate has less than a molar equivalent of carbonate relative to the amount of nickel in the basic nickel carbonate.
89. The nickel particulate form of any of statements 60-88, wherein the nickel particulate form is generated by reduction of basic nickel carbonate, where the basic nickel carbonate has a molar ratio of NiCO<sub>3</sub>:Ni(OH)<sub>2</sub> that is less than approximately 1.
90. The nickel particulate form of any of statements 60-89, wherein the nickel particulate form is generated by reduction of basic nickel carbonate, where the basic nickel carbonate has a mass ratio of Ni:C of at least 6:1, or at least 7:1, or at least 8:1, or at least 9:1, or at least 10:1.
91. The nickel particulate form of any of statements 60-90, wherein the nickel particulate form is generated by reduction of basic nickel carbonate, where the basic nickel carbonate has a mass ratio of Ni:C of 6:1 to about 20:1.
92. The nickel particulate form of any of statements 60-91, wherein the nickel particulate form has been reduced from Ni(II) to zero-valent nickel.

93. The nickel particulate form of any of statements 60-92, wherein the nickel particulate form has been reduced from Ni(II) to zero-valent nickel with hydrogen.
94. The nickel particulate form of any of statements 60-93, wherein the nickel particulate form has been reduced from Ni(II) to zero-valent nickel at 250-400 °C.
95. The nickel particulate form of any of statements 60-94, wherein the nickel particulate form is substantially free of another metal.
96. The nickel particulate form of any of statements 60-95, wherein the nickel particulate form is substantially free of aluminum, copper, tungsten, zinc and/or iron.
97. The nickel particulate form of any of statements 60-96, wherein the nickel particulate form is substantially free of alkali metals and/or alkaline earth metals.
98. The nickel particulate form of any of statements 60-97, wherein the nickel particulate form is substantially free of an anion.
99. The nickel particulate form of any of statements 60-98, wherein the nickel particulate form is substantially free of carbonate, hydroxide and/or oxygen.
100. The nickel particulate form of any of statements 60-99, comprising about 0.01 wt% to about 12 wt% sulfur, relative to the total weight of nickel in the mixture.
101. The nickel particulate form of any of statements 60-100, comprising about 0.1 wt% to about 2 wt% sulfur, relative to the total weight of nickel in the mixture.
102. The nickel particulate form of any of statements 60-101, comprising about 0.2 wt% to about 2 wt% sulfur, relative to the total weight of nickel in the mixture.
103. The nickel particulate form of any of statements 60-102, comprising about 0.4 wt% to about 1 wt% sulfur, relative to the total weight of nickel in the mixture.
104. A complex comprising one or more phosphorus-containing ligands and nickel atoms from the nickel particulate form of any of statements 60-103.
105. The complex of statement 104, having hydrocyanation catalytic activity.
106. The complex of statement 104 or 105, having catalytic activity for hydrocyanation of a compound comprising at least one C=C bond.
107. An organic liquid solution comprising one or more phosphorus-containing ligands and nickel atoms solubilized by complexation therewith, wherein the nickel atoms are from the nickel particulate form of any of statements 60-103.
108. The solution of statement 107, further comprising one or more pentenenitriles.
109. The solution of statement 107 or 108, further comprising a Lewis acid.
110. The solution of statement 109, wherein the Lewis acid is zinc chloride.

111. The solution of any of statements 107-110, having hydrocyanation catalytic activity.
112. The solution of any of statements 107-111, having catalytic activity for hydrocyanation of a compound comprising at least one C=C bond.
113. A method of making a zero-valent nickel complex having catalytic activity, comprising mixing an organic liquid solution comprising one or more phosphorus-containing ligands and the nickel particulate form of any of statements 60-103.
114. The method of statement 113, wherein the organic liquid solution further comprises a Lewis acid.
115. The method of statement 113 or 114, wherein the organic liquid solution further comprises one or more nitriles.
116. The method of any of statements 113-115, wherein at least the one nitrile is a mononitrile.
117. The method of any of statements 113-116, wherein the organic liquid solution comprises one or more pentenenitriles.
118. A method for hydrocyanating a compound having at least one C=C bond comprising contacting the compound with  $\text{HC}\equiv\text{N}$  in the presence of a catalyst comprising a zero-valent nickel complex with one or more phosphorus-containing ligands, wherein the nickel component of the complex is derived from a nickel particulate form of any of statements 60-103.
119. The method of statement 118, wherein one or more phosphorus-containing ligands comprises a phosphite ligand.
120. The method of statement 118 or 119, wherein one or more phosphorus-containing ligands comprises a bidentate phosphite ligand.
- 5 121. The method of statement 120, wherein the bidentate phosphite ligand is Ligand (V):



Ligand (V).

122. A method of identifying whether a basic nickel carbonate test sample will yield a  
 5 nickel particulate form with nickel atoms that complex with one or more phosphorus-  
 containing ligands, comprising:

- (a) calcining a basic nickel carbonate test sample; and
- (b) observing whether the test sample gives off more or less carbon dioxide  
 compared to a control basic nickel carbonate sample;

10 wherein the basic nickel carbonate test sample will yield an active nickel  
 particulate form with nickel atoms that substantially complex with one or more  
 phosphorus-containing ligands within about 2 hours, when the basic nickel carbonate  
 test sample gives off less carbon dioxide than the control basic nickel carbonate; and  
 wherein the control basic nickel will yield a nickel particulate form with nickel  
 15 atoms that substantially do not complex with one or more phosphorus-containing  
 ligands within about 2 hours.

123. A method of identifying whether a nickel test sample will yield a nickel  
 particulate form with nickel atoms that complex with one or more phosphorus-  
 20 containing ligands, comprising:

- (a) reducing the nickel test sample with hydrogen; and
- (b) observing whether the nickel test sample exhibits a single peak of  
 hydrogen absorption between about 350° C and 450° C during reduction;

wherein the nickel test sample will yield an active nickel particulate form with  
 25 nickel atoms that substantially complex with one or more phosphorus-containing

ligands within about 2 hours, when the nickel test sample exhibits a single peak of hydrogen absorption between about 350° C and 450° C during reduction.

124. The method of statement 123, wherein the nickel test sample is basic nickel  
5 carbonate, nickel oxide, nickel hydroxide, or a mixture thereof.

125. The method of statement 123 or 124, further comprising forming a complex  
between the nickel atoms of an active nickel particulate form and one or more  
phosphorus-containing ligands to generate a hydrocyanation catalyst.

10

126. A method of avoiding waste, comprising:

- (a) calcining a basic nickel carbonate test sample; and
- (b) observing whether the test sample gives off more or less carbon dioxide  
compared to a control basic nickel carbonate sample;

15 wherein the basic nickel carbonate test sample will not yield an active nickel  
particulate form with nickel atoms that substantially do not complex with one or more  
phosphorus-containing ligands within about 2 hours, when the basic nickel carbonate  
test sample gives off more carbon dioxide than the control basic nickel carbonate; and  
wherein, after reduction, the control basic nickel carbonate yields a nickel  
20 preparation with nickel atoms that substantially do not complex with one or more  
phosphorus-containing ligands within about 2 hours after mixing in a organonitrile  
solvent.

127. The method of statement 126, wherein waste is avoided by identifying a basic  
25 nickel carbonate test sample that gives off more carbon dioxide than the control basic  
nickel carbonate, and not using the basic nickel carbonate from which the basic nickel  
carbonate test sample was obtained to make a nickel particulate form for use in a  
hydrocyanation catalyst.

30 128. The method of statement 126 or 127, wherein waste is avoided by identifying a  
basic nickel carbonate test sample that gives off more carbon dioxide than the control  
basic nickel carbonate, and by not using the basic nickel carbonate from which the  
basic nickel carbonate test sample was obtained to make a nickel preparation because

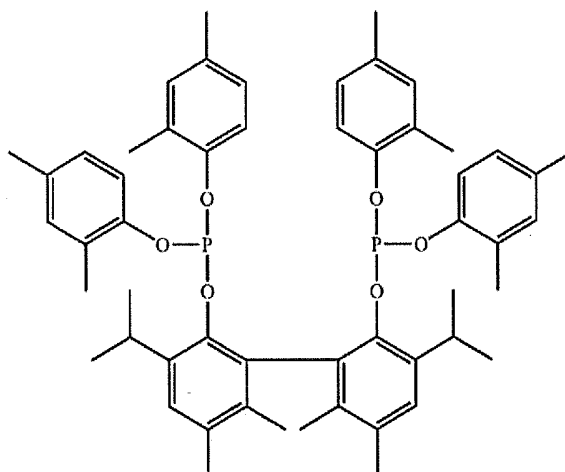
the nickel preparation will not complex with one or more phosphorus-containing ligands within about 2 hours after mixing therewith in a organonitrile solvent.

129. A method of avoiding waste, comprising:

- 5 (a) reducing a nickel-containing test sample; and  
(b) observing whether the nickel test sample exhibits a single peak of hydrogen absorption between about 350° C and 450° C during reduction; wherein the nickel test sample not will yield a nickel particulate form with nickel atoms that substantially complex with one or more phosphorus-containing  
10 ligands within about 2 hours after mixing therewith, when the nickel test sample exhibits two peaks of hydrogen absorption between about 300° C and 450° C during reduction.

130. The method of statement 129, wherein waste is avoided by identifying the nickel  
15 test sample(s) that exhibit two peaks of hydrogen absorption between about 300° C and 450° C during reduction, and not using a nickel source from which the nickel test sample(s) were obtained to generate a hydrocyanation catalyst.

131. The method of any of statements 122 - 130, wherein the one or more  
20 phosphorus-containing ligands is Ligand (V):



Ligand (V).

The foregoing aspects are set forth without any loss of generality to, and  
25 without imposing limitations upon any claimed invention. It is to be understood that

this disclosure is not limited to particular aspects described, as such can vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

5           The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein. As  
10 will be apparent to those of skill in the art upon reading this disclosure, each of the individual aspects described and illustrated herein has discrete components and features that can be readily separated from or combined with the features of any of the other several examples without departing from the scope or spirit of the present disclosure. Where features or aspects of the invention are described in terms of  
15 Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

          All publications and patents cited in this specification are herein incorporated  
20 by reference as if each individual publication or patent were specifically and individually indicated to be incorporated by reference and are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. Applicants reserve the right to physically incorporate into this specification any and all materials and information from any such  
25 cited patents or publications. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present disclosure is not entitled to antedate such publication by virtue of prior disclosure. Further, the dates of publication provided could be different from the actual publication dates that can need to be independently confirmed. All patents and  
30 publications referenced or mentioned herein are also indicative of the levels of skill of those skilled in the art to which the invention pertains.

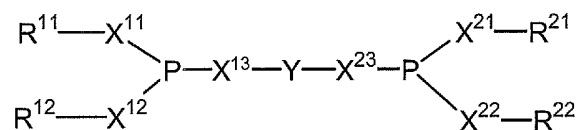
          The following claims describe additional aspects of the invention.

## WHAT IS CLAIMED:

1. A method of generating a complex between nickel atoms and one or more phosphorus-containing ligands comprising:
  - (a) contacting:
    - 5 (i) a nickel starting material with a sulfur source, and generating nickel metal from a mixture of the nickel starting material and the sulfur source to form a particulate sulfur-containing nickel metal; or
    - (ii) a nickel metal with a sulfur source to form a particulate sulfur-  
10 containing nickel metal; and
  - (b) contacting the particulate sulfur-containing nickel metal with one or more phosphorus-containing ligand(s) to thereby form a complex between nickel atoms from the nickel metal and one or more phosphorus-containing  
15 ligands.
2. The method of claim 1, further comprising determining a sulfur content of the nickel starting material or the nickel metal before contacting the nickel metal or the nickel starting material with the sulfur source.
3. The method of claim 2, wherein the nickel metal or the nickel starting material is contacted with the sulfur source if the sulfur content of the nickel metal or the  
20 nickel starting material is less than 0.4 wt% to 0.8 wt% relative to the weight of the nickel metal or the nickel starting material.
4. The method of any of claims 1-3, wherein the nickel metal in step (ii) is simultaneously contacted with the sulfur source and one or more phosphorus-containing ligand(s).
- 25 5. The method of any of claims 1-4, wherein the sulfur source is selected from the group consisting of elemental sulfur, sulfur-containing gases, sulfur-containing salts, sulfur-donating compounds, sulfur-containing ions and combinations thereof.
6. The method of any of claims 1-5, wherein the sulfur source is selected from the group consisting of disulfides, thioacetic acid, thioacetate salts, polysulfides, bis-  
30 alkylamino disulfides, sulfenic sulfonic thioanhydrides, thiosulfonate salts, aminothiosulfonates, acylmethylmercapto azoles, acylmethylmercapto-azolium salts, thiazepines, thiepins, 1,4-dithiins, 1,2-thiazines, 1,3-thiazines, 1,4-thiazines, 1,4,2-dithiazines, 1,3,4-thiadiazines, 1,2,6- thiadiazines, 1,3,5-thiadiazines, dihydro-dithiazines, dihydrothiadiazines, 1,2,3,4-thiatriazoles and combinations thereof.

7. The method of any of claims 1-6, wherein the sulfur source is selected from the group consisting of hydrogen sulfide, nickel sulfate, nickel sulfite, nickel sulfide, nickel hyposulfite, nickel thiosulfate, sulfur trioxide, sulfur dioxide, sulfur monoxide, disulfur dichloride, sulfur dichloride, sulfur tetrachloride, sulfur chloride
- 5 pentafluoride, disulfur decafluoride, sulfur hexafluoride, sulfur tetrafluoride, sulfur trifluoride and combinations thereof.
8. The method of any of claims 1-7, wherein the sulfur source is 95% to 99.9% free of silicon, sodium, potassium, calcium, magnesium, phosphorus, aluminium, copper, tungsten, mercury, iron, and combinations thereof.
- 10 9. The method of any of claims 1-8, wherein the nickel starting material or nickel metal is 95% to 99.9% free of silicon, sodium, potassium, calcium, magnesium, phosphorus, aluminium, copper, tungsten, mercury, iron and combinations thereof.
10. The method of any of claims 1-9, wherein the nickel starting material is basic nickel carbonate, nickel carbonate, nickel bicarbonate, nickel oxalate, nickel formate,
- 15 nickel squarate, nickel hydroxide, nickel oxide, nickel salts or a combination thereof.
11. The method of any of claims 1-10, wherein the nickel metal or the nickel starting material is contacted with the sulfur source before or after reduction of the nickel starting material or the nickel metal to zero valent nickel.
12. The method of any of claims 1-11, wherein the nickel starting material is
- 20 reduced in the presence of hydrogen for a time and at a temperature sufficient to substantially reduce Ni(II) to (Ni(0).
13. The method of any of claims 1-12, wherein a weight percentage of about 0.1 wt% to about 50 wt% sulfur is contacted with the nickel metal or the nickel starting material, wherein the sulfur weight percentage is relative to the total weight of nickel
- 25 in the nickel metal or the nickel starting material.
14. The method of any of claims 1-13, wherein a complex forms between nickel atoms from the particulate sulfur-containing nickel metal and one or more phosphorus-containing ligands in the presence of a Lewis acid.
15. The method of any of claims 1-14, wherein equilibrium of complex formation
- 30 between nickel atoms from the particulate sulfur-containing nickel metal and one or more phosphorus-containing ligands is reached by about 2 hours when about 4% nickel is mixed at about 60 °C to 80 °C in an organonitrile solvent with about 0.5 to 2.5 moles Lewis acid per mole phosphorus-containing ligand.

16. The method of any of claims 1-15, wherein the complex at least partially dissolved in an organonitrile solvent.
17. The method of any of claims 1-16, wherein the organonitrile solvent is a pentenenitrile.
- 5 18. The method of any of claims 1-17, wherein one or more of the phosphorus ligands is a ligand of Formula (III):

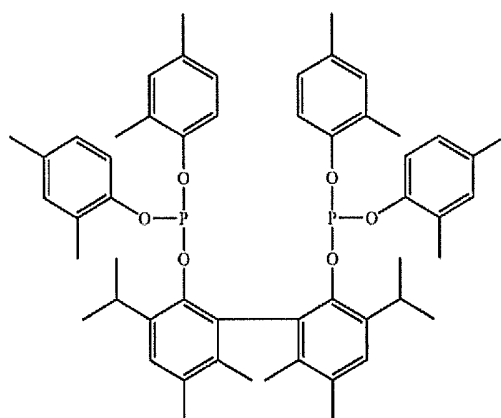


Formula (III)

wherein:

- 10  $\text{X}^{11}$ ,  $\text{X}^{12}$ ,  $\text{X}^{13}$ ,  $\text{X}^{21}$ ,  $\text{X}^{22}$  and  $\text{X}^{23}$  independently represent oxygen or a single direct bond;
- $\text{R}^{11}$  and  $\text{R}^{12}$  independently represent identical or different, single or bridged organic radicals;
- $\text{R}^{21}$  and  $\text{R}^{22}$  independently represent identical or different, single or
- 15 bridged organic radicals; and
- $\text{Y}$  represents a bridging group.

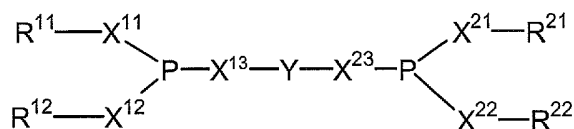
19. The method of any of claims 1-18, wherein one or more of the phosphorus ligands is Ligand (V):



Ligand (V).

20. The method of any of claims 1-19, wherein contacting generates a sulfur to nickel atomic ratio of about 0.003 to about 1.8.

21. The method of any of claims 1-20, wherein the complex formed between nickel atoms from the particulate sulfur-containing nickel metal and one or more phosphorus-containing ligands catalyses hydrocyanation of an olefin.
22. The method of claim 21, wherein the olefin is pentenenitrile.
23. The method of any of claims 1-22, wherein the particulate sulfur-containing nickel metal comprises nickel crystallites with a BET Specific Surface Area of at least about 1 m<sup>2</sup> / gm, and/or wherein on average there are at least about 10<sup>15</sup> surface crystallites present per gram nickel, as calculated for substantially cuboidal crystallites.
24. A catalyst preparation mixture comprising particulate nickel metal, one or more phosphorus-containing ligands and about 0.001 wt% to about 15 wt% sulfur, wherein the sulfur weight percentage is relative to the total weight of nickel in the mixture.
25. The catalyst preparation mixture of claim 24, wherein the mixture is in an organonitrile solvent.
26. The catalyst preparation mixture of claim 24 or 25, further comprising a Lewis acid.
27. The catalyst preparation mixture of any of claims 24-26, further comprising a Lewis acid selected from the group consisting of zinc chloride, ferrous chloride, or a combination thereof.
28. The catalyst preparation mixture of claim 27, comprising a zinc to phosphorus containing ligand molar ratio of about 0.5 to about 2.5.
29. The catalyst preparation mixture of any of claims 24-28, wherein one or more of the phosphorus ligands is a ligand of Formula (III):



Formula (III)

wherein,

X<sup>11</sup>, X<sup>12</sup>, X<sup>13</sup>, X<sup>21</sup>, X<sup>22</sup> and X<sup>23</sup> independently represent oxygen or a single direct bond;

R<sup>11</sup> and R<sup>12</sup> independently represent identical or different, single or bridged organic radicals;

$R^{21}$  and  $R^{22}$  independently represent identical or different, single or bridged organic radicals; and

Y represents a bridging group.

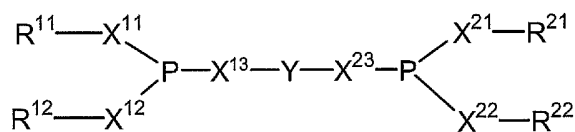
30. The catalyst preparation mixture of any of claims 24-29, comprising a weight percent of the one or more phosphorus containing ligands of about 2 to about 8 wt%.

31. The catalyst preparation mixture of any of claims 24-30, comprising a nickel weight percent of about 1 to about 7 wt%.

32. A complex formed between nickel atoms and one or more phosphorus-containing ligands comprising about 0.00001 wt% to about 15 wt% sulfur, wherein the sulfur weight percentage is relative to the total weight of nickel in the complex.

33. The complex of claim 32, comprising about 0.0001 wt% to about 1 wt% sulfur.

34. The complex of claim 32 or 33, wherein one or more of the phosphorus ligands is a ligand of Formula (III):



Formula (III)

wherein,

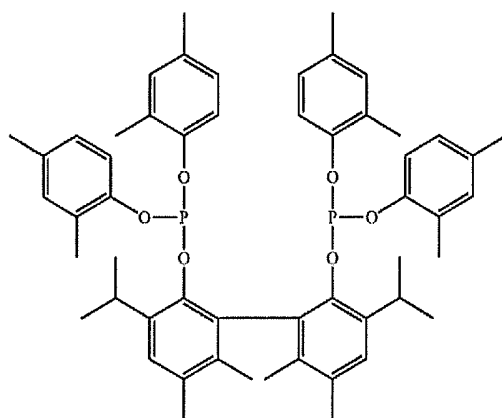
$X^{11}$ ,  $X^{12}$ ,  $X^{13}$ ,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  independently represent oxygen or a single direct bond;

$R^{11}$  and  $R^{12}$  independently represent identical or different, single or bridged organic radicals;

$R^{21}$  and  $R^{22}$  independently represent identical or different, single or bridged organic radicals; and

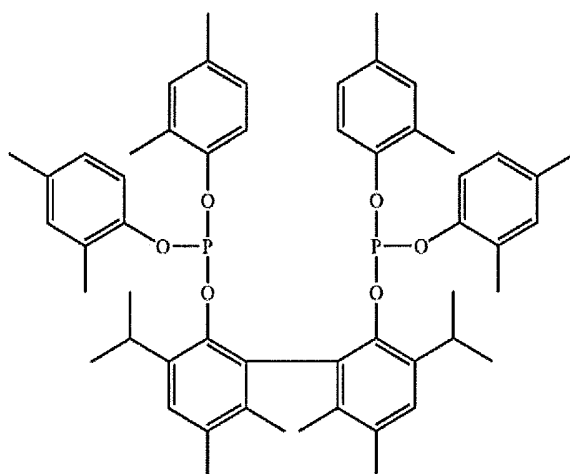
Y represents a bridging group.

35. The complex of any of claims 32-34, wherein one or more of the phosphorus ligands is Ligand (V):



Ligand (V).

36. A nickel particulate form comprising nickel crystallites and about 0.2 wt% to about 12 wt% sulfur, wherein the nickel particulate form has a BET Specific Surface Area of at least about 1 m<sup>2</sup>/gm; at least 10% of the nickel crystallites have a size (C10) that is less than about 20 nm; and the nickel crystallite size distribution span is greater than about 1.0.
37. The nickel particulate form of claim 36, wherein the nickel crystallites have an average crystallite size of no greater than about 100 nm.
38. The nickel particulate form of claim 36 or 37, which has a BET Specific Surface Area / C50 ratio of not less than 0.07 x 10<sup>9</sup> m/gm.
39. The nickel particulate form of any of claims 36-38, which on average has at least about 10<sup>15</sup> surface crystallites per gram of nickel.
40. The nickel particulate form of any of claims 36-39, wherein at least 10% of the particles of the form have a size (D10) of no greater than about 6 μm.
41. The nickel particulate form of any of claims 36-40, wherein on average there are at least about 10<sup>16</sup> surface crystallites per gram nickel that are smaller than or equal to size C10.
42. The nickel particulate form of any of claims 36-41, wherein an equilibrium of complex formation is reached between nickel atoms from the nickel particulate form and Ligand (V) within about 2 hours when about 4 to 5 wt% of the nickel particulate form is mixed with 3-pentenitrile containing approximately 5.25 wt% Ligand (V) and approximately 6300 ppm ZnCl<sub>2</sub>; wherein Ligand (V) has the following formula:



43. A mixture comprising a nickel particulate form with at least one ligand selected from monodentate phosphite ligands, bidentate phosphite ligands and mixtures thereof in the presence of pentenenitriles, wherein the nickel particulate form

5 is characterized by:

- (a) 0.2 wt.% to 12 wt.% sulfur; and
- (b) BET Specific Surface Area of at least 1 m<sup>2</sup>/g.

44. The product formed by mechanically agitating the mixture of claim 43.

45. A homogeneous product formed by mechanically agitating the mixture of

10 claim 43 or 44.

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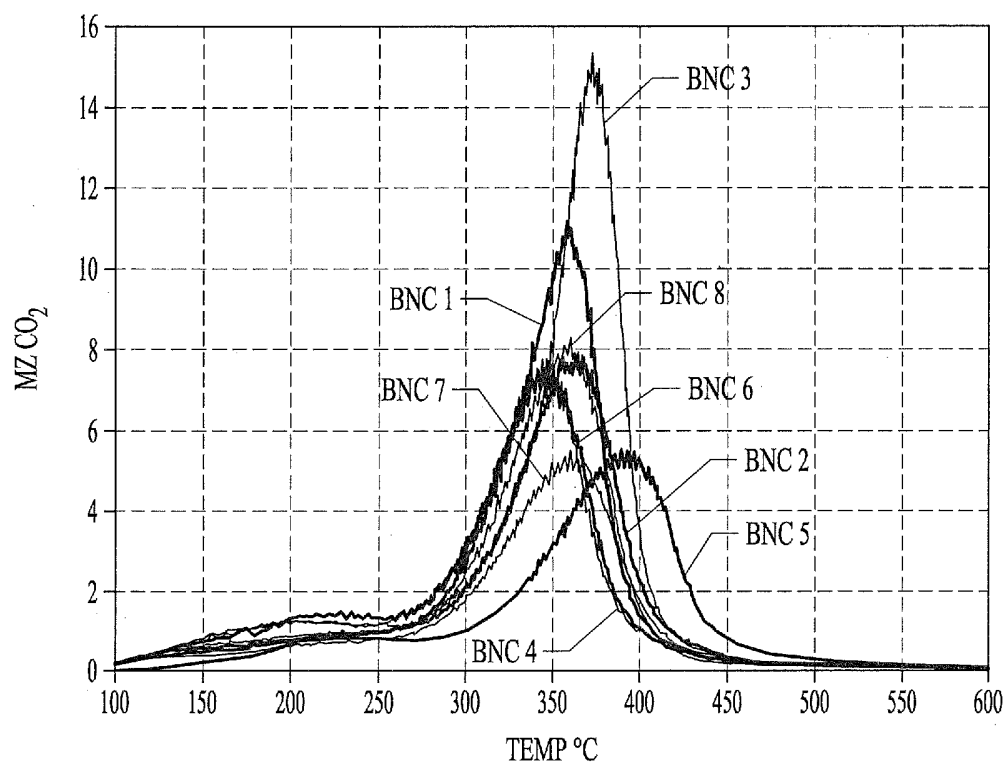


FIG. 1

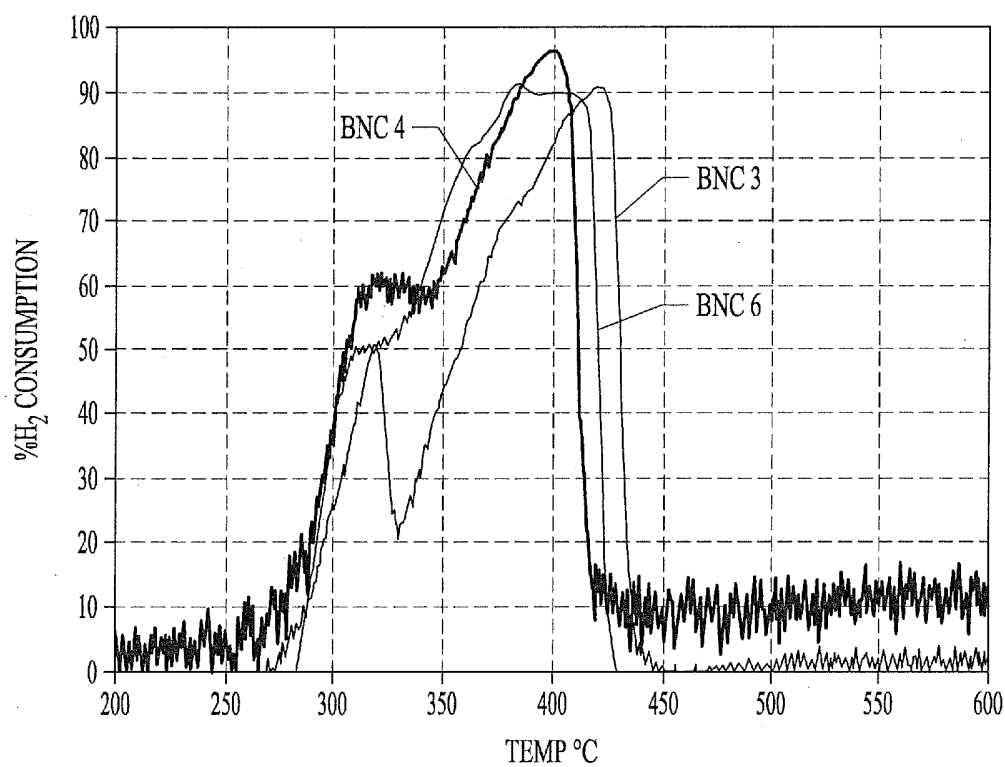
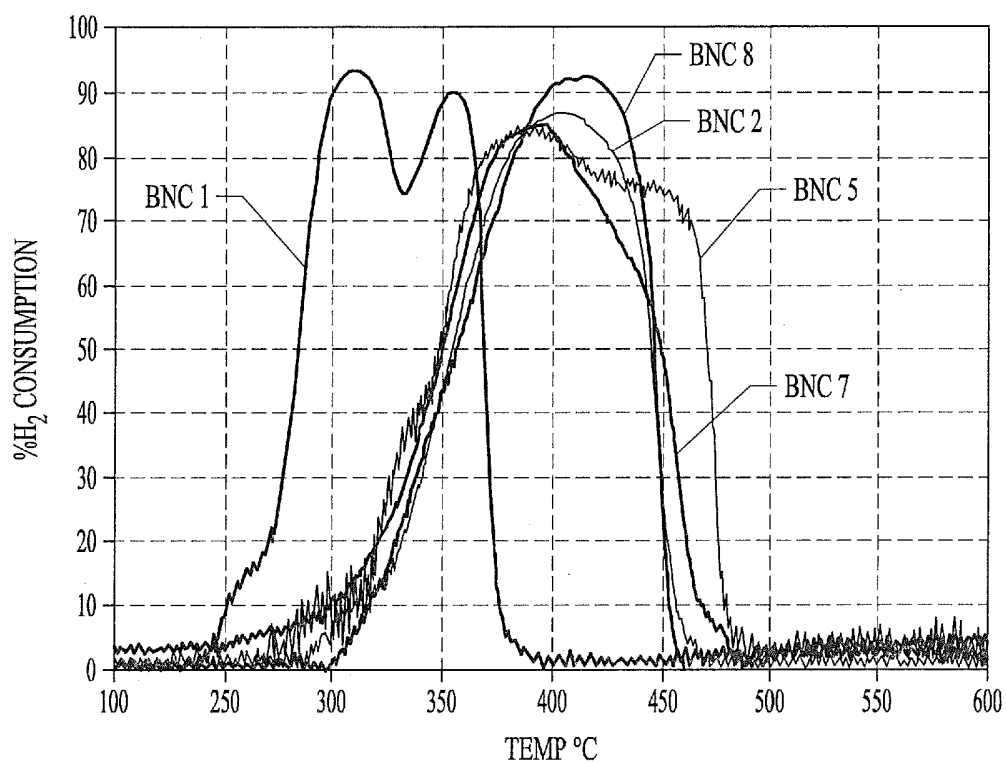
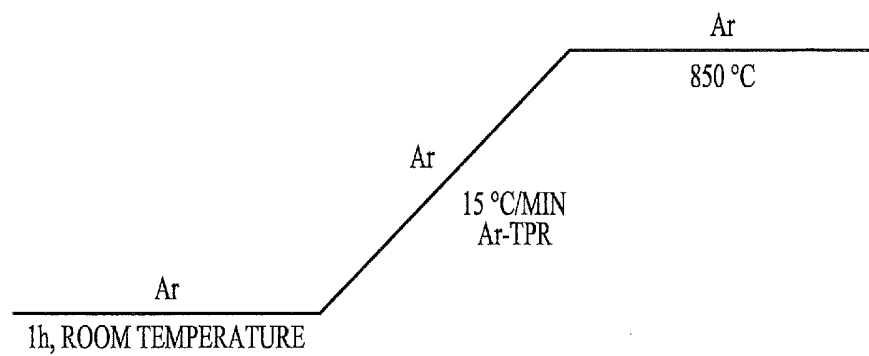
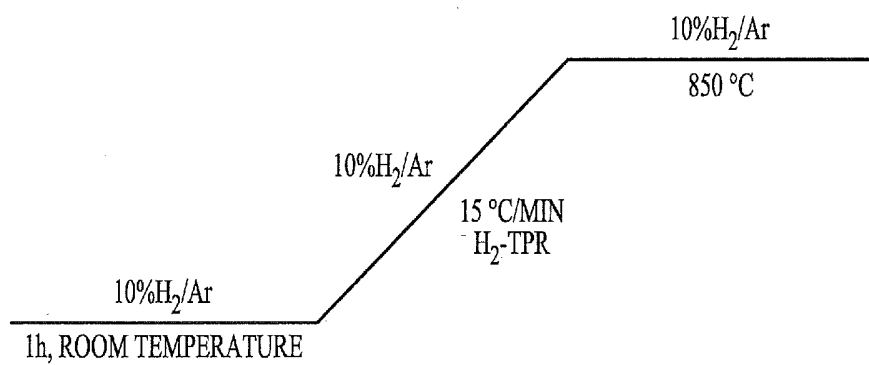


FIG. 2

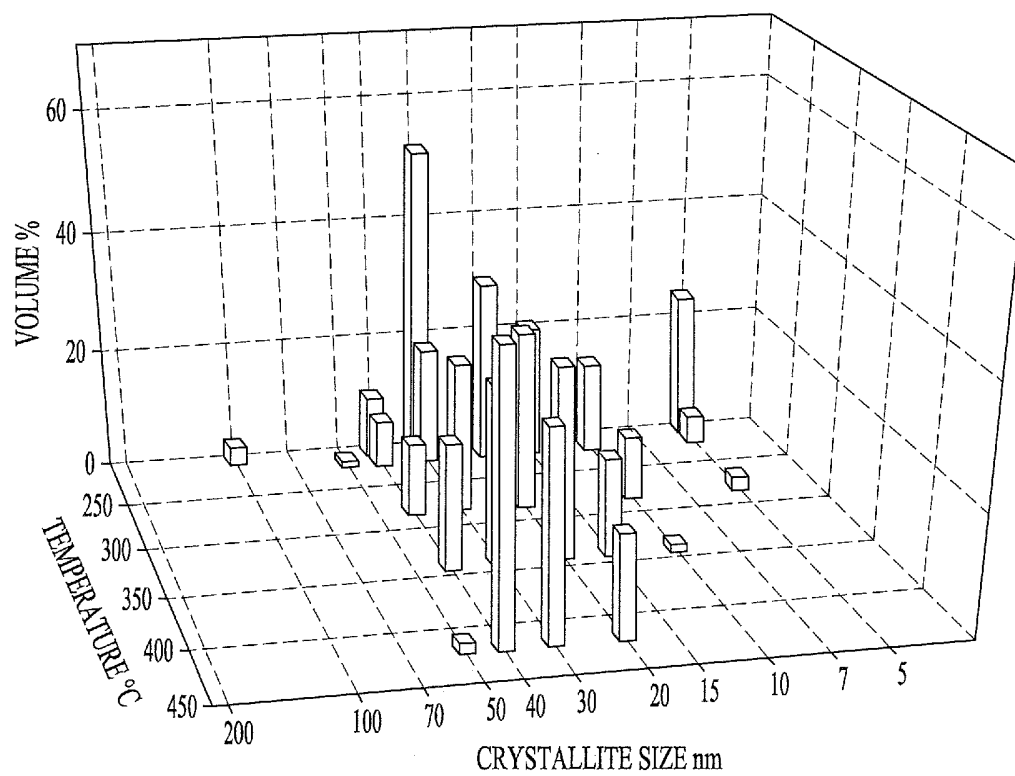
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*FIG. 3A*

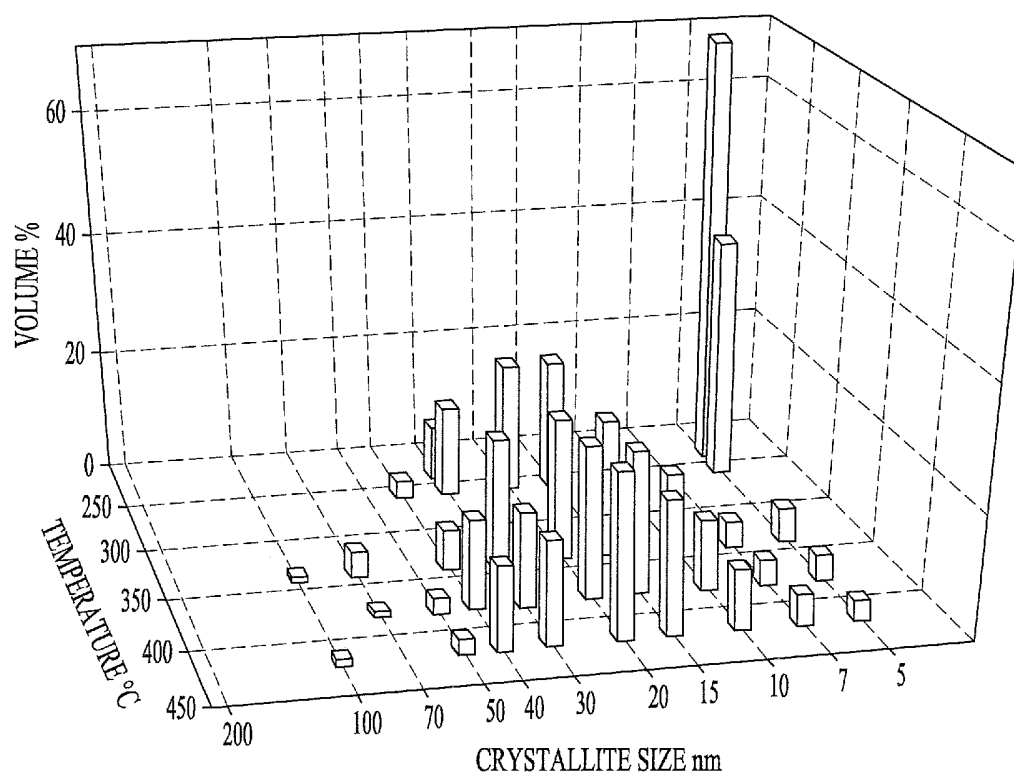
3/20

*FIG. 3B**FIG. 3C*

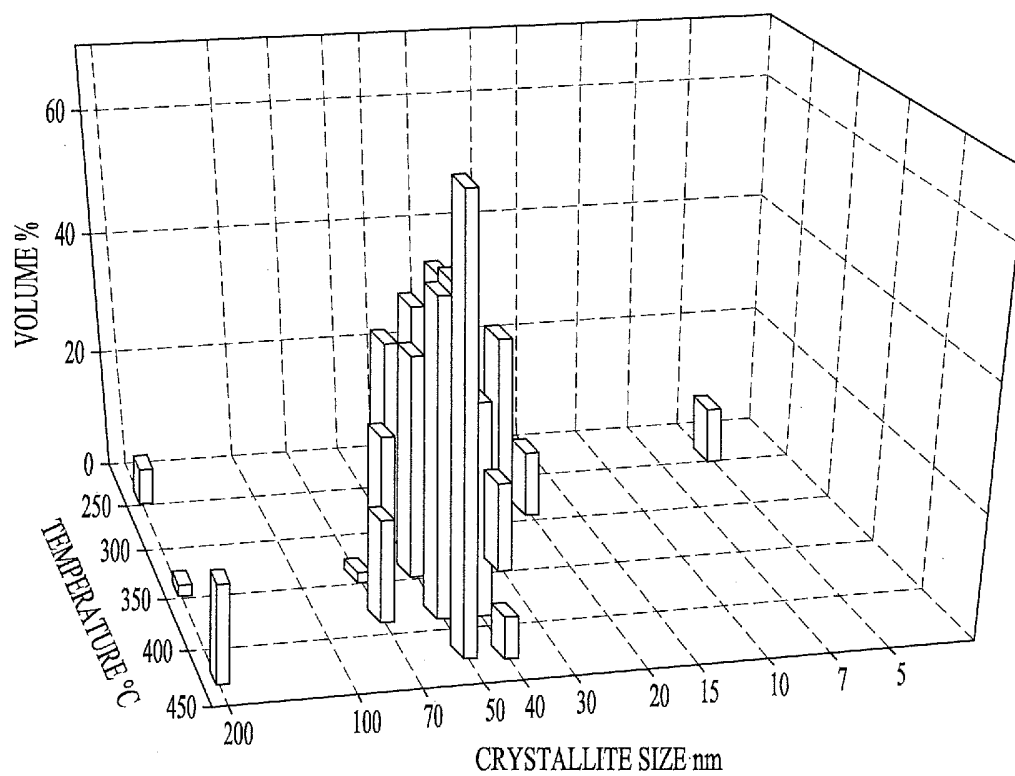
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**FIG. 4**

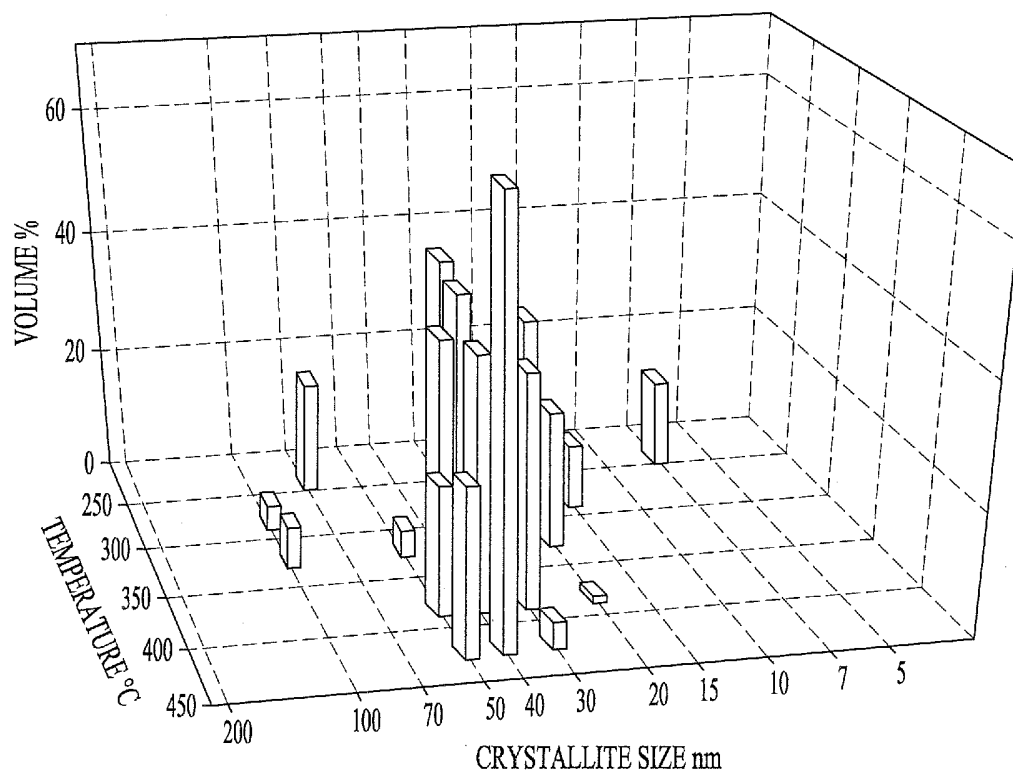
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*FIG. 5*

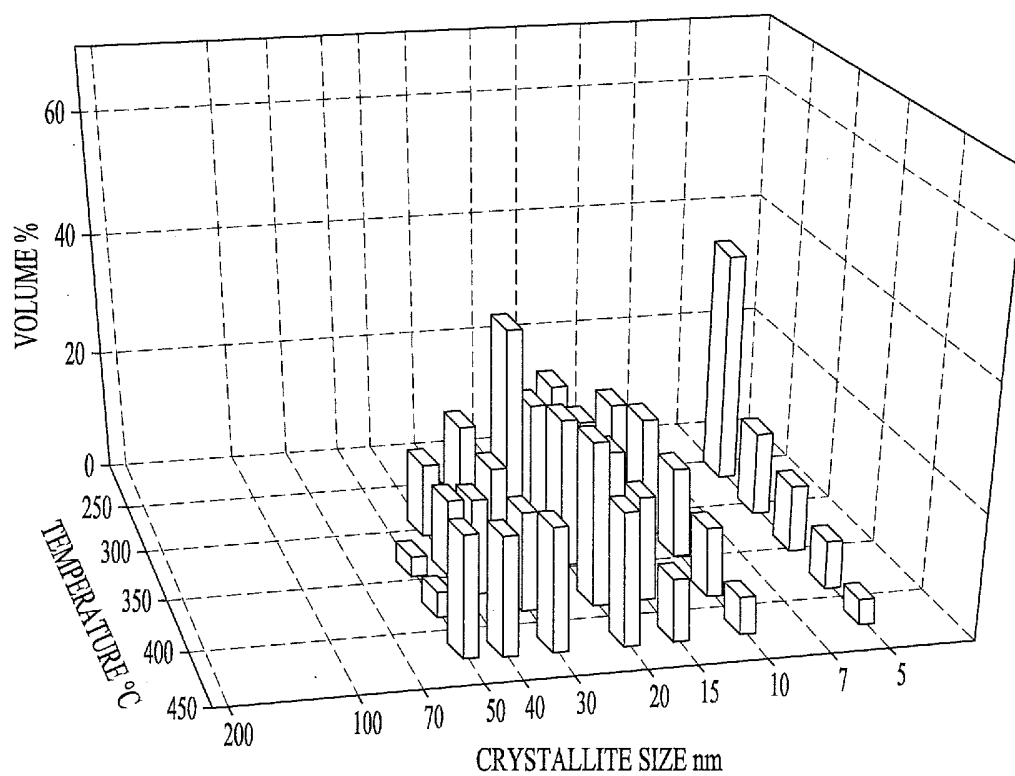
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**FIG. 6**

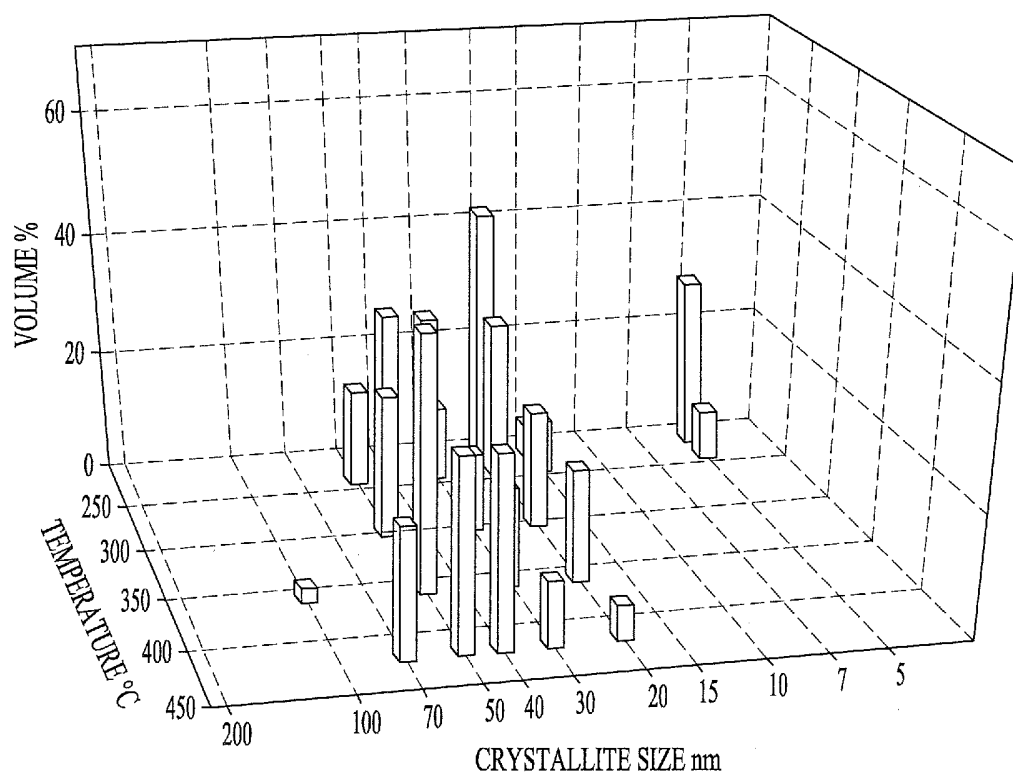
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**FIG. 7**

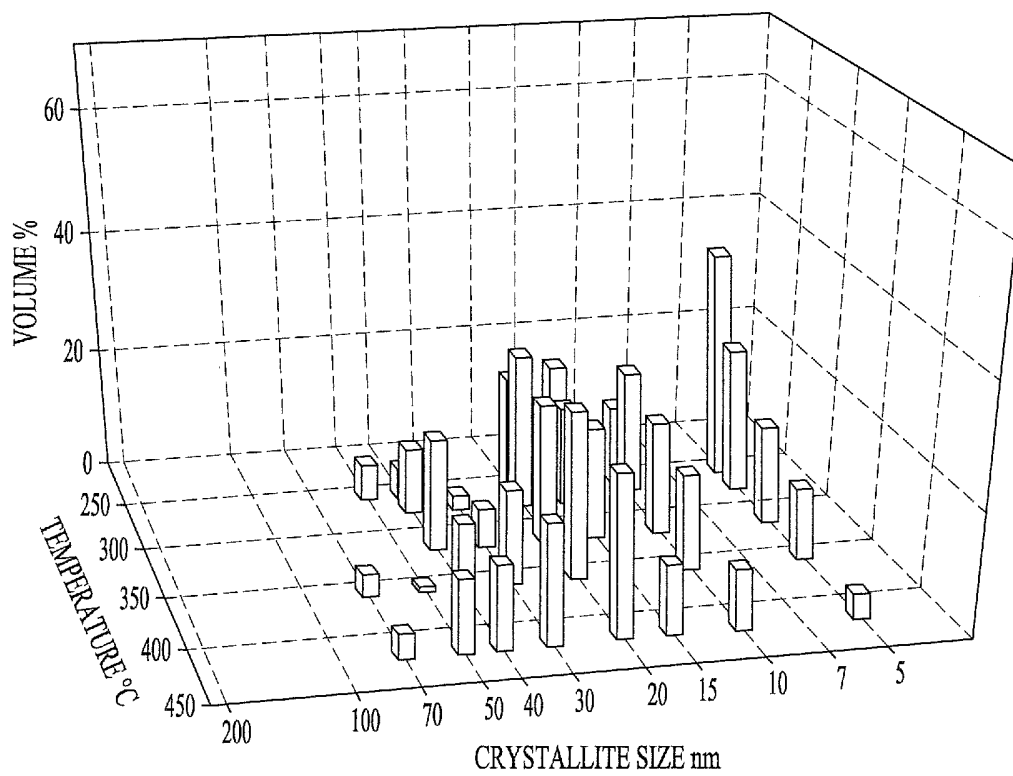
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*FIG. 8*

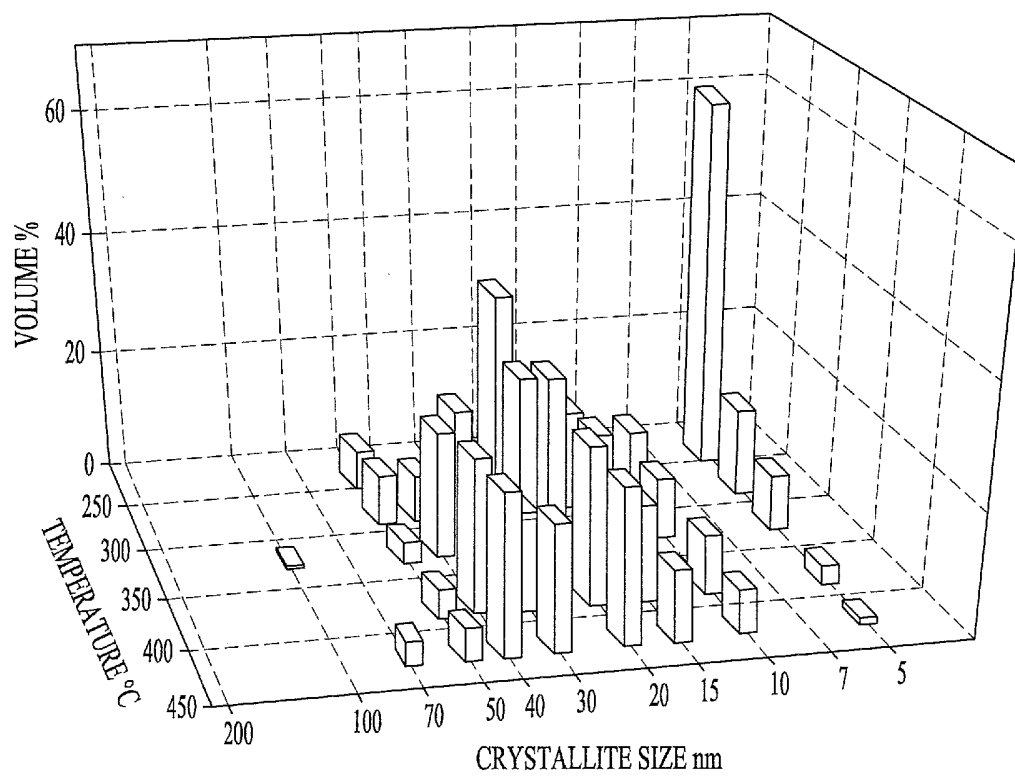
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*FIG. 9*

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*FIG. 10*

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*FIG. 11*

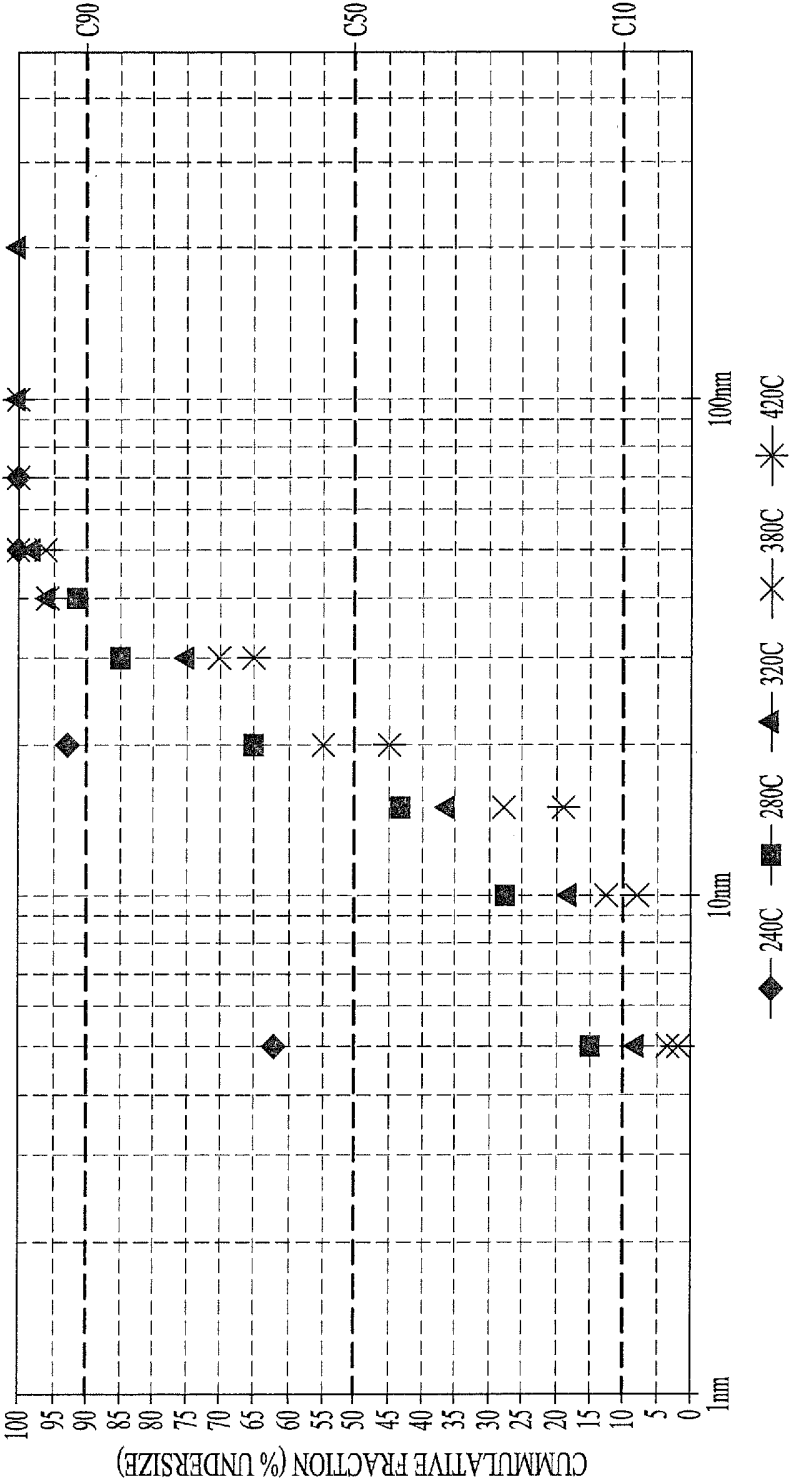
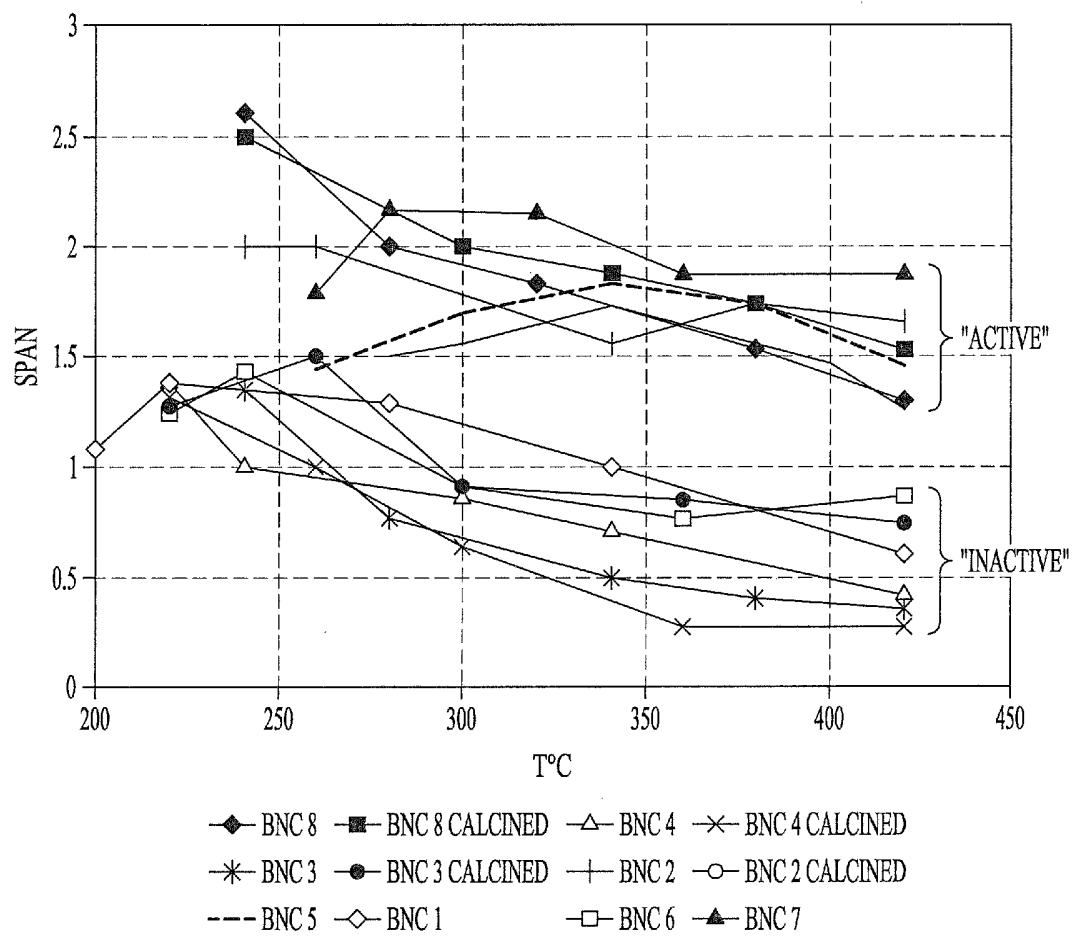


FIG. 12

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*FIG. 13*

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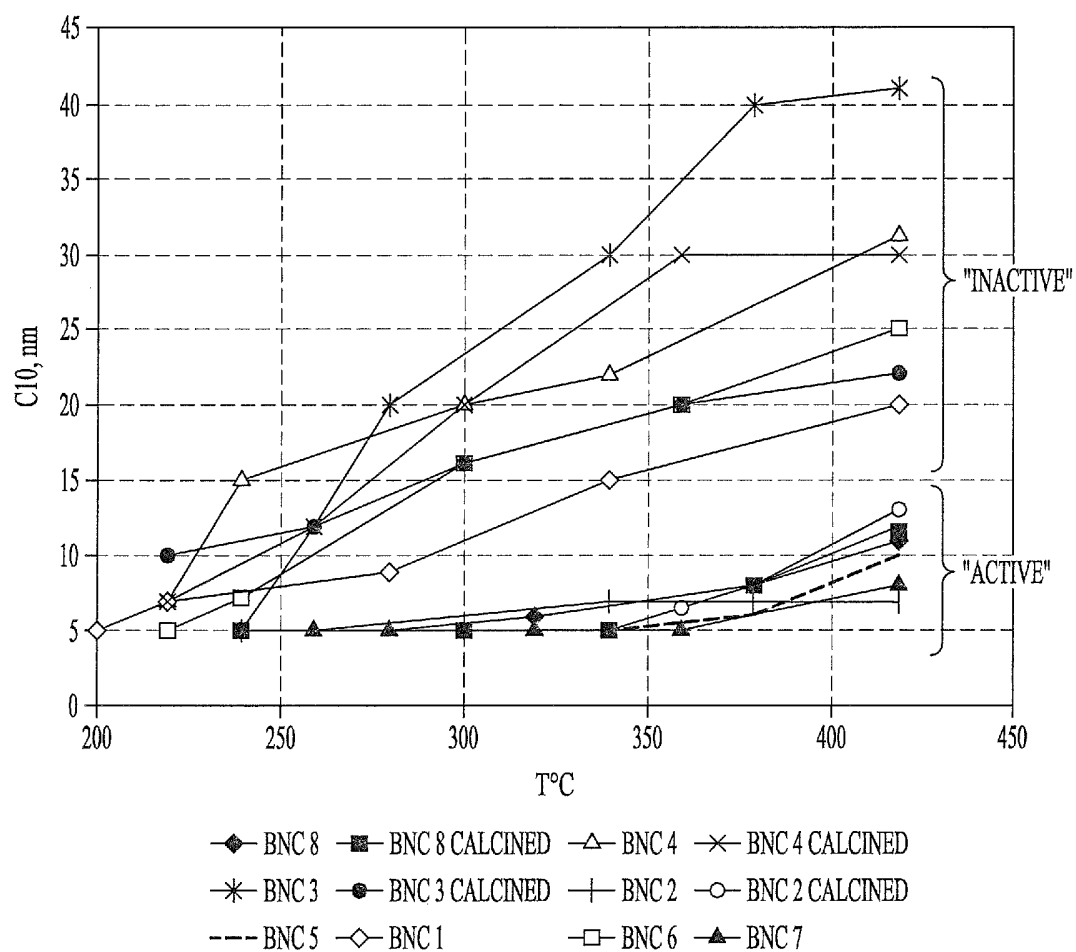
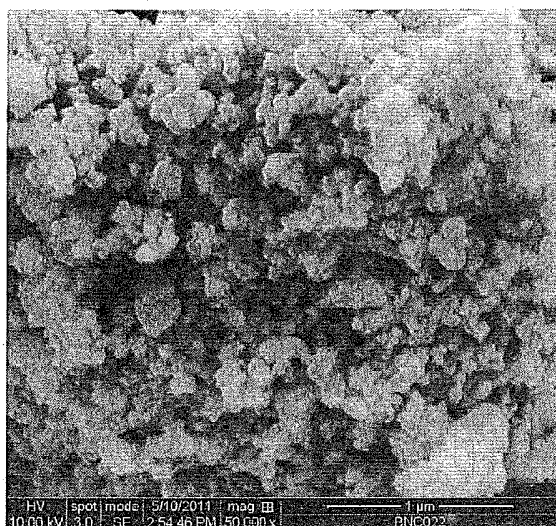
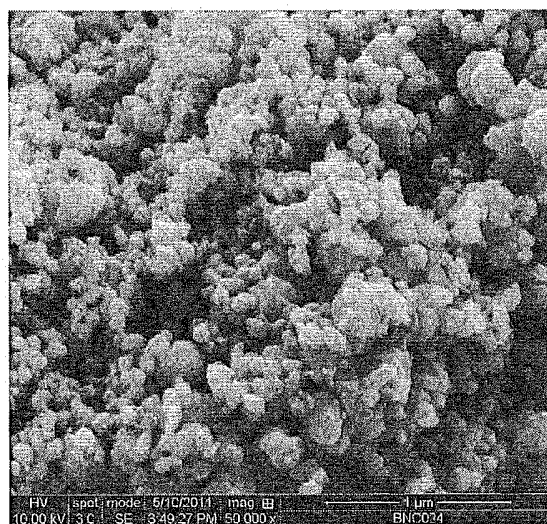
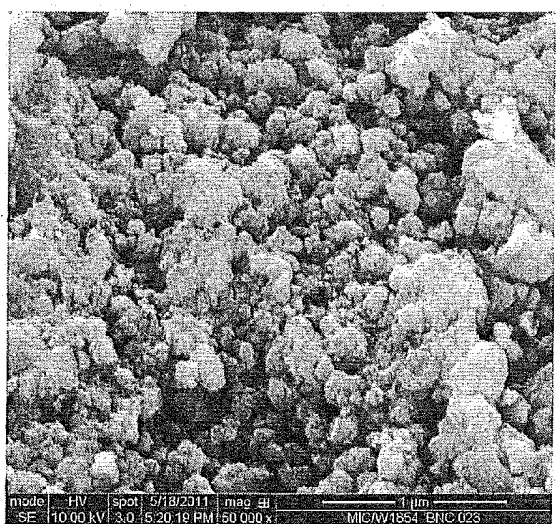
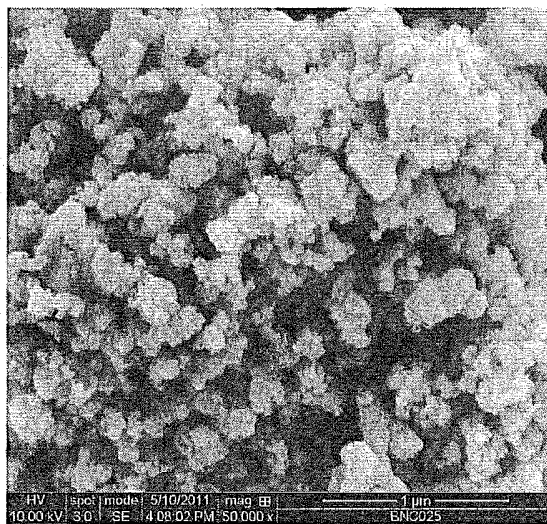
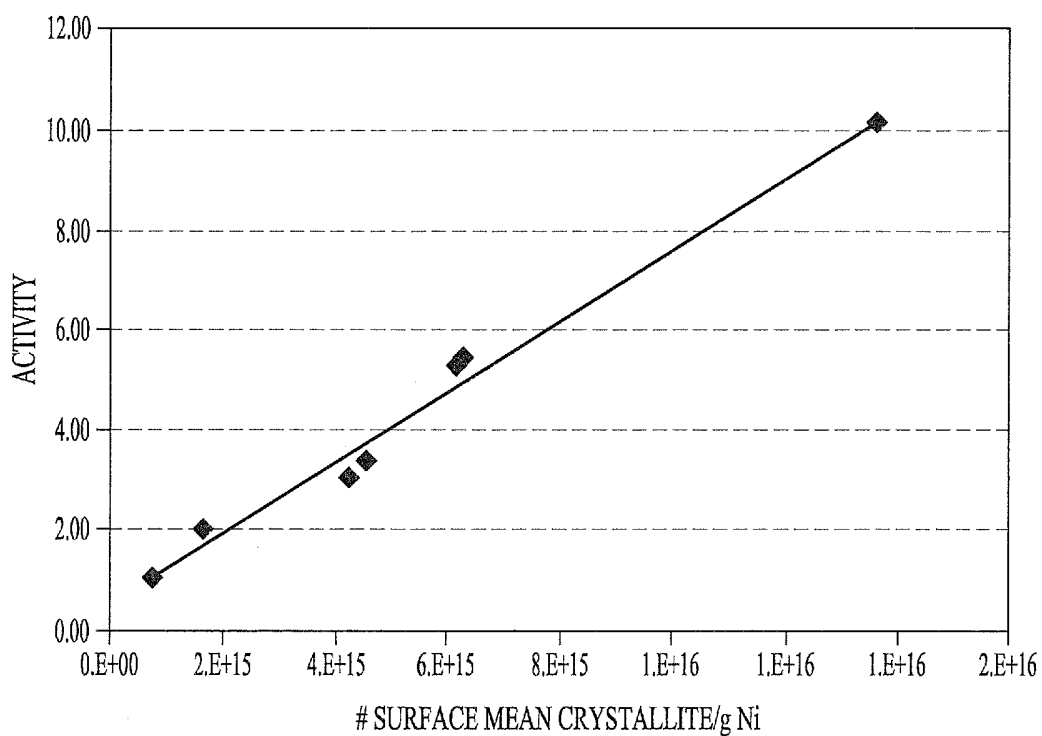
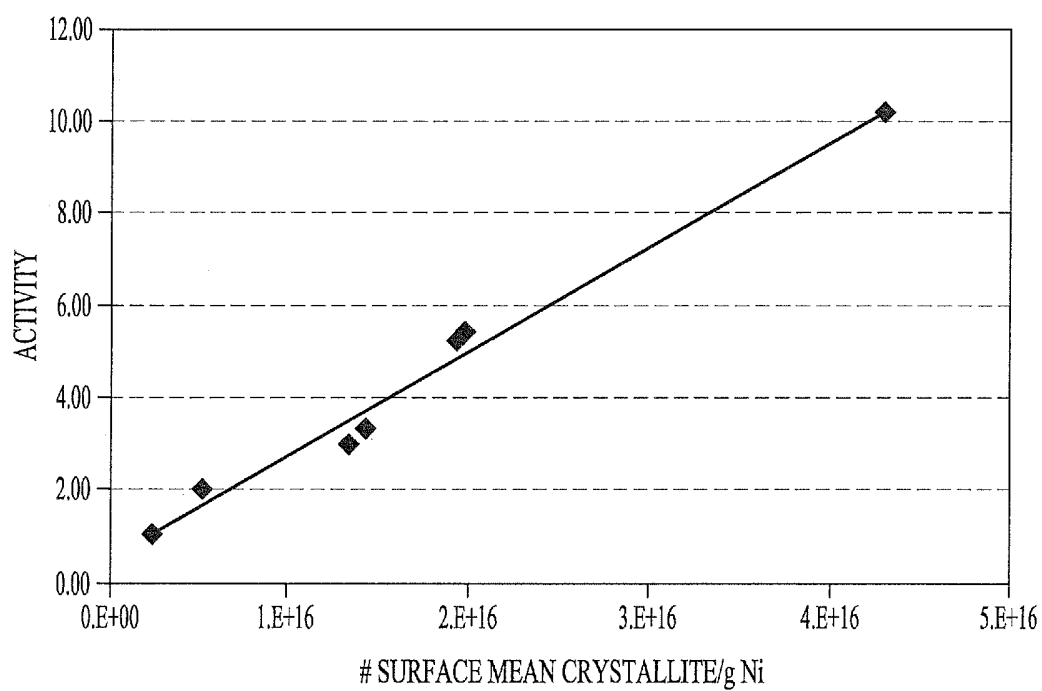


FIG. 14

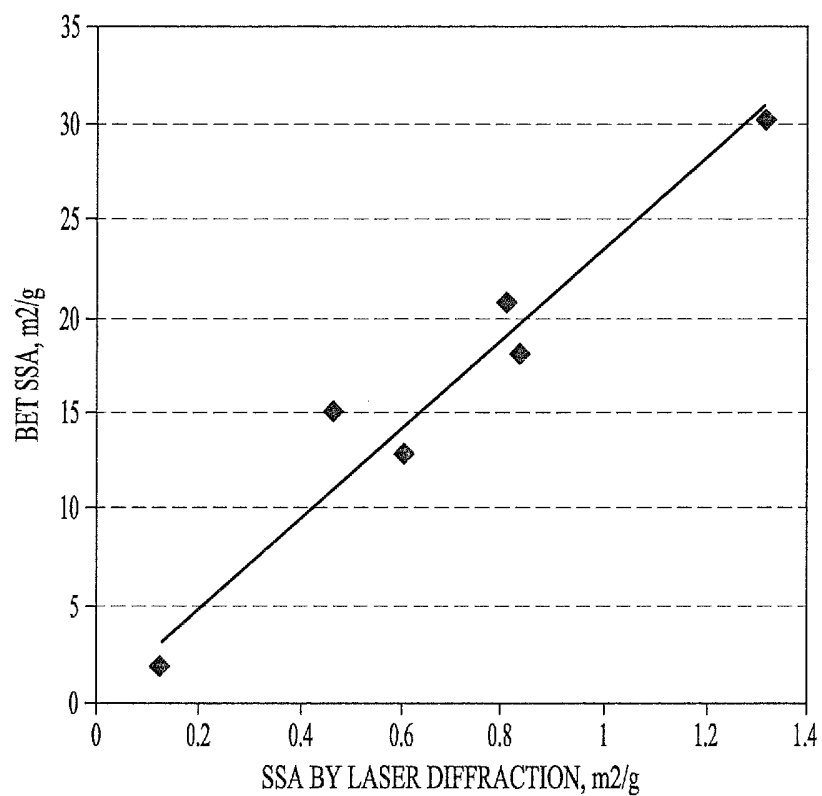
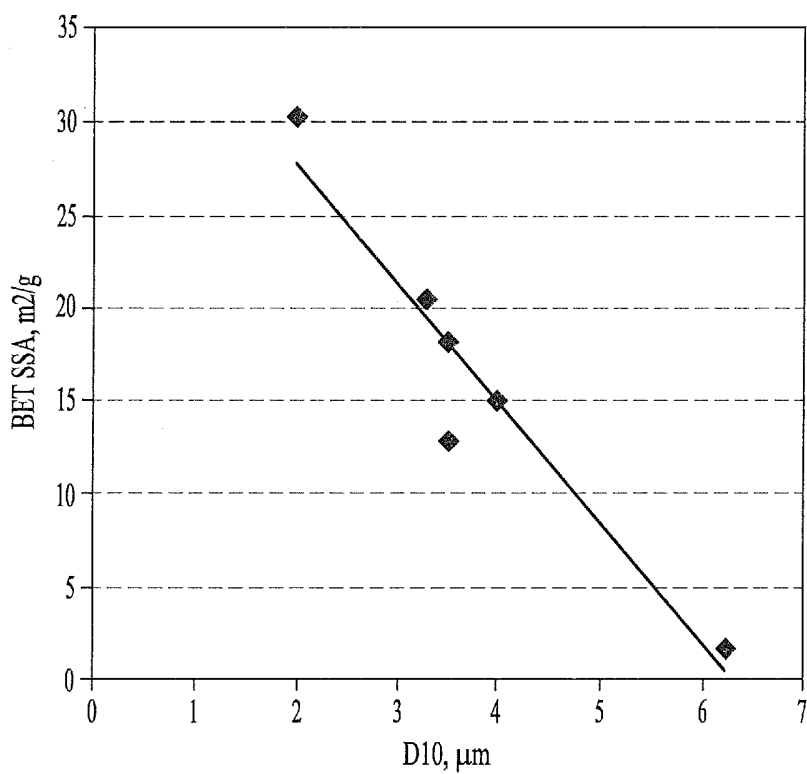
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*FIG. 15A**FIG. 15B**FIG. 15C**FIG. 15D*

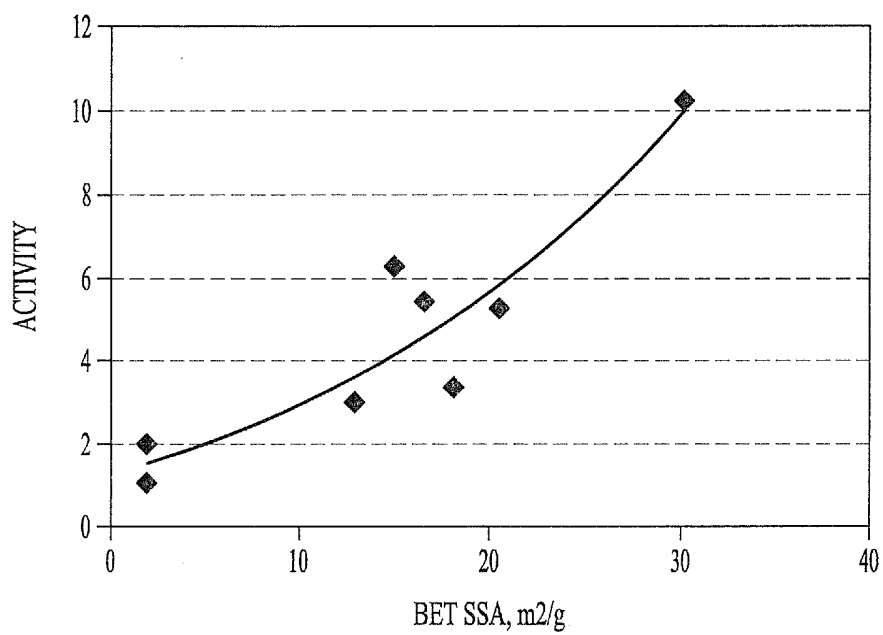
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*FIG. 16A**FIG. 16B*

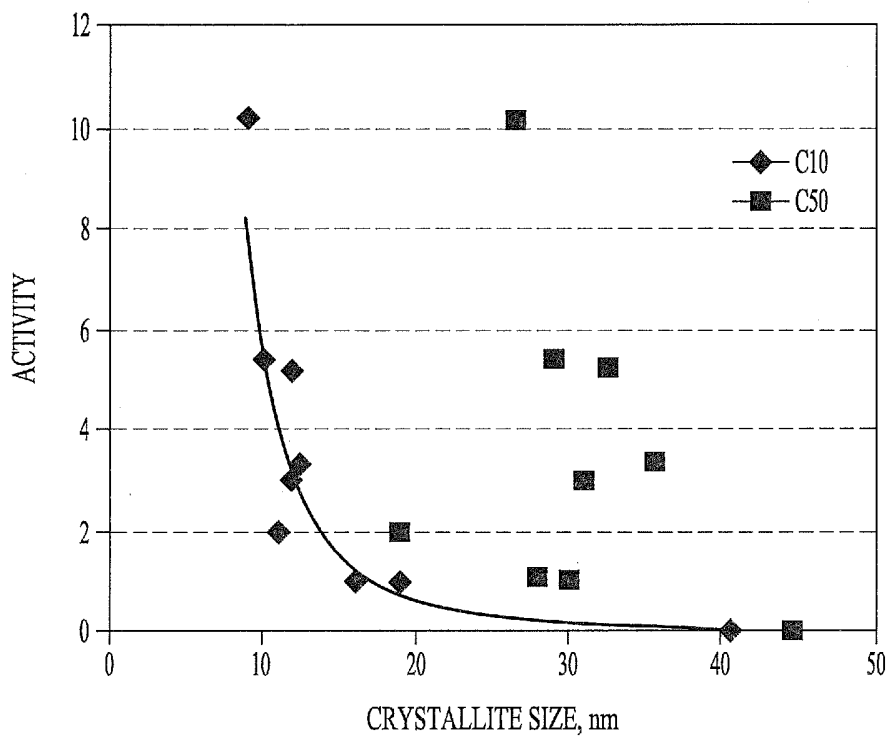
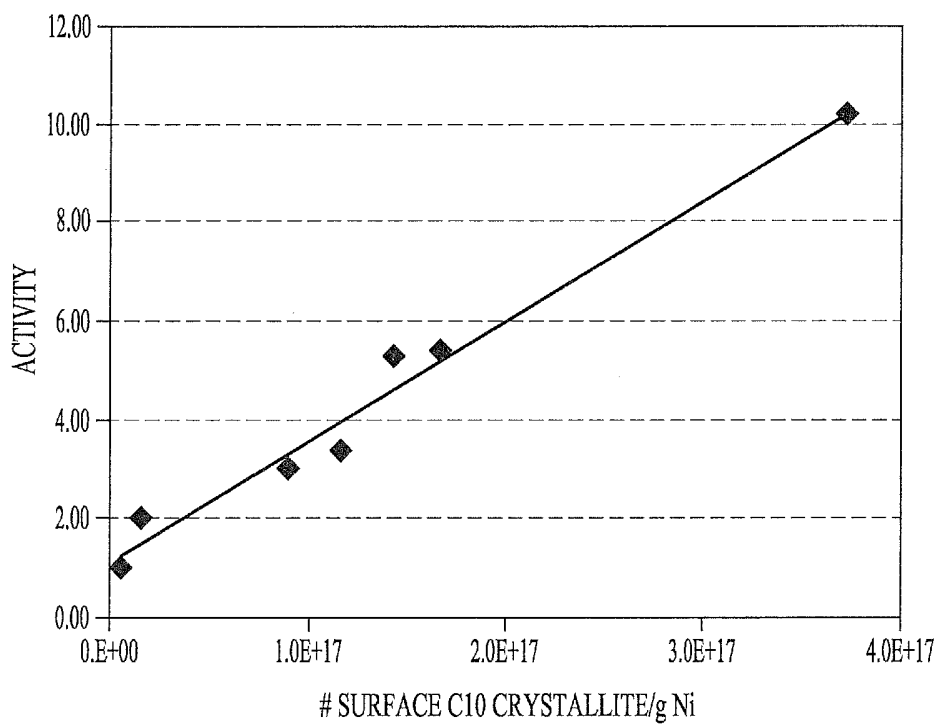
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*FIG. 17A**FIG. 17B*

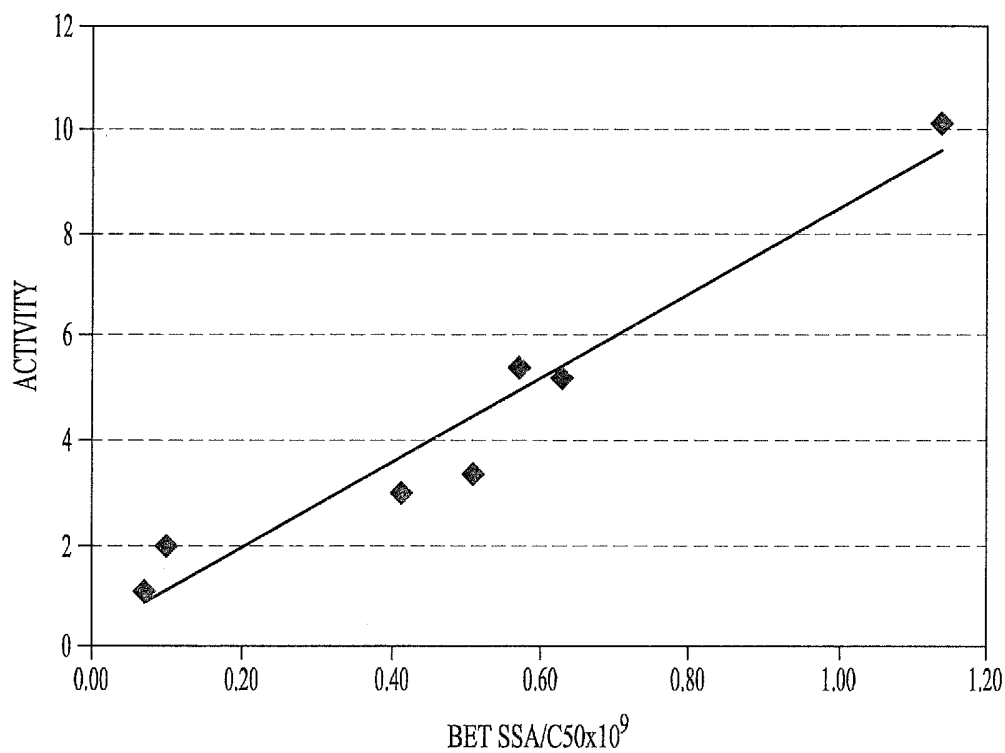
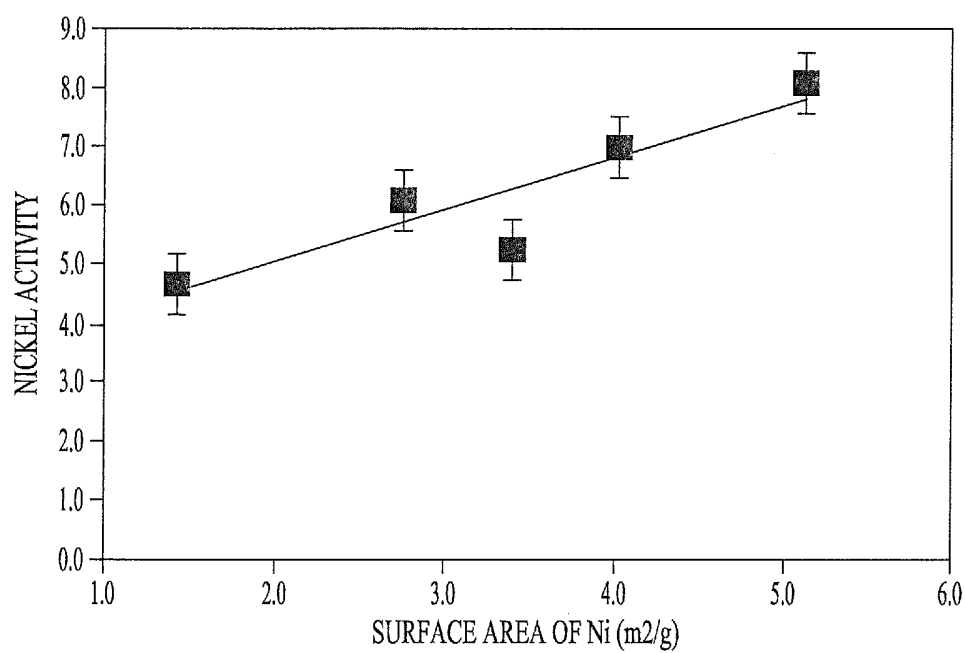
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*FIG. 17C*

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*FIG. 18**FIG. 19*

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*FIG. 20**FIG. 21*



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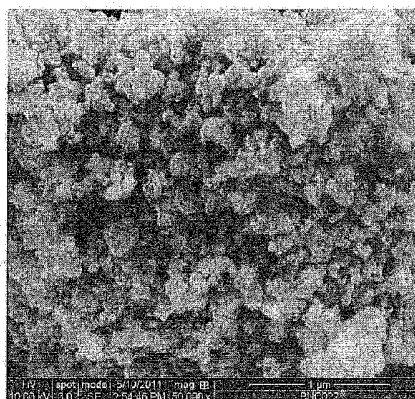
权利要求书5页 说明书74页 附图19页

(54) 发明名称

镍金属配体催化剂形成上的改进

(57) 摘要

用硫处理的镍提供出乎意料地有效的用于产生可用作氢氰化催化剂的镍-含磷配体配合物的镍原子源。



1. 一种在镍原子与一种或多种含磷配体之间产生配合物的方法,所述方法包括:
  - (a) 接触:
    - (i) 将镍原材料与硫源接触,并且由所述镍原材料和所述硫源的混合物产生镍金属以形成含硫镍金属颗粒;或者
    - (ii) 将镍金属与硫源接触以形成含硫镍金属颗粒;和
  - (b) 将所述含硫镍金属颗粒与一种或多种含磷配体接触,从而在来自所述镍金属的镍原子与一种或多种含磷配体之间形成配合物。
2. 权利要求 1 所述的方法,所述方法还包括在将所述镍金属或所述镍原材料与所述硫源接触之前,测定所述镍原材料或所述镍金属的硫含量。
3. 权利要求 2 所述的方法,其中如果所述镍金属或所述镍原材料的硫含量相对于所述镍金属或所述镍原材料的重量为小于 0.4 重量%至 0.8 重量%,则将所述镍金属或所述镍原材料与所述硫源接触。
4. 权利要求 1-3 中任一项所述的方法,其中步骤 (ii) 中的镍金属同时与所述硫源和一种或多种含磷配体接触。
5. 权利要求 1-4 中任一项所述的方法,其中所述硫源选自由以下各项组成的组:单质硫、含硫气体、含硫盐、供硫化合物、含硫离子以及它们的组合。
6. 权利要求 1-5 中任一项所述的方法,其中所述硫源选自由以下各项组成的组:二硫化物、硫代乙酸、硫代乙酸盐、多硫化物、双-烷基氨基二硫化物、次磺酸硫代酸酐、硫代磺酸盐、氨基硫代磺酸酯、酰基甲基巯基唑、酰基甲基巯基-唑盐、硫氮杂草、硫杂草、1,4-二噻英、1,2-噻嗪、1,3-噻嗪、1,4-噻嗪、1,4,2-二噻嗪、1,3,4-噻二嗪、1,2,6-噻二嗪、1,3,5-噻二嗪、二氢-二噻嗪、二氢噻二嗪、1,2,3,4-噻三唑以及它们的组合。
7. 权利要求 1-6 中任一项所述的方法,其中所述硫源选自由以下各项组成的组:硫化氢、硫酸镍、亚硫酸镍、硫化镍、连二亚硫酸镍、硫代硫酸镍、三氧化硫、二氧化硫、一氧化硫、二氯化二硫、二氯化硫、四氯化硫、一氯五氟化硫、十氟化二硫、六氟化硫、四氟化硫、三氟化硫以及它们的组合。
8. 权利要求 1-7 中任一项所述的方法,其中所述硫源是 95%至 99.9%不含硅、钠、钾、钙、镁、磷、铝、铜、钨、汞、铁以及它们的组合。
9. 权利要求 1-8 中任一项所述的方法,其中所述镍原材料或所述镍金属是 95%至 99.9%不含硅、钠、钾、钙、镁、磷、铝、铜、钨、汞、铁以及它们的组合。
10. 权利要求 1-9 中任一项所述的方法,其中所述镍原材料是碱式碳酸镍、碳酸镍、碳酸氢镍、草酸镍、甲酸镍、方酸镍、氢氧化镍、氧化镍、镍盐或它们的组合。
11. 权利要求 1-10 中任一项所述的方法,其中在所述镍原材料或所述镍金属还原成零价镍之前或之后,所述镍金属或所述镍原材料与所述硫源接触。
12. 权利要求 1-11 中任一项所述的方法,其中将所述镍原材料在氢的存在下还原足以基本上将 Ni(II) 还原成 Ni(0) 的时间,并且在足以基本上将 Ni(II) 还原成 Ni(0) 的温度进行。
13. 权利要求 1-12 中任一项所述的方法,其中约 0.1 重量%至约 50 重量%的重量百分比的硫与所述镍金属或所述镍原材料接触,其中所述硫重量百分比相对于所述镍金属或所

述镍原材料中镍的总重量。

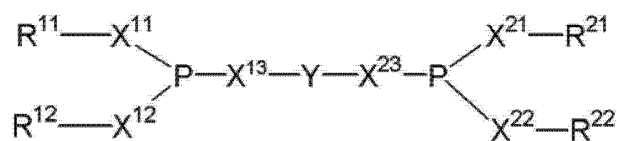
14. 权利要求 1-13 中任一项所述的方法,其中在来自所述含硫镍金属颗粒的镍原子与一种或多种含磷配体之间在路易斯酸的存在下形成配合物。

15. 权利要求 1-14 中任一项所述的方法,其中当将约 4% 镍在约 60℃ 至 80℃ 在有机腈溶剂中与每摩尔含磷配体约 0.5 至 2.5 摩尔的路易斯酸混合时,在来自所述含硫镍金属颗粒的镍原子与一种或多种含磷配体之间在约 2 小时内达到配合物形成的平衡。

16. 权利要求 1-15 中任一项所述的方法,其中所述配合物至少部分地溶解在有机腈溶剂中。

17. 权利要求 1-16 中任一项所述的方法,其中所述有机腈溶剂是戊烯腈。

18. 权利要求 1-17 中任一项所述的方法、其中所述磷配体中的一种或多种是式 (III) 的配体:



式(III)

其中:

$\text{X}^{11}$ 、 $\text{X}^{12}$ 、 $\text{X}^{13}$ 、 $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  独立地表示氧或单个直接键;

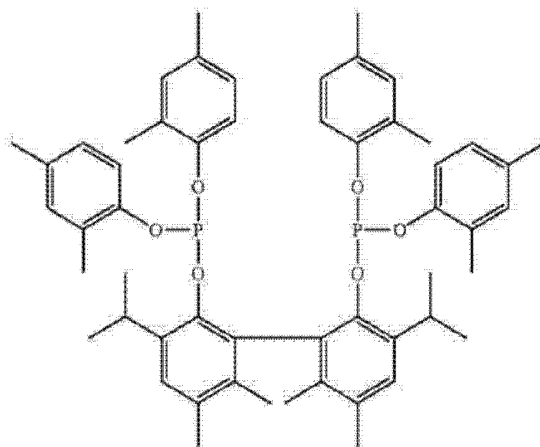
$\text{R}^{11}$  和  $\text{R}^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团;

$\text{R}^{21}$  和  $\text{R}^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团;

并且

Y 表示桥连基。

19. 权利要求 1-18 中任一项所述的方法,其中所述磷配体中的一种或多种是配体 (V):



配体(V)。

20. 权利要求 1-19 中任一项所述的方法,其中接触产生约 0.003 至约 1.8 的硫与镍的原子比。

21. 权利要求 1-20 中任一项所述的方法,其中在来自所述含硫镍金属颗粒的镍原子与

一种或多种含磷配体之间形成的配合物催化烯烃的氢氰化。

22. 权利要求 21 所述的方法,其中所述烯烃是戊烯腈。

23. 权利要求 1-22 中任一项所述的方法,其中所述含硫镍金属颗粒包含具有至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积 of 镍微晶,和 / 或其中对于基本上立方微晶计算,平均存在 :每克镍存在至少约  $10^{15}$  个表面微晶。

24. 一种催化剂制备混合物,所述催化剂制备混合物包含镍金属颗粒、一种或多种含磷配体和约 0.001 重量%至约 15 重量%硫,其中所述硫重量百分比相对于所述混合物中镍的总重量。

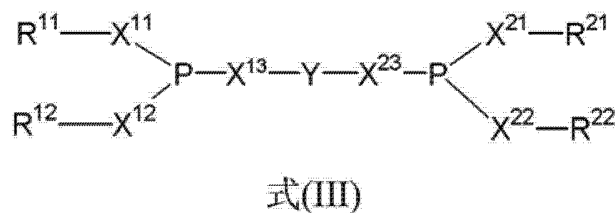
25. 权利要求 24 所述的催化剂制备混合物,其中所述混合物在有机腈溶剂中。

26. 权利要求 24 或 25 所述的催化剂制备混合物,所述催化剂制备混合物还包含路易斯酸。

27. 权利要求 24-26 中任一项所述的催化剂制备混合物,其中所述路易斯酸选自自由以下各项组成的组 :氯化锌、氯化亚铁,或它们的组合。

28. 权利要求 27 所述的催化剂制备混合物,所述催化剂制备混合物包含约 0.5 至约 2.5 的锌与含磷配体的摩尔比。

29. 权利要求 24-28 中任一项所述的催化剂制备混合物,其中所述磷配体中的一种或多种是式 (III) 的配体 :



其中,

$\text{X}^{11}$ 、 $\text{X}^{12}$ 、 $\text{X}^{13}$ 、 $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  独立地表示氧或单个直接键 ;

$\text{R}^{11}$  和  $\text{R}^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团 ;

$\text{R}^{21}$  和  $\text{R}^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团 ;

并且

Y 表示桥连基。

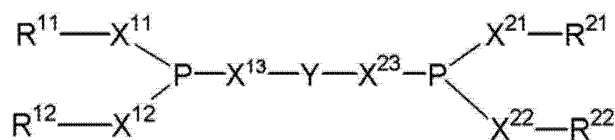
30. 权利要求 24-29 中任一项所述的催化剂制备混合物,所述催化剂制备混合物包含约 2 至约 8 重量%的重量百分比的所述一种或多种含磷配体。

31. 权利要求 24-30 中任一项所述的催化剂制备混合物,所述催化剂制备混合物包含约 1 至约 7 重量%的镍重量百分比。

32. 一种在镍原子与一种或多种含磷配体之间形成的配合物,所述配合物包含约 0.00001 重量%至约 15 重量%硫,其中所述硫重量百分比相对于所述配合物中镍的总重量。

33. 权利要求 32 所述的配合物,所述配合物包含约 0.0001 重量%至约 1 重量%硫。

34. 权利要求 32 或 33 所述的配合物,其中所述磷配体中的一种或多种是式 (III) 的配体 :



式(III)

其中,

$X^{11}$ 、 $X^{12}$ 、 $X^{13}$ 、 $X^{21}$ 、 $X^{22}$  和  $X^{23}$  独立地表示氧或单个直接键;

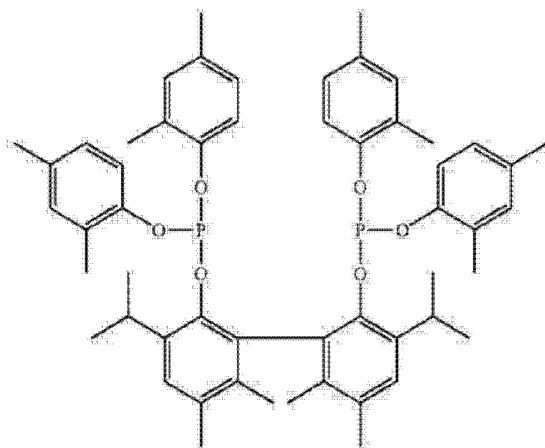
$R^{11}$  和  $R^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团;

$R^{21}$  和  $R^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团;

并且

Y 表示桥连基。

35. 权利要求 32-34 中任一项所述的配合物,其中所述磷配体中的一种或多种是配体(V):



配体(V)。

36. 一种镍颗粒形式,所述镍颗粒形式包含镍微晶和约0.2重量%至约12重量%硫,其中所述镍颗粒形式具有至少约 $1\text{m}^2/\text{gm}$ 的BET比表面积;至少10%的所述镍微晶具有小于约20nm的尺寸(C10);并且所述镍微晶尺寸分布范围大于约1.0。

37. 权利要求36所述的镍颗粒形式,其中所述镍微晶具有不大于约100nm的平均微晶尺寸。

38. 权利要求36或37所述的镍颗粒形式,所述镍颗粒形式具有不小于 $0.07 \times 10^9 \text{m}^2/\text{gm}$ 的BET比表面积/C50的比率。

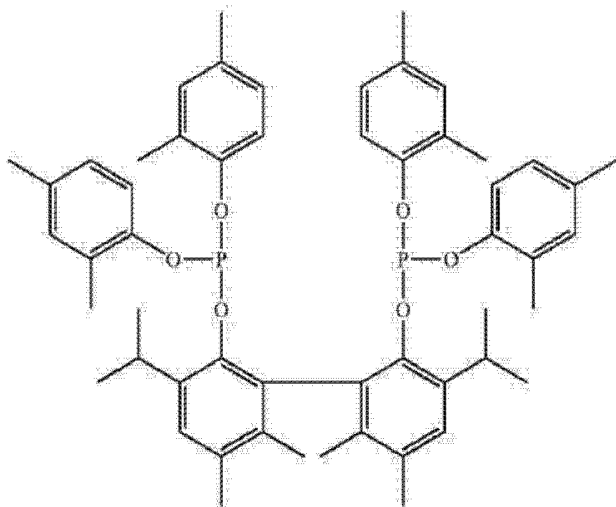
39. 权利要求36-38中任一项所述的镍颗粒形式,所述镍颗粒形式平均具有每克镍至少约 $10^{15}$ 个表面微晶。

40. 权利要求36-39中任一项所述的镍颗粒形式,其中所述形式的至少10%的粒子具有不大于约 $6\mu\text{m}$ 的尺寸(D10)。

41. 权利要求36-40中任一项所述的镍颗粒形式,其中平均具有每克镍至少约 $10^{16}$ 个小于或等于尺寸C10的表面微晶。

42. 权利要求36-41中任一项所述的镍颗粒形式,其中当将约4至5重量%的所述镍颗

粒形式与含有大约 5.25 重量%配体 (V) 和大约 6300ppmZnCl<sub>2</sub> 的 3-戊烯腈混合时,在来自所述镍颗粒形式的镍原子与配体 (V) 之间在约 2 小时内达到配合物形成的平衡;其中配体 (V) 具有下式:



43. 一种混合物,所述混合物在戊烯腈的存在下包含镍颗粒形式与选自以下各项的至少一种配体:单齿亚磷酸酯配体、二齿亚磷酸酯配体和它们的混合物,其中所述镍颗粒形式的特征在于:

(a) 0.2 重量%至 12 重量%硫;和

(b) 至少 1m<sup>2</sup>/g 的 BET 比表面积。

44. 通过机械搅拌权利要求 43 所述的混合物而形成的产物。

45. 一种均相产物,所述均相产物通过机械搅拌权利要求 43 或 44 所述的混合物形成。

## 镍金属配体催化剂形成上的改进

[0001] 本申请要求 2011 年 6 月 10 日提交的美国临时专利申请号 61/495,784 ;2011 年 6 月 13 日提交的美国临时专利申请号 61/496,142 ;2011 年 7 月 1 日提交的美国临时专利申请号 61/503,917 ;2011 年 7 月 13 日提交的美国临时专利申请号 61/507,159 ;和 2011 年 10 月 28 日提交的美国临时专利申请号 61/552,473 的申请日权益,这些申请的内容全部详细地通过引用以它们的全部内容结合在此。

[0002] 发明背景

[0003] 一些类型的镍金属催化剂体系在本领域中是可得的。例如,镍-磷配体催化剂系统用于丁二烯的氢氰化以形成戊烯腈(PN)并用于戊烯腈的氢氰化以形成己二腈(ADN)。催化剂组合物的实例和用于单烯键式不饱和化合物使用零价镍和二齿亚磷酸酯配体在路易斯酸助催化剂的存在下的氢氰化的方法的实例包括,例如美国专利号 5,512,696 ;5,723,641 ;和 6,171,996 中描述的那些。

[0004] 例如,在 GB14607A、GB255884A、GB703826A、EP101733106A、EP0114704、EP0985448A1 中和在美国专利号 4,416,825 ;3,903,1203 ;496,217 ;3,631,191 ;3,816,098 ;3,846,461 ;3,847,959 ;3,903,120 ;4,118,342 ;6,171,996 ;和 6,494,931 中还描述了一些镍制备物和/或镍配合物。

[0005] 氢氰化催化剂的形成可以包括在镍原子与含磷配体之间形成配合物。然而,可商购的镍源通常没有有效地形成这些配合物。此外,来自相同的供应商的镍的不同的批次和批号通常具有不同的组合物并且展现不可预测的用于形成镍-配体配合物的活性。例如,如本文所示,来自不同的批次和不同的商业源的镍原材料在它们与含磷配体形成配合物的能力上可以展现高达 200% 可变性。不同类型的含磷配体在它们与镍形成催化配合物的能力上也不同。由目前可得的镍源和配体在配合物形成上的这种可变性导致低效率催化剂和制造工艺,以及显著的浪费。

[0006] 为解决低效率的镍-配体配合物形成的问题,制造商之前采用活化剂如三氯化磷( $\text{PCl}_3$ )以促进具有单齿含磷配体的催化活性镍配合物的形成。参见,例如,Tam, Kreutzer&McKinney 的美国专利号 5,688,986。然而,这种活化剂可以与一些含磷配体反应并且使配体失活。因此,催化剂的可用寿命时间可以由于活化剂的使用而缩短。因此,需要改善镍金属制备物和制备催化活性镍-配体配合物的方法。

### 发明内容

[0007] 本发明通过提供在没有可以破坏配体的活化剂的情况下制备配合物的方法和通过提供容易地与含磷配体形成配合物的镍的形式解决了寿命短、形成差的镍-配体催化剂配合物的问题。例如,具有本文描述的物理性质的颗粒镍形式可以在不加入破坏配体的活化剂的情况下容易与含磷配体形成配合物。本发明还通过提供用于制备对于配合物形成高度活性的颗粒镍形式的方法解决了镍金属粒子的对于形成镍-配体催化剂配合物的不定活性的问题。例如,如本文所示,多种硫源的加入令人惊讶地将与含磷配体无效地形成配合物的颗粒镍金属转化为展现出色的配合物形成性质的镍颗粒形式。

[0008] 本发明的颗粒镍形式展现所需的物理性质,比如至少约  $1\text{m}^2/\text{gm}$ ,优选至少约  $2\text{m}^2/\text{g}$ ;更优选至少约  $4\text{m}^2/\text{g}$  并且更优选至少约  $10\text{m}^2/\text{g}$  的 BET 比表面积。此外,所需的镍颗粒形式可以还包括不大于约  $100\text{nm}$ ;优选不大于  $70\text{nm}$ ,并且更优选不大于  $50\text{nm}$  的平均微晶尺寸。在所需的镍颗粒形式中,至少 10% 的微晶具有小于约  $20\text{nm}$  的尺寸 (C10)。所需的镍颗粒形式还具有平均每克镍至少约  $10^{16}$  个尺寸 C10 以下的表面微晶。然而,硫源的加入可以恢复或抵消具有不适当的物理性质的镍粒子的差配体配合活性。例如,具有约 0.1 重量%至约 15 重量%硫的颗粒镍金属的组合物有效地与含磷配体配合。因此,当在颗粒镍的制造过程中或者在镍-配体配合物的形成过程中加入硫源时,可以使用具有不适当的物理性质的镍粒子作为用于制备具有出色的催化活性的镍-配体催化剂的颗粒镍的来源。具有高 BET 比表面积、低平均微晶尺寸,低 C10 值,0.1-15 重量%硫含量,或它们的组合的镍颗粒形式与含磷配体最佳地形成配合物。

[0009] 本发明的一个方面是一种在镍原子与一种或多种含磷配体之间产生配合物的方法,所述方法包括:

[0010] (a) 接触:

[0011] (i) 将镍原材料与硫源接触,并且由所述镍原材料和所述硫源的混合物产生镍金属以形成含硫镍金属颗粒;或者

[0012] (ii) 将镍金属与硫源接触以形成含硫镍金属颗粒;和

[0013] (b) 将所述含硫镍金属颗粒与一种或多种含磷配体接触从而在来自所述镍金属的镍原子与一种或多种含磷配体之间形成配合物。

[0014] 这种方法还可以包括在使镍金属或镍原材料与硫源接触之前确定镍原材料或镍金属的硫含量。例如,如果镍金属或镍原材料的硫含量相对于镍金属或镍原材料的重量小于 0.4 重量%至 0.8 重量%,则可以将镍金属或镍原材料与硫源接触。

[0015] 该方法可以包括将约 0.1 重量%至约 50 重量%的重量百分比的硫与镍金属或镍原材料接触,其中硫重量百分比相对于镍金属或镍原材料中镍的总重量。例如,接触步骤可以产生约 0.003 至约 1.8 的硫与镍的原子比。

[0016] 合适的硫源的实例是选自由以下各项组成的组中的那些:单质硫、含硫气体、含硫盐、含硫离子以及它们的组合。硫源的另外地实例包括选自由以下各项组成的组中的那些:硫化氢、硫酸镍、亚硫酸镍、硫化镍、连二亚硫酸镍、硫代硫酸镍、三氧化硫、二氧化硫、一氧化硫、二氯化二硫、二氯化硫、四氯化硫、一氯五氟化硫、十氟化二硫、六氟化硫、四氟化硫、三氟化硫以及它们的组合。硫源可以是 95%至 99.9%不含硅、钠、钾、钙、镁、磷、铝、铜、钨、汞、铁以及它们的组合。

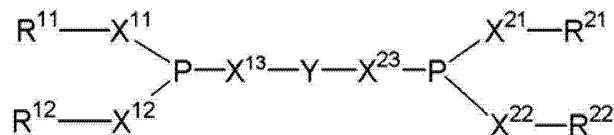
[0017] 镍原材料或镍金属可以是 95%至 99.9%不含硅、钠、钾、钙、镁、磷、铝、铜、钨、汞、铁以及它们的组合。合适的镍原材料的实例包括碱式碳酸镍、碳酸镍、碳酸氢镍、草酸镍、甲酸镍、方酸镍、氢氧化镍、氧化镍、镍盐或它们的组合。

[0018] 在这种方法的过程中,可以在将镍原材料或镍金属还原成零价镍之前或之后将镍金属或镍原材料与硫源接触。可以将镍原材料在氢中在  $200^\circ\text{C}$  至  $400^\circ\text{C}$  还原约 3 至约 5 小时。

[0019] 在来自含硫镍金属颗粒的镍原子与一种或多种含磷配体之间可以在路易斯酸的存在下形成配合物。当产生这种配合物时,步骤 (ii) 中的镍金属可以同时与硫源和一种或

多种含磷配体接触。该方法产生有效地与含磷配体形成配合物的含硫镍金属颗粒。例如，当将约 4% 镍在约 60°C 至 80°C 混合在具有每摩尔含磷配体约 0.5 至 2.5 摩尔路易斯酸的有机腈溶剂中时，来自含硫镍金属颗粒的镍原子与一种或多种含磷配体之间的配合物形成的平衡在约 2 小时（或在约 1 小时内，或者甚至在 30 分钟内）达到。这种配合物可以至少部分地溶解在有机腈溶剂，例如，戊烯腈溶剂中。这种配合物中的磷配体中的一种或多种可以是式 (III) 的配体：

[0020]



式(III)

[0021] 其中：

[0022]  $\text{X}^{11}$ 、 $\text{X}^{12}$ 、 $\text{X}^{13}$ 、 $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  独立地表示氧或单个直接键；

[0023]  $\text{R}^{11}$  和  $\text{R}^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团；

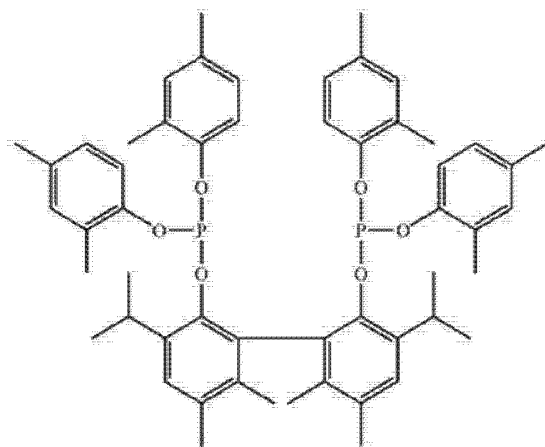
[0024]  $\text{R}^{21}$  和  $\text{R}^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团；

[0025] 并且

[0026] Y 表示桥连基。

[0027] 在另一个实例中，配合物的磷配体中的一个或多个可以是配体 (V)：

[0028]



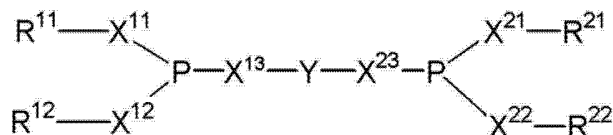
配体(V)。

[0029] 本文描述的方法可以在来自含硫镍金属颗粒的镍原子与一种或多种含磷配体之间形成配合物，其中所述配合物可以催化烯烃的氢氰化。例如，烯烃可以是戊烯腈。

[0030] 本文描述的方法可以产生包含镍微晶的含硫镍金属颗粒，其中所述含硫镍金属具有至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积，和 / 或其中平均地每克镍存在至少约  $10^{15}$  个表面微晶，这是对于基本上立方微晶计算的。含硫镍金属可以具有其他性质和特征，包括本文描述的任意那些性质和特征。

[0031] 本发明的另一方面是一种催化剂制备混合物，所述催化剂制备混合物包含镍金属颗粒、一种或多种含磷配体和约 0.001 重量%至约 15 重量%硫，其中所述硫重量百分比相

对于所述混合物中镍的总重量。这种催化剂制备混合物可以在有机腈溶剂中。催化剂制备混合物还可以包含路易斯酸,例如,选自以下各项组成的组中的路易斯酸:氯化锌、氯化亚铁或它们的组合。例如,催化剂制备混合物可以具有约 0.5 至约 2.5 的锌与含磷配体的摩尔比。催化剂制备混合物中的磷配体中的一种或多种可以是配体 (V) 或式 (III) 的配体:



式(III)

[0033] 其中,

[0034]  $\text{X}^{11}$ 、 $\text{X}^{12}$ 、 $\text{X}^{13}$ 、 $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  独立地表示氧或单个直接键;

[0035]  $\text{R}^{11}$  和  $\text{R}^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团;

[0036]  $\text{R}^{21}$  和  $\text{R}^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团;

[0037] 并且

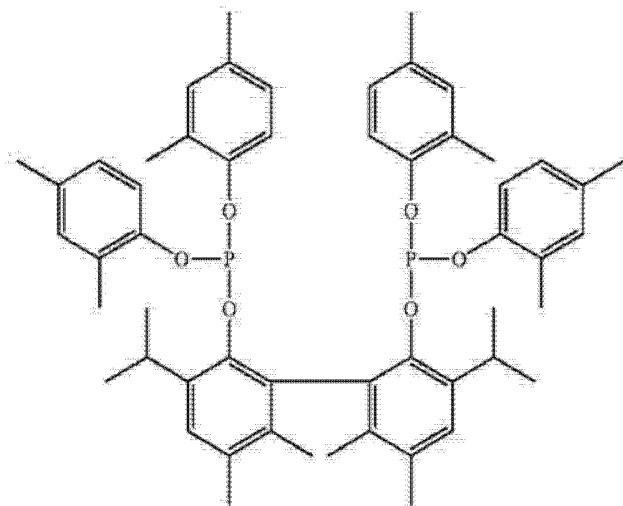
[0038] Y 表示桥连基。

[0039] 催化剂制备混合物内一种或多种含磷配体的重量百分比可以是约 2 至约 8 重量%。催化剂制备混合物内镍重量百分比可以是约 1 至约 7 重量%。

[0040] 本发明的另一方面是在镍原子与一种或多种含磷配体之间形成的配合物,所述配合物包含约 0.00001 重量%至约 15 重量%硫,其中所述硫重量百分比相对于所述配合物中镍的总重量。例如,配合物可以包含约 0.0001 重量%至约 1 重量%硫。在该配合物中可以存在一种或多种磷配体,例如,本文描述的配体 (V) 或式 (III) 的配体。

[0041] 本发明的另一方面是一种镍颗粒形式,所述镍颗粒形式包含镍微晶和约 0.2 重量%至约 12 重量%硫,其中所述镍颗粒形式具有至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积;至少 10% 的所述镍微晶具有小于约 20nm 的尺寸 (C10);并且所述镍微晶尺寸分布范围大于约 1.0。例如,镍颗粒形式中的镍微晶可以具有不大于约 100nm 的平均微晶尺寸。这种镍颗粒形式可以具有不小于  $0.07 \times 10^9 \text{m}^2/\text{gm}$  的 BET 比表面积/C50 的比率。这种镍颗粒形式还可以具有平均每克镍至少约  $10^{15}$  个表面微晶。这种镍颗粒形式可以还包括粒子,其中所述形式的至少 10% 的粒子具有不大于约  $6\mu\text{m}$  的尺寸 (D10)。镍颗粒形式可以还具有大量的表面微晶,例如,平均可以存在每克镍至少约  $10^{16}$  个小于或等于尺寸 C10 的表面微晶,其中 C10 尺寸可以,例如,为小于约 20nm。镍颗粒形式还与一种或多种含磷配体有效地形成配合物。例如,当将约 4 至 5 重量%的镍颗粒形式与含有大约 5.25 重量%配体 (V) 和大约 6300ppm  $\text{ZnCl}_2$  的 3-戊烯腈混合时,镍颗粒形式与配体 (V) 在约 2 小时(或约 1 小时,或甚至约 30 分钟)内达到配合物形成的平衡;其中配体 (V) 具有下式:

[0042]



[0043] 本发明的另一方面是一种混合物,所述混合物在戊烯腈的存在下包含镍颗粒形式与选自以下各项的至少一种配体:单齿亚磷酸酯配体、二齿亚磷酸酯配体和它们的混合物,其中所述镍颗粒形式的特征在于:

[0044] (a) 0.2 重量%至 12 重量%硫;和

[0045] (b) 至少  $1\text{m}^2/\text{g}$  的 BET 比表面积。

[0046] 本发明还涉及通过机械搅拌这种混合物而形成的产物。例如,该产物可以通过机械搅拌这种混合物而形成的均相产物。

[0047] 令人惊讶的是硫处理可以改善镍-配体氢氰化催化剂的形成,原因在于硫已被报道为使催化剂中毒。参见,例如,Chen 等,IND. ENG. CHEM. RES. 27:1391-96(1988)。因此,出乎意料地,令人惊讶地发现当采用本文描述的方法时可以将即使形成镍-配体配合物很差的镍金属的源也可以简单、有效果并且高效率地转化为高度形成镍-配体配合物的镍金属制备物。

[0048] 附图简述

[0049] 图 1 显示表 2 中列出的八个 BNC 样品 #1-#8 的煅烧预处理过程中的二氧化碳 ( $\text{CO}_2$ ) 损失。

[0050] 图 2 是 BNC 样品 #3、4 和 6 的还原过程中的氢吸收的热曲线,其在还原时提供不与本文描述的含磷配体有效地形成配合物的无活性 Ni。

[0051] 图 3A 是 BNC 样品 #1、2、5、7 和 8 的还原过程中氢吸收的热曲线,其在还原时提供不有效地形成如本文描述的具有含磷配体的配合物的活性 Ni。图 3B 显示程序升温解吸-反应-质谱 (TPD-TPR MS),其中测试条件是 Ar 平衡 ( $20\text{cm}^3\text{min}^{-1}$ ,  $> 99\%$  Ar, BOC);总流动速率= $20\text{cm}^3\text{min}^{-1}$ ;内标=Ar ( $m/z=36$ );催化剂质量=50-60mg;速率= $15^\circ\text{C min}^{-1}$ 。图 3C 显示程序升温反应质谱 (TPR-MS),其中测试条件是  $10\%$   $\text{H}_2$  ( $2\text{cm}^3\text{min}^{-1}$ ,  $> 99\%$   $\text{H}_2$ , BOC);Ar 平衡 ( $18\text{cm}^3\text{min}^{-1}$ ,  $> 99\%$  Ar, BOC);总流动速率= $20\text{cm}^3\text{min}^{-1}$ ;内标=Ar ( $m/z=36$ );催化剂质量=50-60mg;速率= $15^\circ\text{C min}^{-1}$ 。

[0052] 图 4 显示对于通过表 2 中列出的 BNC 样品 #1 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。温度轴显示在氢化过程中施加的升温的进行,在这些数据中微晶尺寸轴显示如通过 XRD 测定的微晶尺寸,并且体积-%轴指示每块样品中多种微晶尺寸分类的体积分布。样品序号对应于表 2 中给出的那些。也参见实施例 3。

[0053] 图 5 显示对于通过表 2 中列出的 BNC 样品 #2 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。该图的产生如实施例 3 中所述和对于图 4 所述。

[0054] 图 6 显示对于通过表 2 中列出的 BNC 样品 #3 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。该图的产生如实施例 3 中所述和对于图 4 所述。

[0055] 图 7 显示对于通过表 2 中列出的 BNC 样品 #4 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。该图的产生如实施例 3 中所述和对于图 4 所述。

[0056] 图 8 显示对于通过表 2 中列出的 BNC 样品 #5 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。该图的产生如实施例 3 中所述和对于图 4 所述。

[0057] 图 9 显示对于通过表 2 中列出的 BNC 样品 #6 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。该图的产生如实施例 3 中索书号和对于图 4 所述。

[0058] 图 10 显示对于通过表 2 中列出的 BNC 样品 #7 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。该图的产生如实施例 3 中所述和对于图 4 所述。

[0059] 图 11 显示对于通过表 2 中列出的 BNC 样品 #8 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据。该图的产生如实施例 3 中所述和对于图 4 所述。

[0060] 图 12 是说明了不够尺寸 (undersized) 的 Ni 微晶的累积分数 (%) 作为微晶尺寸的函数关系的图,用于确定从 BNC 样品 #8 通过在所给出的温度还原而制备的镍金属粉末的微晶尺寸分布 (即,微晶尺寸分布 CSD 的宽度)。

[0061] 图 13 显示了微晶尺寸分布 (CSD) 与镍活性相关。对于由表 2 中列出的八个 BNC 样品在所给出的温度还原之后制备的八个 Ni 粉末样品给出 CSD 数据。

[0062] 图 14 图示镍活性与由表 2 中列出的八个 BNC 样品在所给出的温度还原之后产生的多种镍样品的 C10 值之间的关系 (最小 10% 的微晶中以纳米计的最大直径)。

[0063] 图 15A-15D 是镍粒子的扫描电子显微照片。

[0064] 图 16A 图示基于微晶的形状是粗略球体的假设,每克的表面微晶数目相对于 Ni1-Ni3、Ni5-Ni6 和 Ni9-Ni10 样品的镍活性 (表 4)。图 16B 图示基于微晶是基本上正方形截面,即,是立方体或立方形状形状的假设,对于七个镍活性样品 Ni1-Ni3、Ni5-Ni6 和 Ni9-Ni10 的镍活性与每克的平均微晶数目之间的相关性。Ni1-Ni3、Ni5-Ni6 和 Ni9-Ni10 的性质也描述在表 4 中。

[0065] 图 17A-17C 图示镍粒子 / 微晶表面积与镍制备物形成镍 - 配体配合物的活性之间的相关性。图 17A 显示对于镍制备物 Ni1、Ni3、Ni6、Ni7、Ni8 和 Ni9 显示 BET SSA 与 LDS SA 的相关性 (参见表 4)。图 17B 显示样品 Ni1、Ni3、Ni6、Ni7、Ni8 和 Ni9 的 BET SSA 与 D10 粒径之间的相关性 (表 4)。图 17C 图示具有表 4 中描述的性质的镍样品 Ni1-Ni6 和 Ni9-Ni10 的 BET SSA 值相对于镍活性的关系。

[0066] 图 18 图示了对于具有表 4 中列出的性质的样品 Ni1-Ni6 和 Ni8-Ni10 的镍活性相对于 C10 和 C50 值的关系。

[0067] 图 19 图示对于镍样品的不大于 C10 值的尺寸的表面微晶的数目与该样品的镍活性之间的相关性。

[0068] 图 20 图示了对于每个具有如本文定义的至少 1 的活性的镍样品,使用在表 4 中给出的数据的情况下镍活性与 BET SSA/C50 之间的相关性。

[0069] 图 21 图示了对于在相同的条件 (在氢中在 400 °C) 下还原的具有当量硫含量

(1%) 的镍样品的镍活性与 BET SSA 之间的相关性。

[0070] 发明详述

[0071] 镍金属 (例如, 零价镍金属) 粒子用于与一种或多种含磷配体形成配合物, 并且镍原子与含磷配体之间的配合物可以是有效的氢氰化催化剂。这些镍-配体配合物可以溶解在有机介质, 如氢氰化反应介质中。如本文所示, 用硫源处理提高了颗粒镍金属制备物与一种或多种含磷配体形成配合物的能力。

[0072] 物理形式以及颗粒镍金属的制备物中硫的含量影响其与含磷配体形成催化配合物的能力。例如, 具有至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积, 和 / 或在  $300\text{--}400^\circ\text{C}$  还原之后具有小于约  $20\text{nm}$  的 C10 值, 和 / 或具有不大于约  $100\text{nm}$  的平均微晶尺寸的镍颗粒形式展现出良好的与含磷配体形成配合物的活性。然而, 具有更低 BET 表面积和 / 或更高的平均微晶尺寸的镍颗粒形式的硫处理可以显著地提高这些镍颗粒形式与含磷配体形成配合物的能力。所需的颗粒镍物理性质和硫浓度的组合提供最优的配合物形成活性。

[0073] 此外, 与含磷配体形成配合物差的颗粒镍金属的硫处理可以修复结构上不合适的镍制备物的缺陷, 从而制备容易地与含磷配体形成配合物的镍颗粒形式。为实现这种处理, 可以将硫源在镍金属粒子的制造过程中加入至镍原材料, 可以将硫源在镍-配体配合物形成过程中直接加入至颗粒镍金属和一种或多种含磷配体的混合物中, 或者可以将硫源直接加入至含有镍-配体催化剂的氢氰化反应混合物中。

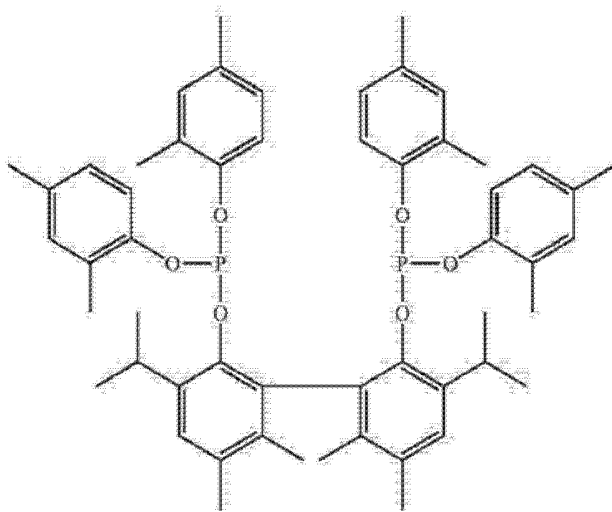
[0074] 用硫源处理的镍粒子更有效地与一种或多种含磷配体结合并且比未处理的镍金属粒子更有效地产生活性氢氰化催化剂。催化剂形成的提高可以是实质性的。例如, 在一种可商购的镍粒子源使用本文描述的方法的处理之后, 根据例如通过镍-配体配合物在有机中的溶解度测量, 在与含磷配体形成配合物方面提高了 14-15 倍。在这种处理之前, 可商购的镍源不可用于制备镍-配体催化剂。用硫源的处理, 使得作为否则可能被抛弃的镍源的镍金属的配合物形成显著地提高, 因而可以有效地用于制备可用于包括氢氰化的制造工艺的出色的催化剂。

[0075] 产生活性镍氢氰化催化剂的方法包括将镍金属或用于制备镍金属的镍原材料与硫源接触。镍原材料可以在镍原材料产生镍金属的处理过程中, 或在产生镍金属之后, 或者甚至镍金属与一种或多种含磷配体形成配合物的过程中与硫源接触。

[0076] 本文提供的所需的镍金属粉末的形式包括由具有给定尺寸、BET 比表面积和激光衍射比表面积、微晶尺寸、微晶尺寸分布、每克的表面微晶以及上述这些的组合的镍微晶构成的镍金属的粒子。例如, 所需的表面积包括具有至少约  $1\text{m}^2/\text{gm}$ , 优选至少约  $2\text{m}^2/\text{g}$ , 更优选至少  $4\text{m}^2/\text{g}$ , 并且再优选至少  $10\text{m}^2/\text{g}$  的 BET 比表面积的那些。所需的镍颗粒形式可以具有选自以下各项组成的组中的至少一种性质: 至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积; 不小于  $0.07 \times 10^9\text{m}^2/\text{gm}$  的 BET 比表面积 / C50 的比率; 小于约  $20\text{nm}$  的 C10; 不大于约  $30\text{nm}$  的平均微晶尺寸; 大于约 1.0 的微晶尺寸分布范围; 平均每克镍至少约  $10^{15}$  个表面微晶; 至少 10% 的粒子形式具有不大于约  $6\mu\text{m}$  的尺寸 (D10); 至少约  $0.4\text{m}^2/\text{gm}$  的激光衍射比表面积; 约  $0.3 \times 10^6\text{m}^2/\text{gm}$  至约  $10.0 \times 10^6\text{m}^2/\text{gm}$  的 BET 比表面积与 D10 的比率; 平均每克镍至少约  $10^{16}$  个尺寸小于或等于 C10 的表面微晶; 以及上述这些的任意组合。优选所需的镍颗粒形式具有这些性质中的至少两种; 更优选, 所需的镍颗粒形式具有这些性质中的至少三种; 再更优选, 所需的镍颗粒形式具有这些性质中的至少四种。

[0077] 当将约 4 至 5 重量%的镍颗粒形式与含有配体 (V) 和  $\text{ZnCl}_2$  的 3-戊烯腈混合时,这种所需的镍颗粒形式在约 2 小时内与配体 (V) 形成配合物;其中配体 (V) 具有下面的化学式:

[0078]



[0079] 虽然这些物理性质是所需的,但是用硫源处理可以显著地提高颗粒镍形式与含磷配体形成配合物的能力。因此,如果将颗粒镍形式在其作为颗粒金属的制备过程中或在颗粒镍金属形式与一种或多种含磷配体的配合物形成过程中用硫源处理,则来自颗粒镍形式的一种或多种所需的物理性质可以缺乏。

[0080] 硫源

[0081] 如本文描述的,与硫源接触的镍原材料和镍金属展现与含磷配体的配合物形成得到改善。

[0082] 所采用的硫源可以包含单质硫、聚合硫、含硫气体、含硫盐、含硫离子以及它们的组合。硫源可以是液体、固体、气体或这些物理形式的组合。硫源可以包括,例如,硫酸盐、亚硫酸盐、硫化物、次硫酸盐、硫代硫酸盐、二氧化硫、一氧化硫、卤化硫等。可以采用的硫源的实例包括硫化氢、硫酸镍、亚硫酸镍、硫化镍、连二亚硫酸镍、硫代硫酸镍、三氧化硫、二硫化硫、一氧化硫、二氯化二硫、二氯化硫、四氯化硫、一氯五氟化硫、十氟化二硫、六氟化硫、四氯化硫、三氯化硫以及它们的组合。可以使用硫的任意这些和其他源来活化镍用于与含磷配体形成配合物。

[0083] 单质硫可以以数种形式,包括固体单质硫、气体硫、聚合硫、硫的聚合链的混合物、环状硫以及它们的组合存在。还存在大数目的硫的同素异形体。在自然界中发现的最常见的形式是黄色正交  $\alpha$ -硫,其含有八个硫原子 ( $\text{S}_8$ ) 的折叠环。此外,硫的其他固体形式含有 6、7、9-15、18 和 20 个原子的硫环。还存在硫气体,如  $\text{S}_2$ 、 $\text{S}_3$ 、 $\text{S}_4$  和  $\text{S}_5$ 。例如,在高压下也可以形成金属状硫形式。这些硫的形式中的任意和全部均是可用于在本文描述的方法中使用的硫源。

[0084] 硫源可以是硫供体。供出硫的化合物的实例包括硫醚、硫代酯、二硫化物等。例如,二硫化物可以选自二硫化物、硫代乙酸、硫代乙酸盐、多硫化物、双-烷基氨基二硫化物、次磺酸硫代酸酐 (sulfenic sulfonic thioanhydride)、硫代磺酸盐、氨基硫代磺酸盐、酰基甲基巯基唑 (acylmethylmercapto azoles) 或唑盐 (azolium salts)、硫氮杂

草、硫杂草 (thiepins)、1,4- 二噻英 (dithiins)、1,2-、1,3-、或 1,4- 噻嗪、1,4,2- 二噻嗪、1,3,4-、1,2,6-、1,3,5- 噻二嗪、二噻嗪或噻二嗪的二氢衍生物、1,2,3,4- 噻三唑以及它们的组合。硫化剂如在以下各项中讨论的硫化剂也是有效的：由 Porter, M. 在橡胶的硫化 (Vulcanization of Rubber) ;Oae, S. Ed. ;硫的有机化学 (Organic Chemistry of Sulfur) ;Plenum :纽约,1977,第 3 章,以及 Hofmann, W 硫化和硫化剂 (Vulcanization and Vulcanizing Agents) ;Palmerton :纽约,1967 年。

[0085] 可以优选的是硫的源不将有机化合物或有机部分引入至镍制备物或镍和含磷配体的混合物。例如,硫源可以不包含含有碳的或含有磷酸 (phosphate) 的化合物和部分。硫的源可以不包括金属污染物 (除镍之外)。例如,硫的源可以不包含显著量的碱和碱土离子或盐。在一些情况下,这些有机化合物或有机部分可以在硫源和镍原材料的混合物的处理过程中被移除。例如,用以从镍原材料产生镍金属粒子的煅烧和 / 或还原过程可以移除一些有机化合物或有机部分。

[0086] 因此,可以采用多种硫源以提高镍活性。具有证实的将镍原材料转化为具有好的镍 - 配体配合物形成性质的镍颗粒形式的能力的硫源包括液体或固体硫酸镍、单质硫 (例如,  $S_8$ ), 以及硫化镍 (例如,  $Ni_3S_2$ )。

[0087] 可以将这种镍源在镍金属粒子的制造过程中加入至镍原材料 (例如, 碱式碳酸镍或氧化镍), 可以在镍 - 配体配合物形成过程中将硫源直接加入至颗粒镍金属和一种或多种含磷配体的混合物, 也可以将硫源直接加入至含有镍 - 配体催化剂的氢氰化反应混合物。

[0088] 镍原材料

[0089] 可以将镍金属 (例如, 零价镍金属) 在与含磷配体形成配合物之前、过程中或之后直接用硫源处理。然而, 也可以将镍原材料与硫源接触, 其中处理镍原材料以产生镍金属。例如, 镍原材料可以包含更高价态的盐形式的镍。因此, 可以在镍原材料制备镍金属粒子的还原之前将硫源加入至镍原材料。

[0090] 很多镍源是可得的并且可以充当制备镍金属的原材料。例如, 镍原材料可以是碱式碳酸镍、碳酸镍、碳酸氢镍、草酸镍、甲酸镍、方酸镍、氢氧化镍、氧化镍、镍盐, 或它们的组合。

[0091] 不同类型的镍原材料可以需要不同的工艺以产生镍金属。用于产生镍金属的工艺是本领域中可得的并且这种工艺的实例在本文被描述。令人惊讶地, 镍原材料用硫源的处理可以在镍金属制备工艺的基本上任意阶段发生。典型地, 用于产生镍金属的工艺包括更高价态形式的镍至零价镍金属的还原。硫源在镍原材料的还原之前的加入是形成有效地与含磷配体形成配合物的镍金属粒子的好的方式。

[0092] 氧化镍也是便利的镍原材料。氧化镍优选是颗粒形式。为产生用于制备镍 - 配体配合物的颗粒镍金属, 将氧化镍从价态 +2 还原成零价镍金属粒子。这种还原可以如本文所描述或通过其他可得的方法进行。

[0093] 如本文所示, 即使在还原之后, 很多可商购的氧化镍源在还原和与含磷配体组合之后不形成有用的催化剂。然而, 当在还原之前、过程中或之后将这种氧化镍用硫源处理时, 所形成的镍可以容易地与含磷配体形成配合物, 形成的程度比在用硫源处理之前由氧化镍产生的镍达到的程度更大。

[0094] 碱式碳酸镍是另一种可用的镍原材料。碱式碳酸镍是可商购的或者它可以如本文所描述制备。当采用碱式碳酸镍作为原材料时,将其还原以产生镍金属。任选地,可以将碱式碳酸镍在还原之前煅烧,从而放出二氧化碳并提供氧化镍组合物。使用这种煅烧步骤以增加镍样品形成在有机腈溶剂中可溶的镍-配体配合物的反应性。然而,当如本文所描述地用硫源处理时,可以不需要煅烧碱式碳酸镍而获得令人满意水平的镍-配体配合物形成。然而,如果进行煅烧,可以将碱式碳酸镍在煅烧以制备氧化镍的过程中,在还原以产生镍金属的过程中或在镍金属产物与含磷配体的配合物形成过程中与硫源接触。

[0095] 如本文所示,即使在煅烧和还原之后,很多商业源的碱式碳酸镍不容易与含磷配体形成配合物。然而,当将这种商业源的碱式碳酸镍在煅烧和/或还原之前、过程中或之后用硫源处理时,即使这些商业源的碱式碳酸镍也可以转化为容易地与含磷配体形成配合物的镍金属制备物。

[0096] 还可以采用甲酸镍作为可用于制备镍金属粒子的原材料。如本文所示,可以将甲酸镍热处理以产生可用于与含磷配体形成配合物的镍金属粒子,尤其是当存在硫(例如,大于约 500ppm 硫,优选约 0.2 重量%至约 15 重量%硫)时。因此,可以将甲酸镍简单地在无含氧气体如氮中热处理,并且可以不需要对甲酸镍进行还原步骤。

[0097] 当将甲酸镍热处理以产生镍金属粒子时,可以将甲酸镍在非-含氧气氛中加热至 350°C 至 450°C 约 1 至 4 小时。如本文所示,可以将甲酸镍便利地在流化床反应器中热处理,其中将甲酸镍悬浮在氮气气氛中并加热至约 400°C 约 2 小时。

[0098] 虽然甲酸镍的还原可以不是必需的,这种还原可以使用本文描述的或本领域中可得的程序进行。如果需要煅烧,也可以使用本文描述的方法煅烧甲酸镍。因此,将甲酸镍在无氧气氛中热处理,可以将甲酸镍在没有煅烧预处理的情况下还原,也可以对其进行煅烧预处理之后还原成零价镍金属粒子。可以将硫源与甲酸镍在任意步骤(热处理、煅烧、还原或配合物形成)组合以产生具有催化活性的镍-磷配体配合物。

[0099] 可用于制备可以容易地与含磷配体形成配合物的镍金属粒子的另一种镍原材料是镍盐。用于制备镍金属粒子的可用的镍盐的一个实例是硫酸镍。当采用硫酸镍作为用于制备镍金属的原材料,可以不需要进一步的硫处理,因为硫酸盐是出色的硫源。因此,硫酸镍可以是用于产生镍金属的有用的原材料。

[0100] 硫酸镍可以是固体(例如,颗粒)形式或在溶液中。当硫酸镍在溶液中时,可以将溶剂移除以产生含有镍(II)的粉末。通常,在还原之前对硫酸镍进行煅烧以产生具有硫酸根离子的氧化镍。硫酸镍的煅烧减少了在还原过程中将形成大量的  $\text{Ni}_3\text{S}_2$  的可能性,  $\text{Ni}_3\text{S}_2$  可能不与含磷配体良好地配合。将通过硫酸镍的煅烧形成的固体和粉末材料中的镍(例如,  $\text{Ni}^{+2}$  和氧化镍)使用本文描述的方法或其他可用的程序还原以产生镍金属(零价镍)。

[0101] 还可以将镍金属用硫源处理。如本文所示,可商购的镍源展现可变的、不可预测的和典型地差的用于制备作为氢氰化催化剂的镍-配体配合物的活性。然而,容易地与含磷配体反应的活性颗粒镍金属可以通过将硫源加入至镍金属粒子容易地制备。例如,可以将硫源加入至镍粒子和含磷配体在传统的溶剂(例如,有机腈溶剂)中的混合物以产生作为有效的氢氰化催化剂的镍-配体配合物。还可以将硫源加入至含有镍-磷配体催化剂的氢氰化反应混合物中。

[0102] 通常,来自商业源的未处理的镍金属展现与含磷配体差的配合物形成。虽然可商

购的镍金属的还原可以提供略微的改进,但是在镍还原过程中,或仅在氢氰化催化剂的形成过程中硫源的加入可靠地将差的镍金属源转化为有效地与含磷配体组合以产生可用的氢氰化催化剂的镍金属的形式。

[0103] 当选择镍金属用于用硫源处理时,镍金属可以是颗粒(粉末)零价镍金属。如果将镍金属部分地氧化,可以将其通过本领域中可得程序,例如,通过如本文描述的热氢处理进行还原。

[0104] 用硫源处理

[0105] 可以将镍金属粒子和镍原材料用可变量的硫源在产生零价镍金属、形成镍-配体配合物和在氢氰化反应过程中保持有效的镍-配体催化剂的不同的阶段进行处理。例如,可以将硫源在煅烧之前、过程中或之后加入至镍原材料。可以将硫源在还原之前、过程中或之后加入至镍原材料。还可以在镍-配体配合物形成过程中和采用镍-配体催化剂的氢氰化反应过程中包含硫源。

[0106] 镍原材料或镍金属在用硫源的处理过程中可以是溶液、悬浮液或颗粒形式。例如,镍可以是液体介质或气体流内的颗粒形式。因此,镍原材料或镍金属可以在悬浮液中。镍金属的溶解性在很多液体溶剂中通常非常低。然而镍金属可以悬浮在液体中或通过气体悬浮。备选地,可以将固体颗粒形式的镍原材料或镍金属与硫源简单地混合。

[0107] 可以将硫源与镍原材料或镍金属组合和/或混合不同的时间。例如,镍原材料或镍金属和硫源可以在一起混合约1分钟至约72小时,或约1分钟至24小时,或约1分钟至12小时,或约1分钟至4小时,或约1分钟至2小时,或约1分钟至1小时。当将硫源加入至要经历包括混合,如煅烧,还原或者甚至催化剂配合物形成的进一步的处理的镍原材料时,可能最初需要很少的混合。

[0108] 在镍原材料或镍金属用硫源的处理过程中,可以将混合物保持在约4℃至约450℃。可能需要少量的或不需另外的加热或孵育以用硫源处理镍金属或镍原材料,因为镍金属的形成或镍-配体催化剂配合物的形成中的各个步骤为镍的硫处理提供足够的加热和混合。因此,可以将硫源加入至镍金属或镍-配体配合物的制备中所包括的基本上任意方便的步骤。

[0109] 例如,可以将硫源直接加入至催化剂配合物形成混合物,该混合物含有在有机溶剂(例如,有机腈溶剂)中的镍金属粒子和一种或多种含磷配体,将其混合并升温至约60℃-80℃。可以将硫源便利地加入至任意镍原材料中并且可以将镍原材料以通常方式处理为颗粒镍金属,例如,通过还原(煅烧典型地是任选的)进行。

[0110] 可以将镍和镍原材料用变化量的硫源有效地处理。例如,硫与镍的摩尔比可以在约0.003至约1.8的范围内;优选摩尔比为约0.004至约0.2;并且更优选这种硫与镍摩尔比为约0.01至约0.05。

[0111] 与镍和镍原材料的组合的硫的有效量可以在相对于组合物的总重量约0.1重量%硫至约50重量%硫之间变化,或优选相对于组合物的总重量约0.2%至约4重量%硫,优选相对于组合物的总重量约0.3%至约2重量%硫。

[0112] 例如,零价颗粒镍制备物中硫的有效量可以在相对于镍的重量约0.1重量%硫至约50重量%硫之间变化。硫的重量百分比可以在约0.2重量%硫至约15重量%硫,或约0.2重量%硫至约10重量%硫变化。优选地,零价颗粒镍制备物中硫的量可以为相对于镍

的重量约 0.5 重量%硫至约 5 重量%硫,或更优选相对于镍重量的约 0.6%至约 1%硫。如本文所示,颗粒镍金属制备物中有效量的硫为相对于镍重量的约 0.8%硫。

[0113] 可以将镍原材料如碱式碳酸镍、碳酸镍、碳酸氢镍、草酸镍、甲酸镍、方酸镍或它们的组合用相对于组合物的总重量约 0.1 重量%至约 25 重量%硫,或相对于组合物的总重量约 0.2 重量%至约 10 重量%硫,相对于组合物的总重量约 0.3 重量%至约 3 重量%硫处理。优选地,将这种镍原材料用相对于组合物的总重量约 0.3 重量%至约 1 重量%范围内的硫的硫源处理,或相对于组合物的总重量约 0.3 重量%至约 0.5 重量%硫的硫源处理。如本文所示,碱式碳酸镍中有效量的硫为相对于组合物的总重量约 0.4 重量%硫。可以将相似的镍原材料用相对于组合物的总重量约 0.4 重量%硫处理。

[0114] 可以将镍原材料如碱式碳酸镍 (BNC)、碳酸镍、碳酸氢镍、甲酸镍、草酸镍或方酸镍与硫源混合以使得硫含量为基于镍至少 0.1 重量%,或基于镍至少 0.2 重量%,或基于镍至少 0.3 重量%,或基于镍至少 0.4 重量%,或基于镍至少 0.5 重量%,或基于镍至少 0.6 重量%,或基于镍至少 0.7 重量%,或基于镍至少 0.8 重量%,或基于镍至少 0.9 重量%,或基于镍至少 1.0 重量%,或基于镍至少 2 重量%,或基于镍至少 3.0 重量%。

[0115] 可以使用比用于碱式碳酸镍稍微更多硫处理氧化镍。例如,可以将氧化镍用相对于组合物的总重量约 0.2 重量%至约 30 重量%硫处理,或用相对于组合物的总重量约 0.3 重量%至约 10 重量%硫处理,用相对于组合物的总重量约 0.4 重量%至约 5 重量%硫处理。优选地将氧化镍用相对于组合物的总重量约 0.4 重量%至约 1 重量%硫,或相对于组合物的总重量约 0.5 重量%至约 0.7 重量%硫处理。如本文所示,与氧化镍的混合物中硫的有效量为相对于组合物的总重量约 0.6%硫。可以将相似的镍原材料用相对于组合物的总重量约 0.6%硫处理。

[0116] 氧化镍与硫源一起以使得硫含量为基于镍至少 0.2 重量%,或基于镍至少 0.3 重量%,或基于镍至少 0.4 重量%,或基于镍至少 0.5 重量%,或基于镍至少 0.6 重量%,或基于镍至少 0.7 重量%,或基于镍至少 0.8 重量%,或基于镍至少 0.9 重量%,或基于镍至少 1.0 重量%,或基于镍至少 2 重量%,或基于镍至少 3.0 重量%。

[0117] 当使用含硫盐作为硫源时,可以将含硫盐作为固体或作为水溶液与镍原材料或镍金属接触。当盐作为水溶液使用时,溶液的浓度可以是约 0.01M 至约 2M,或约 0.05M 至约 1.5M,或约 0.1M 至约 1.5M,或者浓度可以是 1M。例如,  $\text{NiSO}_4$  可以作为 1M 水溶液使用。可以采用重量比约 1 : 2 至约 1 : 8 的镍原材料与 1M 硫盐溶液用于镍原材料的有效处理。例如,如本文所示,采用 1 : 5 重量比的碱式碳酸镍与 0.05 至 1M 硫酸镍溶液可以产生颗粒镍金属制备物(在干燥和还原之后),该颗粒镍金属制备物与一种或多种含磷配体有效地形成配合物。测试证实可以采用 1 : 5 重量比的镍原材料 1M 硫酸镍溶液用于数种类型的镍原材料如碱式碳酸镍、氧化镍和钝化的(涂布  $\text{NiO}$  的)镍。

[0118] 也如本文所示,可以将约 0.4%至 2%单质硫或硫化镍(以相对于全部组合物的重量%硫计)加入至碱式碳酸镍或氧化镍以形成颗粒镍金属制备物(在还原之后),该颗粒镍金属制备物与含磷配体有效地组合以形成镍-配体配合物。

[0119] 可以将含有硫的镍原材料还原以制备用于在催化剂中使用的颗粒零价镍金属。煅烧是典型地任选的,然而,如果使用硫酸镍作为镍原材料,可能所需的是硫酸镍在还原之前煅烧。

[0120] 当要与硫接触的镍是零价颗粒镍金属时,可以将硫源直接加入至溶剂中含有颗粒镍金属和一种或多种含磷配体的催化剂制备混合物。路易斯酸(例如,氯化锌)也通常存在于催化剂制备混合物中。这种路易斯酸可以促进配合物形成。与镍相比所使用的硫源的量可以变化,采用相对于镍的量约 0.1 重量%硫至约 50 重量%硫,或约 0.2 重量%硫至约 25 重量%硫,或约 0.5 重量%硫至约 15 重量%硫。如本文所示,少至 150ppm 单质硫或硫酸镍向催化剂制备混合物中的加入将镍-配体配合物形成提高约 3 至 5 倍。约 11%至 12% S<sub>8</sub>(相对于镍含量)向催化剂制备混合物中的加入将镍-配体配合物形成提高约 4- 至约 12- 倍。

[0121] 因此,镍用硫源的有效处理的方法是简单的、灵活的并且容易实施。

[0122] 制备镍原材料

[0123] 颗粒镍金属可以得自更高价态的镍原材料如含有 Ni(II) 的原材料。镍原材料的实例包括碱式碳酸镍、碳酸镍、碳酸氢镍、草酸镍、甲酸镍、方酸镍、氢氧化镍、氧化镍、镍盐或它们的组合。更高价态的镍原材料的一种经常采用的实例是镍盐如碱式碳酸镍,也称为 BNC 或 BNC 镍。BNC 可以在下面描述的方法中使用以制备本发明的 Ni 金属颗粒形式。

[0124] 碱式碳酸镍是商业可得的。例如,碱式碳酸镍可以由该材料的美国销售商 MetChem Corporation 获得。根据卖主,所提供的碱式碳酸镍通过将碱式碳酸镍从包含镍、氨、碳酸铵和水的水溶液中沉淀制备。根据卖主,碱式碳酸镍由包含镍和碱式碳酸镍的矿石制备并且还可以包含选自以下各项组成的组中的至少一种元素:铝、钙、钴、铜、铁、镁、锰、钠、硫和锌。例如,按从供应商收到的 MetChem 碱式碳酸镍的分析显示它具有表 1 中给出的组成。

[0125] 表 1:对于 MetChem 碱式碳酸镍粉末的分析结果

|        |          |          |          |           |
|--------|----------|----------|----------|-----------|
| [0126] | 镍 47 重量% |          |          |           |
|        | 钴 65 ppm | 铜 20 ppm | 铁 55 ppm | 锌 12 ppm  |
|        | 镁 60 ppm | 钙 60 ppm | 钠 60 ppm | 硫 175 ppm |

[0127] 没有硫处理,由 MetChem 获得的碱式碳酸镍典型地不形成与含磷配体以商业可接受速率(例如,在数分钟至数小时内)形成配合物的镍金属。然而,当将 MetChem 碱式碳酸镍在镍金属制备过程中或在配合物形成过程中用硫源处理时,得自 MetChem 碱式碳酸镍的镍金属与含磷配体在商业可接受的时间内(例如,在约 15 分钟至约 3 小时内)形成配合物。

[0128] 可能需要的是制备碱式碳酸镍而不是从商业源获得它。例如,通过使用所选择的反应物和制造条件下的碱式碳酸镍的制造,可以避免杂质并可以控制碱式碳酸镍的组成。

[0129] BNC 可以用以下化学式描述

[0130]  $[\text{Ni}(\text{CO}_3)_x(\text{OH})_y]_z(\text{H}_2\text{O})_n$ ,

[0131] 其中  $x=z-(y/2)$ ;  $y=2z-2x$ ;  $z=1$  至  $100$ ; 和  $n=0$  至  $400$ 。BNC 可以包含镍(II)离子、碳酸根离子、氢氧化物离子和水分子。BNC 可以使用可得的程序合成。

[0132] 所选择的 BNC 镍原材料可以具有低碳酸盐含量。例如,所选择的 BNC 镍原材料可以具有小于约 1 的  $\text{NiCO}_3 : \text{Ni}(\text{OH})_2$  的摩尔比,其中至少约 10 : 1 的 Ni : C 的质量比,或它们的任意组合。这种 BNC 可以制造具有低水平的碳杂质的 Ni(0),包括低水平的碳杂质如碳酸盐杂质。

[0133] 颗粒镍金属由具有低碳酸盐含量的 BNC 镍的制备,如小于约 1 的  $\text{NiCO}_3 : \text{Ni(OH)}_2$  的摩尔比,至少约 10 : 1 的 Ni : C 的质量比,或它们的任意组合,在煅烧过程中可以更容易地产生  $\text{CO}_2$  并且因此可以导致更复杂的至 NiO 的转化,在 NiO 中具有更少的碳杂质。通过制备具有更低碳含量的 NiO,包括更低碳酸盐含量,可以在 Ni(O) 产物中存在更少的碳杂质,或 Ni(O) 产物可以如本文所定义的更加“活性”,或同时存在这两种情况。

[0134] BNC 可以通过 (i) 将沉淀剂溶液与镍溶液在沉淀反应器中接触以形成反应混合物;和 (ii) 将镍盐从反应混合物沉淀而制备,其中镍溶液包含镍(II)离子和水,并且沉淀剂溶液选自以下各项组成的组:(a) 碳酸氢根离子和水,(b) 碳酸根离子和水,以及(c) 它们的混合物。

[0135] 进料结束时反应混合物中碳酸氢根离子与镍(II)离子的摩尔比可以在 0 : 1 至 2 : 1,包括约 0 : 1 至约 1.6 : 1,约 0 : 1 至约 1.2 : 1,约 1.0 : 0 至约 1.9 : 1,约 1.2 : 1 至约 1.9 : 1,约 0.8 : 1 至约 1.4 : 1,约 1.0 : 1 至约 1.8 : 1,约 1.0 : 1 至约 1.6 : 1,约 1.0 : 1 至约 1.4 : 1,约 0.8 : 1 至约 1.4 : 1,以及约 0.8 : 1 至约 1.2 : 1 的范围内。进料结束时反应混合物中碳酸根离子与镍离子的摩尔比可以在 0 : 1 至 1.6 : 1,包括约 0 : 1 至约 1.4 : 1,约 1.0 : 0 至约 1.2 : 1,约 0.8 : 1 至约 1.4 : 1,约 1.0 : 1 至约 1.6 : 1,约 1.0 : 1 至约 1.6 : 1,约 1.0 : 1 至约 1.4 : 1,约 0.8 : 1 至约 1.4 : 1,以及约 0.8 : 1 至约 1.2 : 1 的范围内。在沉淀剂溶液也可以使用碳酸氢盐和碳酸盐的共混物。

[0136] 用于制备前体 BNC 样品的沉淀反应器可以是任意合适的容器如槽、容器或管。BNC 的沉淀可以以分批或连续方式进行。可以将反应混合物在镍组合物的沉淀之前和/或过程中搅拌。例如,搅拌可以通过机械搅拌、泵循环回路、流通静态混合器或超声波进行。沉淀过程中高剪切的使用可以防止粒子结块并且可以给出更小的所得到的 BNC 粒子。反应器设计、搅拌设计以及高能量搅拌的使用是可以在沉淀过程中产生反应混合物的高剪切搅拌的因素的实例。

[0137] 可以将 BNC 在外加的二氧化碳的存在下从反应混合物沉淀。例如,可以将二氧化碳加入至沉淀反应器,加入至镍溶液,加入至沉淀剂溶液,加入至反应混合物,以及上述这些的任意组合。虽然本发明不受理论叙述的限制,但是加入二氧化碳可以通过间接影响中和化学计量比而改变 BNC 的硫含量。同样,可以将沉淀剂溶液在如约 30 分钟至约 60 分钟的时间内进料至沉淀反应器,并且这种加入可以以半连续或连续方式进行。也可以将沉淀剂溶液以半连续或连续方式,例如,通过使用渐进添加加入至沉淀反应器中的镍溶液。

[0138] BNC 可以在约 0°C 至约 90°C,包括约 20°C 至约 90°C,约 20°C 至约 70°C,约 20°C 至约 50°C,约 50°C 至约 90°C,约 60°C 至约 80°C,以及约 65°C 至约 75°C 的温度范围内沉淀。沉淀过程中增加的温度可以降低所得到的 BNC 中碳酸根离子的比率,这对于产生可用的氢化催化剂可以是有用的。

[0139] 沉淀过程中更高 pH 的使用可以减少所得到的 BNC 沉淀物中碳酸根离子的比率。例如,可以使用约 4、5、6、7、8 或约 9 以上的 pH 值。在一个实例中, pH 在沉淀过程中从约 4.9 增加至约 5.8。

[0140] 也可以将反应混合物在接触沉淀剂溶液之后通过将反应混合物在约 50°C 至约 90°C 加热约 0.25 小时至约 24 小时的期间煮解为镍溶液。沉淀可以在煮解之前、过程中或

之后发生,或这些过程的任意组合下发生。其他合适的温度范围包括约 60°C 至约 80°C,和 / 或约 65°C 至约 75°C。其他合适的煮解时间可以在约 2 小时至约 24 小时,包括约 4 小时至约 20 小时,约 6 小时至约 16 小时,以及约 8 小时至约 12 小时的范围内。更长的煮解时间可以导致所得到的沉淀物中更大的 BNC 粒子。

[0141] BNC 制备方法还可以包括,在沉淀步骤之后,用水洗涤沉淀的 BNC;和部分地干燥沉淀的 BNC。例如,可以将沉淀的 BNC 通过过滤或倾析从反应混合物分离,可以将所得到的沉淀的 BNC 通过过滤或倾析用水洗涤,和 / 或可以将所得到的 BNC 通过 60°C 至 100°C 之间的水蒸发干燥。干燥可以在环境压力下或在真空下,并且在惰性气体如氮的存在下进行。

[0142] 包含镍(II)离子和水的 BNC 的制备中使用的镍溶液可以通过将镍(II)盐溶解在水中制备。镍盐可以是在水中可溶的任意盐,例如  $\text{NiCl}_2$ 、 $\text{NiSO}_4$  和  $\text{Ni}(\text{NO}_3)_2$ 。备选地,可以将商业 BNC 通过如下过程纯化:首先将粗 BNC 溶解在酸谁溶液如盐酸、硫酸或硝酸中,之后使用该溶液用于如本文描述的纯化的 BNC 的再沉淀。可以将其他水不溶 Ni(II)源以类似方式转化为可溶材料并且用作适合用于本发明的镍活性颗粒形式的制备物的 BNC 的源。

[0143] 包含碳酸氢根离子的沉淀剂溶液可以通过将碳酸氢盐,例如,  $\text{NaHCO}_3$  和  $\text{NH}_4\text{HCO}_3$  溶解在水中制备。备选地,沉淀剂溶液可以通过将  $\text{CO}_2$  和碱金属氢氧化物或氨采用已知方法溶解在水中而原位制备。类似地,包含碳酸根离子的沉淀剂溶液可以通过溶解碳酸盐,例如  $\text{Na}_2\text{CO}_3$  制备。沉淀剂溶液还可以通过将  $\text{CO}_2$  和碱金属氢氧化物采用已知的方法溶解在水中而原位制备。可以选择镍盐的阴离子和碳酸氢盐或碳酸盐的阳离子以使得包含来自反应混合物的阳离子和阴离子两者的由沉淀产生的盐,(例如  $\text{NaCl}$ ) 在反应混合物的水中可溶。这种选择提供用于从沉淀的 BNC 分离阴离子和阳离子的方法。

[0144] 如前所述,碳酸氢根或碳酸根离子相对于所加入的用于制备 BNC 的镍(II)离子的量可以影响所得到的零价镍粒子与含磷配体,例如,配体(V)的镍反应性。因为镍的高成本,BNC 型镍组合物的制造者将被引导加入过量的沉淀剂溶液以便经济上可行地回收尽可能多的镍。然而,令人惊讶地发现过量沉淀剂的使用产生对于磷-配体配合物反应低反应性的镍金属。当使用减少量的沉淀剂时产生高反应性镍,其中允许大概更多的镍(II)离子保持溶解在所得到的反应混合物的水中并且可以不沉淀。

[0145] 还发现的是使用碳酸氢根离子制备的沉淀的镍组合物比使用碳酸根离子制备的沉淀的镍组合物过滤快得多并且令人惊讶地洗涤快得多。此外,使用碳酸氢根离子制备的过滤的沉淀的镍组合物干燥为具有小收缩的软粉。因为这些原因,使用碳酸氢根离子制备含镍固体进一步提供用于下游处理和干燥沉淀的镍 BNC 组合物的操作所需的性质。

[0146] 含镍材料的还原

[0147] 镍金属的产生可以包括特定镍原材料的直接还原或镍金属制备物的还原。然而,镍还原的程度典型地是不关键的。合适的镍金属制备包括完全还原或部分地还原的那些。还原的程度可以由本领域技术人员使用本文描述的或本领域可利用的程序容易地测定和选择。

[0148] 可以将各种镍原材料还原如 BNC、方酸镍、草酸镍、硫酸镍、氧化镍、草酸镍,以及部分地氧化的镍金属,或镍金属。通常,可以将这种镍原材料和 / 或镍金属用还原剂(例如,氢、甲烷、CO) 在升高的温度还原。

[0149] 可以将镍原材料在还原之前煅烧,也可以将它们用氢或另一种还原剂在升高的温

度直接还原。煅烧可以移除吸附的气体如二氧化碳、二氧化硫等。

[0150] 如本文描述的,可以将硫源在还原过程中与镍金属或镍原材料混合。

[0151] 还原可以在方便的还原或反应器容器中,如流化床反应器、膨胀的固定床、旋转炉、旋转盘或本领域技术人员已知的任意这种设备进行。为促进镍金属和 / 或镍原材料对还原剂的最佳暴露,可以采用流化床还原容器。

[0152] 例如,可以采用流化床反应器以将镍原材料和 / 或镍金属煅烧和还原至零价镍金属粉末。可以将镍原材料和 / 或镍金属装入至流化床反应器并且可以将反应器关闭。之后可以开始还原 ( 和 / 或煅烧 ) 程序。对于还原过程,可以在引入还原剂之前将反应器用惰性气体吹扫以从反应器移除氧。

[0153] 在还原过程中,水蒸气也可以是还原剂的混合物的组分。当比如在还原过程中使用水蒸气时,如此产生的镍金属粉末可以是自由流动的,其促进从反应容器的产物移除并且进一步促进镍金属的处理。水蒸气在用于制备反应性镍金属产物的大部分条件下不是必须的,但它防止还原的镍产物的聚集和结块。

[0154] 对于向零价镍金属的还原,流动通过镍原材料或镍金属的床的气体含有还原剂,优选在惰性载气中。还原剂可以是可以将镍离子还原为镍金属的任意气体或颗粒物质。可以将镍离子还原为镍金属的还原剂的实例包括,例如,氢、甲烷和一氧化碳。所需的还原剂是氢。例如,流化气体可以含有足以将流化的含镍材料中镍的至少一部分还原为镍金属的量的氢。该过程中的气体流动速率可以由用于还原的设备类型决定,并且其选择在本领域技术人员的知识范围内。

[0155] 惰性载气基本上不含氧。可以采用的惰性载气的实例包括氮、氩和氦。氮是便宜并且方便的惰性载气源。

[0156] 用于还原的气体或气体的混合物还可以含有水蒸气,这可以促进自由流动的镍金属产物的产生。在用于制备反应性镍金属产物的大部分条件下水蒸气不是必需的,但是它确实防止还原的镍产物的聚集和结块,从而促进从还原容器的产物移除和镍金属的进一步处理。还原气体中水蒸气的百分比可以为约 0.1% 至 80 体积%,或约 0.1% 至 70 体积%,或约 0.1% 至 50 体积%,或约 0.1% 至 30 体积%。流化气体可以含有约 0.1% 至 20% 体积百分比的水蒸气,或约 1% 至约 20% 体积百分比的水蒸气。处于蒸汽形式的水蒸气的存在制备自由流动的镍粉末中是有效的。

[0157] 足以将镍原材料和 / 或镍金属还原为零价镍金属的条件包括升高的温度以及足以基本上还原含镍固体以形成包含镍金属的第三含镍固体的还原剂 ( 例如,氢气体 ) 的量和时间这两者。

[0158] 还原步骤在 200℃ 至 500℃,例如,200℃ 至 450℃,或 225℃ 至 425℃,或 250℃ 至 400℃ 的温度有益地进行。这些范围 ( 例如,200℃ 以下 ) 的下限的温度需要更长的还原时间。在高温 ( 例如,500℃ 以上 ) 还原可以给出具有与含磷配体的配合物形成减少的镍金属粉末。

[0159] 用于还原的时间可以稍微随温度变化、其中还原在更高的温度进行得稍微更快。通常,进行还原约 30 分钟至 8 小时,优选约 1 至 6 小时,更优选约 2 至 5 小时并且最优选约 4 小时。

[0160] 所观察到的是,对于约 300℃ 至 475℃ 或约 250℃ 至 400℃ 的温度,还原步骤在约四

个小时内基本上完成,条件是至少一个当量的氢与氧化镍反应。可能所需的是加入过量的氢(例如,大于一当量),以确保完成还原。可以采用的温度的范围因此受还原的时间和所提供的氢的量影响。可接受的温度范围包括表示落入 200℃至 500℃之间的温度范围的整数的任意数值范围。然而,优选的温度是约 250℃至 400℃,或约 250℃和 350℃,持续约四个小时。

[0161] 当使用氢作为还原剂时,氢向流化反应容器的引入可以导致含镍固体的床中的温度立刻升高,例如,依赖于氢的浓度升高约 10–50℃。本领域技术人员明白这种升高可以发生并且可以按需要调节还原条件。

[0162] 通常,使足够的还原剂(例如,氢)通过反应器以将含镍固体转化为镍金属粉末。还原气体中有效的水蒸气浓度可以为约 1%至约 80 体积%。例如,有效的氢浓度可以为约 10%至约 95 体积%。载气可以以约 20%至约 85 体积%的浓度存在。有效用于还原的气体组合物的实例包含以体积百分比(体积测量)计约 10–20%水蒸气,约 10–20%氢,以及作为余量的氮。

[0163] 还原步骤过程中的反应器压力不是关键的。因此,还原可以在约 0.1 个大气压至 20 个大气压,或在约 0.5 个大气压至 10 个大气压,或在约 0.5 个大气压至 2 个大气压压力进行。还原可以方便地在约一个大气压的压力进行。

[0164] 在还原步骤的结束时,将反应器用氮,或另一种惰性气体填充,以有效移除残留的氢。惰性气体被选择为与镍金属粉末无反应性。氧在该阶段与镍金属接触可以至少将镍粒子的表面氧化为氧化镍,从而潜在地降低催化剂形成步骤中的反应性。

[0165] 在还原之前,可以将含有含镍固体(例如,镍原材料和/或镍金属)的流化床反应器用基本上不含氧的惰性气体吹扫,以从该装置中以及从该含镍固体中移除分子氧。可以之后将还原剂或还原实际(例如,氢气体)引入至流化气体中使得还原剂和惰性载气的混合物用于流化并基本上支撑固体。还原过程中的气体流动速率不是关键的并且可以被调节以支撑镍金属或镍原材料和/或由用于还原的设备类型决定。

[0166] 在反应完成之后,床温度可以降低约 10℃。在升高的床温观察的时间期间可以对应于加入化学计量量的将镍原材料和/或镍金属还原成零价镍金属的氢所需的时间。可以将反应器中的零价镍金属粉末在非-含氧气氛中冷却并且其可以展现铁磁性。所产生的镍金属的量及其纯度可以通过使用本领域技术人员已知的方法的金属分析测定。类似地,本文描述的方法中使用的任意含镍组合物中镍的量可以通过使用本领域技术人员已知的方法的金属分析测定。

[0167] 镍金属粉末制备物的合适性可以通过在溶剂或液体底物(例如,3-戊烯腈(3PN))中制备零价镍-配体配合物评定。在将混合物升温所选时间之后,测量溶液中已溶解的镍-配体配合物的水平,例如,通过液体色谱测量。如果需要评价,则可以将未反应的镍金属通过过滤或离心从环境移除。镍与含磷配体的配合并且保持在溶剂如 3PN(其也为氢氰化底物)的溶液中,因为它形成合适的零价镍-配体配合物。

[0168] 合适的镍金属粉末制备物可以与单齿或二齿含磷配体在腈溶剂中反应以有效地制备镍配合物,该镍配合物可以作为用于共轭二烯烃至单腈的氢氰,以及不饱和腈至二腈的氢氰化的均相催化剂使用。

[0169] 煅烧

[0170] 还原步骤可以直接对镍原材料进行。备选地,可以对镍原材料进行煅烧步骤并且之后可以进行还原步骤。

[0171] 在还原步骤之前,可以对镍原材料如碱式碳酸镍、碳酸镍、碳酸氢镍、草酸镍、甲酸镍、方酸镍、氢氧化镍、氧化镍、硫酸镍、镍盐或它们的组合进行煅烧步骤。煅烧可以从镍原材料移除挥发物和气体物质。例如,煅烧通过碳酸镍(或碳酸氢镍)的热分解将 BNC 至少部分地转化为氧化镍,同时放出二氧化碳( $\text{CO}_2$ )气体和水。煅烧还可以从硫酸镍移除二氧化硫和/或三氧化硫以产生氧化镍。

[0172] 煅烧可以在方便的容器中,如流化床反应器、膨胀的固定床、旋转炉、旋转盘或本领域技术人员已知的任何这种设备上进行。为促进镍原材料均匀暴露于热并最优地移除可能吸附至镍原材料上的挥发物和气体物质,可以采用流化床还原容器。

[0173] 通常,煅烧可以在与镍组合物无反应性的任意气体气氛中,例如,在不形成不适宜的镍化合物的气体中进行。用于煅烧步骤的合适的便利的气体包括空气和氮;其他可以包括氩和氦。在煅烧步骤过程中可以存在水蒸气(水的蒸气)。

[0174] 一般地,煅烧可以在足以煅烧镍原材料的时间和热条件下进行。

[0175] 为进行煅烧,可以将镍原材料放置在闭合的反应器中,可以采用流动气体如空气、氮、氩或它们的混合物来支撑一种或多种镍原材料。空气是适合用于煅烧步骤的廉价且便利的气体。

[0176] 温度可以升高至所需的煅烧温度,例如,约  $200^\circ\text{C}$  至  $600^\circ\text{C}$ 。在煅烧温度  $300^\circ\text{C}$ – $450^\circ\text{C}$ ,或更高的温度,可以使具有或不具有水蒸气的空气在约 1 至 2 小时的时间内通过反应器,同时将挥发物和气体物质从镍原材料移除。例如,当使用 BNC 作为镍原材料并且将 BNC 煅烧时,可以移除二氧化碳并且可以将 BNC 转化为氧化镍。类似地,硫酸镍的煅烧可以释放二氧化硫或三氧化硫以产生氧化镍。

[0177] 煅烧步骤可以在约  $200^\circ\text{C}$  至  $600^\circ\text{C}$  的温度进行。低于  $200^\circ\text{C}$ ,煅烧过程可以是慢的或不完全的,并且因此未反应的镍前体可以保留在产物中。高于  $600^\circ\text{C}$ ,可以出现氧化镍过度塌陷,必然降低镍粉末产物的反应性。用于煅烧步骤的时间可以在  $600^\circ\text{C}$  几十秒至  $200^\circ\text{C}$  数小时的范围内。合适的煅烧温度可以包括,例如,约  $300^\circ\text{C}$  至约  $475^\circ\text{C}$  的温度。在约  $300^\circ\text{C}$  至约  $475^\circ\text{C}$  或约  $325^\circ\text{C}$  至  $450^\circ\text{C}$  的温度,煅烧在合理的时间段,如约 1.25 至 2 小时中基本上完成。

[0178] 在煅烧之后,可以将镍原材料(例如,氧化镍)还原。例如,可以将反应器用氮气吹扫足够的时间以基本上移除所有氧(例如,98%至 99.9%的氧)并且可以将煅烧镍原材料如本文所描述地还原。

[0179] 颗粒镍制备物

[0180] 本文描述新型镍金属制备物,其与配体高度反应性而形成零价镍-磷配体配合物。这种配合物被用作催化剂,例如,作为氢氰化催化剂。本发明的镍金属颗粒形式与有机液体,如用于氢氰化反应的有机腈液体或烯烃前体中的二齿亚磷酸酯配体是高度反应性的。当将镍-配体催化剂混合物与 HCN 接触时,以良好的产率产生烯烃的氢氰化产物。

[0181] 本发明的镍颗粒形式具体表达了下面和附图中描述的一种或多种特征。本发明提供用于具有二齿含磷配体的零价镍配合物的形成的镍颗粒形式,其中镍颗粒形式具有如通过由镍粒子吸附的气体分子的量测量的大表面积(例如,经由 BET 比表面积测量)并且镍

颗粒形式具有大量的小微晶。

[0182] 例如,镍颗粒形式可以具有至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积;更优选,至少约  $2\text{m}^2/\text{gm}$  的 BET 比表面积;再更优选,至少约  $4\text{m}^2/\text{gm}$  的 BET 比表面积;再更优选,至少约  $10\text{m}^2/\text{gm}$  的 BET 比表面积。

[0183] 所需的镍颗粒形式可以具有物理特性的组合。例如,优选的镍颗粒形式可以具有以下性质中的两种以上的组合:至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积;如通过程序化升温的 X 射线衍射 (TP-XRD) 测定的不大于约  $100\text{nm}$  的平均尺寸的镍微晶;在  $300\text{--}400^\circ\text{C}$  还原之后小于约  $20\text{nm}$  的 C10 值;每克镍至少约  $10^{16}$  个尺寸为 C10 以下的表面微晶;如对于立方微晶计算的至少每克约  $2 \times 10^{15}$  个表面微晶;大于 1.0 的镍微晶尺寸分布范围。

[0184] 通常,具有这些性质中的两个以上的镍颗粒形式可以与含磷配体有效地形成配合物。更优选,具有这些性质中的三个以上的镍颗粒形式与含磷配体有效地形成配合物。

[0185] 镍颗粒形式的 BET 比表面积可以是对于镍颗粒形式的相关的物理性质。通常,具有更高的 BET 比表面积的镍颗粒形式展现提高的与含磷配体的配合物形成。因此,当与其他所需的特征组合时,镍颗粒形式可以具有至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积。然而,镍颗粒形式优选具有大于  $2\text{m}^2/\text{gm}$  的 BET 比表面积,更优选镍颗粒形式可以具有大于  $4\text{m}^2/\text{gm}$  的 BET 比表面积,再更优选镍颗粒形式可以具有大于约  $10\text{m}^2/\text{gm}$  的 BET 比表面积。所需的镍颗粒形式可以具有  $100\text{m}^2/\text{gm}$  以上的 BET 比表面积。例如,镍颗粒形式可以具有大于  $11\text{m}^2/\text{gm}$ ,或大于  $12\text{m}^2/\text{gm}$ ,或大于  $13\text{m}^2/\text{gm}$ ,或大于  $14\text{m}^2/\text{gm}$ ,或大于  $15\text{m}^2/\text{gm}$ ,或大于  $16\text{m}^2/\text{gm}$ ,或大于  $17\text{m}^2/\text{gm}$ ,或大于  $18\text{m}^2/\text{gm}$ ,或大于  $20\text{m}^2/\text{gm}$  的 BET 比表面积。例如,镍颗粒形式可以具有约  $1\text{m}^2/\text{gm}$  至约  $100\text{m}^2/\text{gm}$ ,或  $1\text{--}100\text{m}^2/\text{gm}$  之间或  $10\text{--}50\text{m}^2/\text{gm}$  之间的任意数值的 BET 比表面积。

[0186] 虽然不希望束缚于理论,但是来自具有,例如,如通过 BET 比表面积测量的大表面的镍颗粒形式的镍原子可以更容易地从颗粒镍释放并与含磷配体结合。备选地,含磷配体可以对具有更高的 BET 比表面积的镍颗粒形式的更大表面积具有更大的可接近性。

[0187] BET 表面积或气体吸收,可以使用测量技术测量样品中存在的粒子的表面积和多孔性。被吸附气体的分子在真空室内的受控的条件下被物理吸附至粒子表面上,包括任何孔或微晶的表面。例如,BET 比表面积 (BETSSA) 可以在将样品在真空下于  $105^\circ\text{C}$  脱气过夜之后通过使用 Tristar3000 氮吸附仪观测氮吸附而测量。可以使用  $0.05\text{--}0.3P/P_0$  的分压范围进行多点 BET 测量。吸附等高线可以通过作为引入至室中的气体体积的函数测量样品上方气体的压力获得。之后可以使用吸附等高线的线性区域,使用 BET 理论确定形成跨越可得的粒子表面积的单层所需的气体的体积,如通过以下公式描述的:

$$[0188] \quad \frac{1}{v[(P/P_0)-1]} = \frac{c-1}{v_m} \left( \frac{P}{P_0} \right) + \frac{1}{v_m c}$$

[0189] 其中  $v$  是气体的体积, $P$  是压力, $P_0$  是饱和压力, $v_m$  是形成单层所需的气体的体积,而  $c$  是 BET 常数。关于压力作图,  $\phi (=P/P_0)$ , 并且体积允许由线的梯度和截距测定单层的体积。

[0190] 镍颗粒形式的表面积还可以通过激光衍射比表面积技术测量。镍颗粒形式可以具有至少约  $0.4\text{m}^2/\text{gm}$  的激光衍射比表面积。同样,至少 10% 的镍粒子 (D10) 可以具有不大于约  $4\mu\text{m}$  的直径。

[0191] 激光衍射比表面积 (LD SSA) 和粒径分布 (PSD) 可以用 Mastersizer2000 粒径分析仪 (例如, 来自 Malvern Instruments Ltd, 使用 Hydro2000MU 附件和水作为分散剂) 测量。具有以微米测量的特定波长的光由更小尺寸的粒子衍射。衍射的角度将依赖于所存在的尺寸的范围。可以使用以下公式报告比表面积 (SSA) :

$$[0192] \quad SSA = \frac{6 \sum \frac{V_i}{d_i}}{\rho \sum V_i} = \frac{6}{\rho D[3,2]}$$

[0193] 其中  $V_i$  是具有  $d_i$  的平均等级直径的等级  $i$  中的相对体积,  $\rho$  是材料的密度, 并且  $D[3,2]$  是表面积重均直径。该计算可以在激光衍射系统软件中自动进行。LD SSA 提供快速估计粒子表面积的方式。在进行该计算中, 通常假设的是粒子基本上是球体, 实心球体。

[0194] 由微晶构成的镍粒子的表面特征可以使得 BET 比表面积与激光衍射比表面积的比率为 15 至 25。

[0195] 镍颗粒形式可以平均每克具有每克镍至少约  $10^{15}$  个表面微晶, 优选每克镍至少约  $5 \times 10^{15}$  个表面微晶, 更优选每克镍至少约  $10^{16}$  个表面微晶, 再更优选每克镍至少约  $5 \times 10^{16}$  个表面微晶, 并且更优选每克镍至少约  $10^{17}$  个表面微晶。通过“表面微晶”意指镍粒子上或内的镍微晶, 其中微晶的至少一侧或边暴露于环境。虽然不希望束缚于理论, 但是本文的发明人相信具有至少约  $10^{15}$  至  $10^{17}$  个表面微晶存在的镍颗粒形式的合适性与众多微晶边缘的粒子表面的展现相关, 其据信比平面微晶面更加具有反应性。微晶边缘更大的反应性可以在溶液中的配体接近固体镍颗粒形式的表面的相互作用上与空间因素、电子因素, 或两者相关。

[0196] 所需的镍颗粒形式可以具有如通过程序化升温的 X 射线衍射 (TP-XRD) 测定的不大于约 70nm (例如, 代替 100nm) 的平均尺寸的镍微晶; 或优选镍微晶具有不大于约 50nm (代替 100nm 或 70nm) 的平均微晶尺寸; 或更优选镍微晶具有不大于约 30nm (代替 100nm、70nm 或 50nm) 的平均微晶尺寸。通常, 具有更小的镍微晶的镍颗粒形式, 尤其是当与其他所需的物理性质组合时, 是优选的。

[0197] 本发明的镍形式的高度反应性据认为, 至少部分地, 由形成粒子的镍金属微晶的性质所引起的。本发明的镍粒子可以由微晶, 即在更大的、无序的粒子内的局部晶体有序的区域组成, 其中平均微晶尺寸 (直径) 可以为不大于约 20-25nm。更优选的镍颗粒形式可以包括具有 0.1 至 10nm 的范围内的直径的镍微晶尺寸。

[0198] 镍颗粒形式可以具有甚至更多所需的物理性质的组合。例如, 所需的镍颗粒形式可以具有平均每克镍具有至少约  $5 \times 10^{16}$  个尺寸 C10 以下的表面微晶 (例如, 代替  $10^{16}$  个表面微晶)。更优选, 所需的镍颗粒形式可以具有平均每克镍具有至少约  $10^{17}$  个尺寸 C10 以下的表面微晶 (例如, 代替  $10^{16}$  或  $5 \times 10^{16}$  个表面微晶)。

[0199] 此外, 镍微晶尺寸分布范围可以大于 1.5。微晶尺寸典型地作为微晶例如沿主要维度的直径测量。

[0200] 镍颗粒形式可以具有的其他物理性质包括其中至少 10% 的粒子具有不大于约  $6 \mu\text{m}$  或优选不大于约  $4 \mu\text{m}$  的直径 (D10) 的那些。由微晶构成的镍粒子的表面特性可以使得镍粒子的 BET 比表面积与 D10 的比率为约  $0.3 \times 10^6 \text{m}^2/\text{gm}$  至约  $10.0 \times 10^6 \text{m}^2/\text{gm}$ , 或约  $0.5 \times 10^6 \text{m}^2/\text{gm}$ 。

gm 至约  $5 \times 10^6$  m/gm。

[0201] 镍颗粒形式是零价,即,金属镍。

[0202] 镍颗粒形式可以是基本上干燥的,例如,粉末或颗粒形式。镍颗粒形式可以悬浮、溶解或部分地溶解在溶剂中。溶剂典型地是非水溶剂。溶剂可以是有机溶剂。例如,用于镍颗粒形式的溶剂可以是具有一个或多个双键的支链或非支链的 C2-C20 烃。用于镍颗粒形式的溶剂可以是有机腈液体如被至少一个腈 (CN) 基团取代的支链或非支链的 C2-C20 烷基或亚烷基。溶剂的实例包括戊烯腈如 2- 戊烯腈、3- 戊烯腈、4- 戊烯腈、2- 甲基 -3- 丁烯腈和 2- 甲基 -2- 丁烯腈。

[0203] 镍颗粒形式可以是干燥形式或悬浮或溶解在溶剂中的基本上纯的镍。例如,可以将镍颗粒形式分离,但没有,或基本上没有,伴随的离子(例如,没有阴离子)或金属(例如,没有铝、铜、钨、锌和/或铁)。镍颗粒形式可以没有杂质如含碳、含硅和/或含氮部分和/或化合物。镍颗粒形式可以基本上没有杂质如钠、钙、镁、钾和/或其他碱金属和/或碱土金属。例如,镍颗粒形式可以具有小于 10% 杂质,或小于 7% 杂质,或小于 5% 杂质,或小于 4% 杂质,或小于 3% 杂质,或小于 2% 杂质,或小于 1% 杂质,或小于 0.7% 杂质,或小于 0.6% 杂质,或小于 0.5% 杂质,或小于 0.4% 杂质,或小于 0.3% 杂质,或小于 0.2% 杂质,或小于 0.1% 杂质,或小于 0.07% 杂质,或小于 0.05% 杂质,或小于 0.03% 杂质,或小于 0.01% 杂质。除了它们的硫含量之外,镍颗粒形式可以是 95% 至 99.9% 纯度,或 98% 至 99.99% 纯度。

[0204] 这种镍颗粒形式可以与含磷配体,例如,本文描述的那些中的任一种组合。

[0205] 含磷配体

[0206] 在本文作为术语使用的“含磷配体”是指含有至少一个磷原子的配体,其适合用于与过渡金属如镍形成配合物,其中配合物可以拥有用于有机反应如烯烃的氢氰化反应,如丁二烯的氢氰化以产生戊烯腈,或戊烯腈的氢氰化以产生己二腈的催化活性。

[0207] 本文提供的氢氰化催化剂由镍和至少一种含磷(含 P)配体组成。含 P 配体可以,例如,是亚磷酸酯、亚膦酸酯、次磷酸酯、膦,以及混合的含 P 配体或这些成员的组合。含 P 配体可以是单齿的或多齿的,例如,二齿或三齿。

[0208] 含 P 配体可以化学键连至金属,例如,镍,作为包含金属和一种或多种含 P 配体的配合物。

[0209] 术语“单齿”是本领域中已知的并且意指配体(其可以每个分子含有一个或多个磷原子)的仅一个磷原子可以连接至单个金属(例如,镍)原子。两个单齿配体可以分别连接至金属原子,或者一个单齿配体和一个多齿配体可以各自连接至金属原子。

[0210] 术语“二齿”是本领域中已知的并且意指配体(其可以每分子含有两个以上磷原子)的两个磷原子可以连接至单个金属(例如,镍)原子。二齿含 P 配体可以,例如,选自由以下各项组成的组:二齿亚磷酸酯、二齿亚膦酸酯、二齿次磷酸酯、二齿膦或混合二齿配体。

[0211] 混合二齿配体可以,例如,选自由以下各项组成的组:亚磷酸酯-亚膦酸酯、亚膦酸酯-次磷酸酯、亚磷酸酯-膦、亚膦酸酯-次磷酸酯、亚膦酸酯-膦和次磷酸酯-膦。

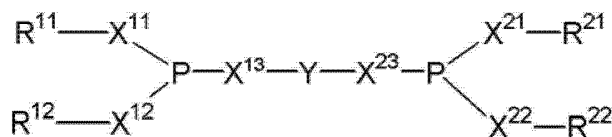
[0212] 术语“三齿”意指配体(其可以每分子含有三个以上磷原子)的三个磷原子可以连接至单个金属(例如,镍)原子。也可以将术语“二齿”和“三齿”称为螯合配体。

[0213] 亚含磷配体可以是单齿亚磷酸酯、单齿亚膦酸酯、单齿次磷酸酯、单齿膦、二齿亚

磷酸酯、二齿亚磷酸酯、二齿次磷酸酯或二齿膦,以及这些成员的任意组合。此外,含磷配体可以是单齿亚磷酸酯以形成单齿亚磷酸酯的镍配合物,之后可以将单齿亚磷酸酯的镍配合物与二齿含磷配体组合。类似的,含磷配体可以是还包含单齿亚磷酸酯的二齿亚磷酸酯。例如,合适的含磷配体包括一种或多种选自以下成员的混合物:单齿亚磷酸酯配体、二齿亚磷酸酯配体以及单齿和二齿亚磷酸酯配体的混合物。

[0214] 用于催化剂的合适的含磷配体包括选自由以下各项组成的组中的那些:式(III)、式(IV)、式(IVa)的化合物或它们的组合。式(III)具有如下结构:

[0215]



式(III)

[0216] 其中,

[0217]  $\text{X}^{11}$ 、 $\text{X}^{12}$ 、 $\text{X}^{13}$ 、 $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  独立地表示氧或单(直接)键;

[0218]  $\text{R}^{11}$  和  $\text{R}^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团;

[0219]  $\text{R}^{21}$  和  $\text{R}^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团;

[0220] 并且

[0221] Y 表示桥连基。

[0222] 例如,  $\text{X}^{11}$ 、 $\text{X}^{12}$ 、 $\text{X}^{13}$ 、 $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  可以各自为氧。在这种情况下,桥连基 Y 键连至亚磷酸酯基团。备选地,  $\text{X}^{11}$  和  $\text{X}^{12}$  可以各自为氧并且  $\text{X}^{13}$  为单键,或者  $\text{X}^{11}$  和  $\text{X}^{13}$  可以各自为氧并且  $\text{X}^{12}$  是单键,以使得被  $\text{X}^{11}$ 、 $\text{X}^{12}$  和  $\text{X}^{13}$  环绕的磷原子是亚磷酸酯的中心原子。在这种情况下,  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  可以各自为氧,或者  $\text{X}^{21}$  和  $\text{X}^{22}$  可以各自为氧并且  $\text{X}^{23}$  是单键,或者  $\text{X}^{21}$  和  $\text{X}^{23}$  可以各自为氧并且  $\text{X}^{22}$  是单键,或者  $\text{X}^{23}$  可以是氧并且  $\text{X}^{21}$  和  $\text{X}^{22}$  各自是单键,或者  $\text{X}^{21}$  可以是氧并且  $\text{X}^{22}$  和  $\text{X}^{23}$  各自是单键,或者  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  可以各自为单键,以使得由  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  环绕的磷原子可以是亚磷酸酯、亚膦酸酯、次磷酸酯或膦,优选亚膦酸酯的中心原子。优选地  $\text{X}^{13}$  可以是氧并且  $\text{X}^{11}$  和  $\text{X}^{12}$  各自可以是单键,或者  $\text{X}^{11}$  可以是氧并且  $\text{X}^{12}$  和  $\text{X}^{13}$  各自可以是单键,以使得由  $\text{X}^{11}$ 、 $\text{X}^{12}$  和  $\text{X}^{13}$  环绕的磷原子是亚膦酸酯的中心原子。在这种情况下,  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  可以各自为氧,或者  $\text{X}^{23}$  可以是氧并且  $\text{X}^{21}$  和  $\text{X}^{22}$  各自是单键,或者  $\text{X}^{21}$  可以是氧并且  $\text{X}^{22}$  和  $\text{X}^{23}$  各自是单键,或者  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  可以各自为单键,以使得由  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  环绕的磷原子可以是亚磷酸酯、次磷酸酯或膦,优选次磷酸酯的中心原子。在一些情况下,  $\text{X}^{11}$ 、 $\text{X}^{12}$  和  $\text{X}^{13}$  可以各自为单键,以使得由  $\text{X}^{11}$ 、 $\text{X}^{12}$  和  $\text{X}^{13}$  环绕的磷原子是膦的中心原子。在这种情况下,  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  可以各自为氧,或者  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  可以各自为单键,以使得由  $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  环绕的磷原子可以是亚磷酸酯或膦,优选膦的中心原子。桥连基 Y 特别是,例如被  $\text{C}_1$ - $\text{C}_4$ -烷基、卤素、如氟、氯、溴、卤化的烷基如三氟甲基、亚芳基如亚苯基取代的亚芳基,或者这种亚芳基是未取代的。亚芳基可以是在芳族体系中具有 6 至 20 个碳原子的基团,尤其是焦儿茶酚、双(苯酚)或双(萘酚)。  $\text{R}^{11}$  和  $\text{R}^{12}$  基团可以各自独立地是相同的或不同的有机基团。有益的  $\text{R}^{11}$  和  $\text{R}^{12}$  基团可以是芳基,优选具有 6 至 10 个碳原子的那些,其可以是未取代的或单-或多取代的,尤其是被  $\text{C}_1$ - $\text{C}_4$ -烷基、卤素如氟、氯、溴,卤代烷基如三氟甲基,芳基如苯基,或未取代

的芳基取代。 $R^{21}$  和  $R^{22}$  基团可以各自独立地是相同的或不同的有机基团。有益的  $R^{21}$  和  $R^{22}$  基团可以是芳基,尤其是具有 6 至 10 个碳原子的那些,其可以是未取代的或单-或多取代的,尤其是被  $C_1$ - $C_4$ -烷基、卤素如氟、氯、溴、卤代烷基如三氟甲基、芳基如苯基或未取代的芳基取代。 $R^{11}$  和  $R^{12}$  基团可以各自为分离的或桥连的。 $R^{21}$  和  $R^{22}$  基团也可以各自为分离的或桥连的。 $R^{11}$ 、 $R^{12}$ 、 $R^{21}$  和  $R^{22}$  基团可以以所描述的方式各自为分离的,两个可以是桥连的并且两个分离的,或全部四个可以是桥连的。

[0223] 式 (IV) 具有如下结构,

[0224]  $P(X^1R^1)(X^2R^2)(X^3R^3)$

[0225] 式 (IV)

[0226] 其中,

[0227]  $X^1$ 、 $X^2$  和  $X^3$  独立地表示氧或单个直接键;并且

[0228]  $R^1$ 、 $R^2$  和  $R^3$  各自独立地为相同的或不同的有机基团。

[0229] 例如, $R^1$ 、 $R^2$  和  $R^3$  可以各自独立地为优选具有 1 至 10 个碳原子的烷基,如甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基、叔丁基,或芳基如苯基、邻-甲苯基、间-甲苯基、对-甲苯基、1-萘基、2-萘基,或优选具有 1 至 20 个碳原子的烃基,如 1,1'-联苯酚、1,1'-联萘酚。 $R^1$ 、 $R^2$  和  $R^3$  基团可以直接键合在一起,即不仅经由中心磷原子连接。可以优选的是  $R^1$ 、 $R^2$  和  $R^3$  基团不直接键合在一起。 $R^1$ 、 $R^2$  和  $R^3$  基团也可以是选自由以下各项组成的组中的基团:苯基、邻-甲苯基、间-甲苯基和对-甲苯基。尤其是, $R^1$ 、 $R^2$  和  $R^3$  基团中的最多两个应当是苯基。 $R^1$ 、 $R^2$  和  $R^3$  基团中的最多两个可以是邻-甲苯基。可以使用的特定的化合物是下面的式 (IVa) 的化合物:

[0230]  $(\text{邻-甲苯基}-O-)_w(\text{间-甲苯基}-O-)_x(\text{对-甲苯基}-O-)_y(\text{苯基}-O-)_zP$

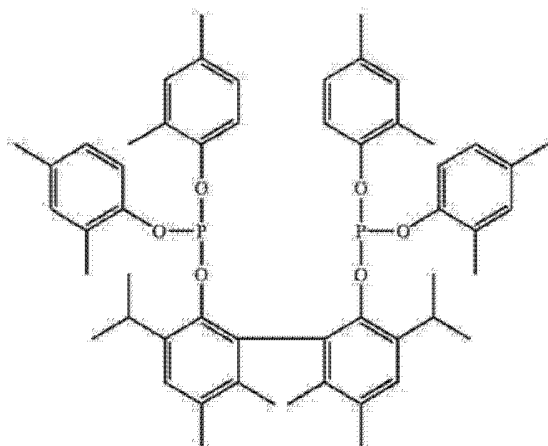
[0231] 式 (IVa)

[0232] 其中  $w$ 、 $x$ 、 $y$ 、 $z$  各自是自然数并且满足以下条件: $w+x+y+z=3$  并且  $z$  小于或等于 2。

[0233] 式 (IVa) 的化合物的实例是  $(\text{邻-甲苯基}-O-)_3P$ 、 $(\text{对-甲苯基}-O-)(\text{苯基}-O-)_2P$ 、 $(\text{间-甲苯基}-O-)(\text{苯基}-O-)_2P$ 、 $(\text{邻-甲苯基}-O-)(\text{苯基}-O-)_2P$ 、 $(\text{对-甲苯基}-O-)_2(\text{苯基}-O-)P$ 、 $(\text{间-甲苯基}-O-)_2(\text{苯基}-O-)P$ 、 $(\text{邻-甲苯基}-O-)_2(\text{苯基}-O-)P$ 、 $(\text{间-甲苯基}-O-)(\text{对-甲苯基}-O-)(\text{苯基}-O-)P$ 、 $(\text{邻-甲苯基}-O-)(\text{对-甲苯基}-O-)(\text{苯基}-O-)P$ 、 $(\text{邻-甲苯基}-O-)(\text{间-甲苯基}-O-)(\text{苯基}-O-)P$ 、 $(\text{对-甲苯基}-O-)_3P$ 、 $(\text{间-甲苯基}-O-)(\text{对-甲苯基}-O-)_2P$ 、 $(\text{邻-甲苯基}-O-)(\text{对-甲苯基}-O-)_2P$ 、 $(\text{间-甲苯基}-O-)_2(\text{对-甲苯基}-O-)P$ 、 $(\text{邻-甲苯基}-O-)_2(\text{对-甲苯基}-O-)P$ 、 $(\text{邻-甲苯基}-O-)(\text{间-甲苯基}-O-)(\text{对-甲苯基}-O-)P$ 、 $(\text{间-甲苯基}-O-)_3P$ 、 $(\text{邻-甲苯基}-O-)(\text{间-甲苯基}-O-)_2P$ 、 $(\text{邻-甲苯基}-O-)_2(\text{间-甲苯基}-O-)P$  或这些化合物的混合物。

[0234] 可用的二齿亚磷酸酯配体的实例是如下所示的配体 (V)

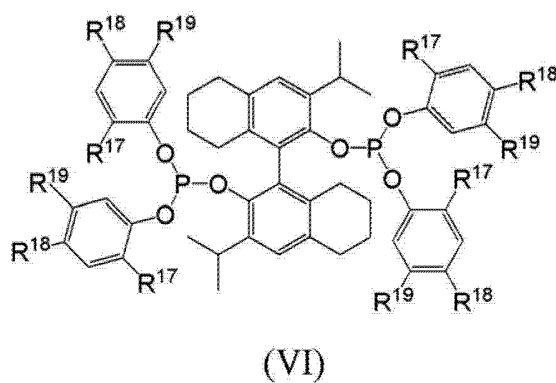
[0235]



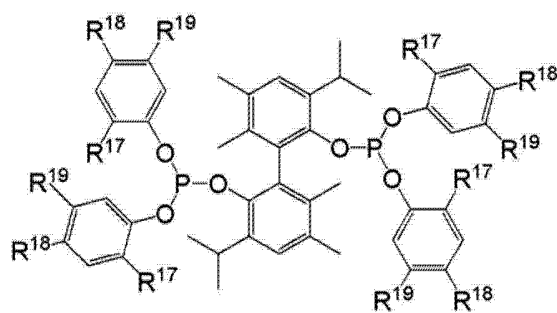
配体(V)。

[0236] 在本发明的方法中可用的二齿亚磷酸酯配体的另外的实例包括具有如下所示的式 (VI) 至 (IX) 的那些, 其中对于每个式,  $R^{17}$  是选自由甲基、乙基或异丙基组成的组, 并且  $R^{18}$  和  $R^{19}$  独立地选自 H 或甲基:

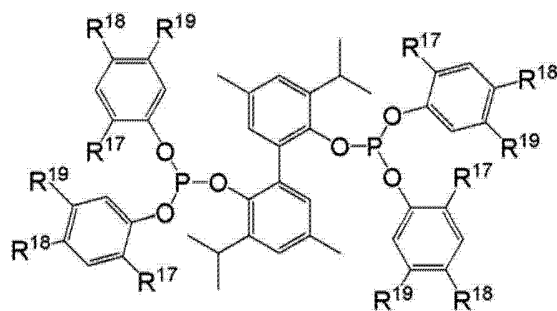
[0237]



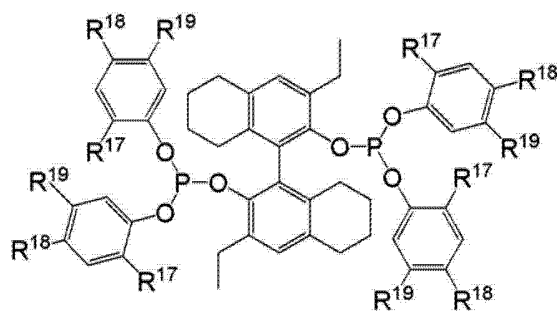
[0238]



(VII)



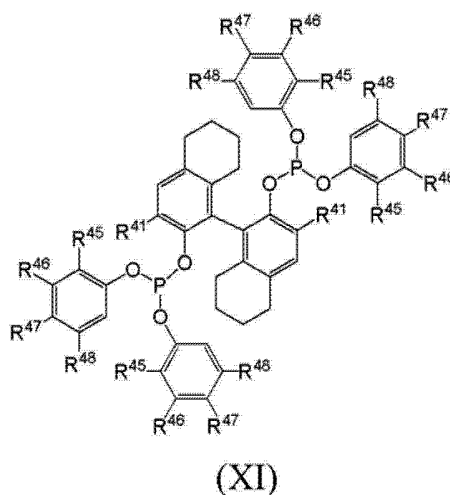
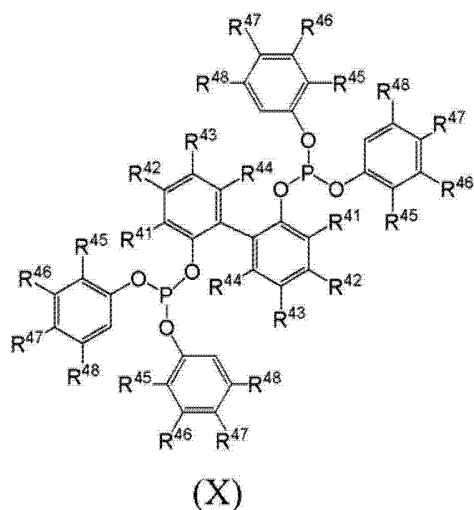
(VIII)



(IX)

[0239] 在本发明的方法中可用的二齿亚磷酸酯配体的另外的实例包括选自由式 (X) 和 (XI) 表示的组的成员的配体, 其中所有相同的标记字母具有相同的含义, 除非有另外明确地限定:

[0240]



[0241] 其中,

[0242]  $R^{41}$  和  $R^{45}$  独立地选自由以下各项组成的组:  $C_1$  至  $C_5$  烷基, 并且  $R^{42}$ 、 $R^{43}$ 、 $R^{44}$ 、 $R^{46}$ 、 $R^{47}$  和  $R^{48}$  的每一个独立地选自由以下各项组成的组: H 和  $C_1$  至  $C_4$  烷基。如本文所使用的, “烷基”特别是烷基或环烷基。

[0243] 例如, 二齿亚磷酸酯配体可以选自由式 (X) 和式 (XI) 表示的组的成员, 其中

[0244]  $R^{41}$  是甲基、乙基、异丙基或环戊基;

[0245]  $R^{42}$  是 H 或甲基;

[0246]  $R^{43}$  是 H 或  $C_1$  至  $C_4$  烷基;

[0247]  $R^{44}$  是 H 或甲基;

[0248]  $R^{45}$  是甲基、乙基或异丙基; 并且

[0249]  $R^{46}$ 、 $R^{47}$  和  $R^{48}$  是独立地选自由 H 和  $C_1$  至  $C_4$  烷基组成的组。

[0250] 作为另外的实例, 二齿亚磷酸酯配体可以选自由式 (X) 表示的组的成员, 其中

[0251]  $R^{41}$ 、 $R^{44}$  和  $R^{45}$  是甲基;

[0252]  $R^{42}$ 、 $R^{46}$ 、 $R^{47}$  和  $R^{48}$  是 H; 并且

[0253]  $R^{43}$  是  $C_1$  至  $C_4$  烷基;

[0254] 或者

[0255]  $R^{41}$  是异丙基;

[0256]  $R^{42}$  是 H;

[0257]  $R^{43}$  是  $C_1$  至  $C_4$  烷基;

[0258]  $R^{44}$  是 H 或甲基;

[0259]  $R^{45}$  是甲基或乙基;

[0260]  $R^{46}$  和  $R^{48}$  是 H 或甲基; 并且

[0261]  $R^{47}$  是 H、甲基或叔-丁基;

[0262] 或者二齿亚磷酸酯配体可以是选自由式 XI 表示的组的成员, 其中

[0263]  $R^{41}$  是异丙基或环戊基;

[0264]  $R^{45}$  是甲基或异丙基; 并且

[0265]  $R^{46}$ 、 $R^{47}$  和  $R^{48}$  是 H。

[0266] 作为再另一个实例, 二齿亚磷酸酯配体可以由式 (X) 表示, 其中  $R^{41}$  为异丙基;  $R^{42}$ 、

$R^{46}$  和  $R^{48}$  是 H; 并且  $R^{43}$ 、 $R^{44}$ 、 $R^{45}$  和  $R^{47}$  是甲基。

[0267] 将认识到的是, 式 (V) 至 (XI) 是三维分子的二维表示并且绕化学键的旋转可以在分子中出现, 从而给出与所给出的那些构型不同的构型。例如, 分别绕式 (V) 至 (XI) 的联苯基、八氢联萘基和或联萘基桥连基的 2- 和 2' - 位之间的碳 - 碳键旋转可以使得每个式的两个磷原子彼此更紧密接近并且可以允许亚磷酸酯配体以二齿方式连接至镍。术语“二齿”是本领域中公知的并且意指配体的两个磷原子都键连至单个镍原子。此外, 用于  $R^{41}$  的光学活性部分如仲丁基的使用可以带来光活性的催化剂。

[0268] 二齿含磷配体合成

[0269] 配体 (V) 是二齿含磷配体的实例。配体 (V) 可以通过本领域中已知的任何合适的合成方式制备。例如, 3,3'-二异丙基 -5,5',6,6'-四甲基 -2,2'-联苯酚可以通过美国公布的专利申请号 2003/0100802 中公开的程序制备, 其中 4-甲基麝香草酚可以在氯氢氧化铜 -TMEDA 配合物 (TMEDA 是 N,N,N',N'-四甲基乙二胺) 和空气的存在下经过氧化偶联为取代的联苯酚。2,4-二甲苯酚的磷氯化物  $[(CH_3)_2C_6H_3O]_2PCl$  可以, 例如, 通过美国已公开专利申请号 2004/0106815 中公开的程序制备。为选择性形成该磷氯化物, 可以将无水三乙胺和 2,4-二甲苯酚在温度 - 受控的条件下以受控的方式分别和同时加入至溶解在合适的溶剂中的  $PCl_3$  中。该磷氯化物与 3,3'-二异丙基 -5,5',6,6'-四甲基 -2,2'-联苯酚形成所需的配体 (V) 的反应可以, 例如, 根据美国专利号 6,069,267 中公开的方法进行。可以将磷氯化物与 3,3'-二异丙基 -5,5',6,6'-四甲基 -2,2'-联苯酚在有机碱的存在下反应以形成配体 (V), 其可以根据本领域中可利用的技术分离, 例如如美国专利号 6,069,267 中描述的技术。

[0270] 另外的双齿配体、配体配合物, 以及其制备方法公开在通过引用以其全部内容结合在此的美国专利号 6,171,996 中。

[0271] 镍 - 磷配体配合物形成

[0272] 镍 - 磷配体配合物可以是有效的氢化催化剂。这种镍 - 磷配体配合物可以通过将镍金属粒子和一种或多种含磷配体在有机腈溶剂中混合形成。在镍金属 - 磷配体配合物形成溶液中还可以包含路易斯酸。如本文描述的, 可以将硫源加入至镍金属粒子和一种或多种含磷配体的混合物中以改善镍原子与含磷配体之间的配合物形成。

[0273] 一种或多种含磷配体可以是本文描述的那些中的任意一种或多种。

[0274] 可以将用于配合物形成的镍金属用如本文描述的硫源预处理, 或者可以将其当在镍金属 - 磷配体配合物形成溶液中时用硫源处理。

[0275] 用于与一种或多种含磷配体的配合物形成使用的镍金属可以是颗粒 (粉化的) 镍金属。颗粒镍金属可以具有一定粒径范围。“镍粒子”是离散的粒子, 典型地在扫描电子显微照片中可见。例如, 至少 10% 的镍粒子可以具有小于约  $6\mu m$  的直径 (D10)。术语“D10”是指粒子的样品中最小 10% 的粒子的最大粒径。可用的颗粒镍原材料可以具有表面微晶。“微晶”是镍粒子内或上的局部晶体有序的区域。“表面微晶”是指粒子内包含的微晶, 但其中微晶的一部分暴露至粒子周围的环境, 如含有配体的有机液体。每个镍粒子理想地具有大数目的微晶。例如, 镍可以具有平均每克镍至少约  $10^{15}$  个表面微晶。镍金属粒子还可以具有至少约  $1m^2/gm$  的 BET 比表面积, 或者用于镍金属粒子的 BET 比表面积可以是至少约  $10m^2/gm$ 。可以将这种镍金属粒子在与一种或多种含磷配体的配合物形成之前, 或在与一种或多

种含磷配体的配合物形成的过程中用硫源处理。

[0276] 有机腈溶剂可以选自由以下各项组成的组中的一个或多个成员：2-戊烯腈、3-戊烯腈、4-戊烯腈、2-甲基-3-丁烯腈、2-甲基-2-丁烯腈、己二腈、2-甲基戊二腈和乙基丁二腈。例如，有机腈可以是戊烯腈或戊烯腈的混合物。

[0277] 路易斯酸可以选自由以下各项组成的组：无机或有机金属化合物，其中阳离子选自包括以下各项的组：钪、钛、钒、铬、锰、铁、钴、铜、锌、硼、铝、钇、锆、铌、钼、镉、铯、镧、铪、铊、铋、锡和它们的混合物。路易斯酸可以选自由以下各项组成的组：氯化锌；氯化亚铁；或氯化锌、氯化亚铁和它们的混合物的组合。例如，路易斯酸可以是氯化锌。

[0278] 镍金属、硫源、路易斯酸、含磷配体和 / 或有机腈溶剂可以基本上不含金属如铝、铜、钨、汞和 / 或铁。例如，镍粒子、硫源、路易斯酸、含磷配体和 / 或有机腈溶剂可以基本上没有含硅部分和 / 或化合物。镍粒子、硫源、路易斯酸、含磷配体和 / 或有机腈溶剂也可以基本上没有钠、钙、镁、钾，和 / 或其他碱金属和 / 或碱土金属。

[0279] 与含磷配体混合的镍和 / 或硫源可以基本上没有烃、二氧化碳和其他含碳化合物。例如，与含磷配体混合的镍和 / 或硫源可以基本上不含硅、钠、钾、钙、镁、磷、铝、铜、钨、汞和 / 或铁杂质。与含磷配体混合的镍和 / 或硫源可以具有少于 10% 杂质，或少于 7% 杂质，或少于 5% 杂质，或少于 4% 杂质，或少于 3% 杂质，或少于 2% 杂质，或少于 1% 杂质，或少于 0.7% 杂质，或少于 0.6% 杂质，或少于 0.5% 杂质，或少于 0.4% 杂质，或少于 0.3% 杂质，或少于 0.2% 杂质，或少于 0.1% 杂质，或少于 0.07% 杂质，或少于 0.05% 杂质，或少于 0.03% 杂质，或少于 0.01% 杂质。

[0280] 可以将镍粒子、路易斯酸和一种或多种含磷配体与有机腈溶剂在足以用于镍原子与含磷配体之间的配合物形成的温度和时间混合。例如，可以将镍粒子、路易斯酸和一种或多种含磷配体与有机腈溶剂在 0℃ 至 150℃ 的温度混合约 15 分钟至约 24 小时。例如，足以用于配合物形成的温度可以是约 4℃ 至约 130℃，或约 10℃ 至约 110℃，或约 15℃ 至约 100℃，或约 20℃ 至约 100℃，或约 40℃ 至约 100℃，或约 60℃ 至约 80℃。

[0281] 足以用于配合物形成的时间是在镍-含磷配体的形成中用于达到平衡的时间。例如，用于达到平衡的时间可以是约 5 分钟至约 24 小时，或约 10 分钟至约 12 小时，或约 15 分钟至约 8 小时，或约 20 分钟至约 4 小时，或约 20 分钟至约 2 小时。优选的用于达到平衡的时间可以是约 20 分钟至约 40 分钟，或约 30 分钟。

[0282] 镍-磷配体配合物可以典型地在非氧气氛下形成。例如，可以采用氮氛。

[0283] 用于镍-磷配体配合物形成的测定

[0284] 为评价镍制备物用于氢氰化催化剂的制备的适合性，评价镍制备物以确定镍制备物中的镍金属是否与一种或多种含磷配体以足于在制造过程中使用的速率形成配合物。

[0285] 可以使用测定以评价镍制备物用于氢氰化催化剂的制备的适合性。这种测定包括将镍测试样品（例如，相对于反应混合物的总重量 1-7 重量% 镍）与一种或多种含磷配体和路易斯酸在有机腈溶剂中混合。含磷配体可以是本文描述的任意含磷配体。优选地，含磷配体可以是二齿亚磷酸酯配体如配体 (V)。路易斯酸可以是氯化锌。有机腈溶剂可以是戊烯腈。

[0286] 已知质量的镍粉末（例如，4 重量% 镍）的样品可以在 3-戊烯腈 (3PN) 溶液中与每摩尔二齿亚磷酸酯配体（例如，配体 (V)）约 0.5 至 2.5 摩尔路易斯酸（如氯化锌）接触。

可以将混合物升温数小时的时间,在该时间过程中,通过液相色谱 (LC) 测量溶液中已溶解的镍的水平。在测定混合物中配体和 / 或氯化锌的量可以是相对于所加入的镍粉末的量化学过量。然而,需要的是相对于所加入的镍粉末的量限制测定混合物中配体和 / 或氯化锌的量。因此,测定混合物中配体和 / 或氯化锌的浓度可以相对于所存在的镍粉末的量限定。

[0287] 当镍与含磷配体形成配合物时,它在有机腈溶剂 (例如,氢氰化底物如 3PN) 中变得可溶。可以将未反应的镍金属从混合物通过过滤或离心移除。

[0288] 为避免与空气接触,配备有电磁搅拌棒的反应器瓶可以在用于干燥氮氛操作的真空气氛干燥盒内装有反应物。加入该瓶中的反应物可以包含所要测试的镍制备物、一种或多种含磷配体 (例如配体 (V)), 其中溶剂是 3- 戊烯腈。也可以将氯化锌加入至测定混合物中。

[0289] 为标准化测试程序,将 4-5 重量%镍在约 60°C 至 80°C 在含有每摩尔二齿含磷配体约 0.5 至 2.5 摩尔氯化锌的 3- 戊烯腈 (3PN) 溶液中混合。例如,可以将 4 重量%镍制备物与大约 5.25 重量%配体 (V) 和 6300ppm  $\text{ZnCl}_2$  在 3- 戊烯腈的溶液中混合。那么所采用的锌与配体 (V) 的摩尔比为约 0.75。

[0290] 可以将反应器瓶密封,从干燥箱移除,并且移动至实验室通风橱中,在此,可以将其放置在电磁搅拌板上。之后可以将反应瓶内的反应混合物加热至 60°C -80°C (例如, 60°C)。可以使用足够的搅拌以将含镍固体悬浮在该反应混合物中。

[0291] 可以将从反应混合物过滤的液体样品以 5 分钟至一小时的间隔从反应器瓶移除。可以在 24 小时之后取出最终的样品。使用液相色谱 (LC) 测量样品中可溶镍的量。用于该测定的检测的该极限为约 20-50ppm 配体 (V) 的可溶镍配合物形式的可溶镍。

[0292] 镍制备物的活性因此通过其形成可溶零价镍金属磷配体配合物的倾向而测量。对于可溶零价镍金属磷配体配合物的形成,镍制备物的活性可以在该测定中与对照镍制备物相当。例如,对照镍制备物可以是测定为具有不足的活性的镍制备物。活性镍制备物因此是具有比无活性负对照镍制备物更高活性的镍形式。对照镍制备物可以是测定为具有好活性的镍制备物。活性镍制备物因此是具有与活性正对照镍制备物大约相同或更高活性的镍形式。

[0293] 对照镍制备物的一个实例是来自 MetChem BNC 使用一步氢化法 (即,不包括煅烧预处理) 获得的镍粉,其中在 400°C 进行氢化。由 MetChem BNC 制备的这种镍制备物描述在表 1 中,并且具有的镍活性典型地低于能够有效制备适合用于在包括氢氰化催化剂的制造过程中使用的零价镍配合物。

[0294] 采用用于催化剂 - 制备测定中 Ni 溶解的经验速率方程,以提供在以下反应中的镍“活性” (与配体 (V) 成为可溶催化剂配合物的能力) 的数值指示:

[0295]



[0296] 以下公式描述镍 - 配体 (V) 催化剂形成的速率:

$$[0297] \quad r = a * k' * W_{\text{Ni}} * C_A^{a'} * C_B^{b'} * [1 - C_c / (K_{\text{eq}} * C_A * C_B)] * 2 * (C_A / C_{A0}) / [1 + (C_A / C_{A0})]$$

[0298] 其中:

[0299]  $a$  = 镍的活性

[0300]  $W_{\text{Ni}}$  = 镍的重量负载量 (镍的重量 / 溶液的重量)

- [0301]  $k'$  = 阿雷尼乌斯 (Arrhenius) 速率常数 :
- [0302]  $[(\text{毫摩尔 Ni/升})^{0.5/\text{hr}}] = 1.539 \times 10^{10} \exp[-6832.1/T(\text{K})]$
- [0303]  $C_A$  = 配体 (V) 的浓度 (mmol/L)
- [0304]  $C_{A0}$  = 配体 (V) 的初始浓度 (mmol/L)
- [0305]  $C_B$  =  $\text{ZnCl}_2$  的浓度 (mmol/L)
- [0306]  $a'$  = 关于 D80 的反应级数 = 0
- [0307]  $b$  = 关于  $\text{ZnCl}_2$  的反应级数 = 0.5
- [0308]  $K_{eq}$  = 化学反应的平衡常数
- [0309]  $[\text{升}/\text{mmol}] = \exp[11555/T(\text{K}) - 35.231]$
- [0310]  $T$  = 以绝对温度计的温度。
- [0311] 所假设的是 3-戊烯腈远远过量, 所以其关于 3-戊烯腈溶解的速率的反应级数被认为是零。与镍的负载量的反应级数认为是 1。
- [0312] 速率常数  $k'$  对于在 400°C 在纯氢下还原为镍的标准 MetChem BNC 定义。然而, 为考虑到可以具有不同性质的镍的其他来源, 使用称为镍溶解的活性的因子。该‘活性’数在以下具体条件下被选择为 1: 对于在 400°C 还原为镍的 MetChem BNC, 在 80°C 溶解在具有 0.8 的  $\text{ZnCl}_2$ /配体 (V) 摩尔比和 4 重量% 镍负载的催化剂-制备物溶液中, 其中溶解速率为 980ppmNi/h。原理上, 对于给定镍, 越高的活性, 基本上越高的速率常数。为了不用对于每种类型的镍分别测定速率常数, 定义活性术语来消除 (get around) 该问题。
- [0313] 使用该公式, 如果镍制备物具有至少 2.0, 优选至少 3.0 并且更优选至少 4.0 的活性, 则它是活性的。
- [0314] 如果镍制备物以适合用于在包括氢氰化催化剂的制造过程中使用的速率有效地形成零价镍磷配体配合物, 则该镍制备物也是活性的。合适的速率是在镍金属磷配体配合物的形成中用于达到平衡的时间不大于 8 小时, 不大于 6 小时, 不大于 5 小时, 不大于 4 小时, 不大于 3 小时, 不大于 2 小时, 不大于 1 小时, 或不大于 30 分钟。与含磷配体非常慢地 (例如, 需要数天或一周来形成) 形成配合物的镍制备物不是可用于产生氢氰化催化剂的活性镍制备物。
- [0315] 用于催化剂储存和运输的容器
- [0316] 可以将多种尺寸和形状 of 容器如桶、鼓用于镍、含磷配体和 / 或催化剂的储存和运输。尤其是, 可以使用允许对大气和其他氧源暴露最小的内含物的进入和离开的容器。聚合材料特别用于与镍和 / 或配体催化剂的任何接触。适合用于镍和 / 或催化剂配体储存和运输的轴环鼓描述在 2011 年八月 4 日公开的并且授让给 Auburn, Maine USA 的 Pack-Gen 的 W02011/094411 中。
- [0317] 用于这种容器并且与镍和 / 或催化剂配体进行接触的材料包括聚合物如聚对苯二甲酸乙二醇酯 (PET)、聚萘二甲酸乙二醇酯 (PEN)、聚丙烯和聚乙烯以及耐配体催化剂泄漏的金属容器。
- [0318] 具有氧清除芯层的容器描述在颁布给 Chevron 的美国专利 7,056,565 中, 并且可以利用容器的多种结构和化学组成方面来储存和传输配体化合物。
- [0319] 用于氧敏感产物的容器描述在颁布给 Sonoco 的美国专利 7,854,973 中, 其中在第一外层中提供氧化催化剂以消耗扩散至内部的氧。可以使用美国专利 7,854,973 的多种结

构和化学组成方面作为容器,条件是用于清除氧的机构不氧化镍和 / 或配体。提供壁层,其可以是乙烯 - 乙烯醇共聚物、聚酰胺均聚或共聚物、聚丙烯腈共聚物、聚氯乙烯基 (PVC) 或具有低氧渗透性的其他聚合物。

[0320] 可以使用颁布给 Amoco 的美国专利 4,946,068 和颁布给 Exxon-Mobil 的 W02006/052677 中描述的用于催化剂储存、运输和分配的催化剂容器结构来进行镍和 / 或配体的储存和运输。

[0321] 用于危险液体填充物的储存和运输的热塑性容器描述在颁布给德国 Bruhl 的 Mauser-Werke 的 EP0673841 中。

[0322] 惰性气氛包装 (IAP) 或改性气氛包装 (MAP) 一般可用于本文描述的配体和 / 或镍金属制备物的储存和运输。因此,用于储存或运输的配体 / 溶剂混合物向合适容器中的装入通过使得液体表面上方的顶部空间保持为惰性或非常低的反应性气氛而完成;或者用于储存或运输的配体 / 溶剂混合物装入合适容器中,之后使得液体表面上方的顶部空间保持为惰性或非常低的反应性气氛;或上述两者。

[0323] 定义

[0324] 如说明书和所附权利要求中使用的,单数形式“一个”、“一种”和“所述”包括复数引用,除非上下文清楚地有另外指出。

[0325] 在本文献中,使用术语“或”指代非排除性的,或使得“A 或 B”包括“A 但不是 B”、“B 但不是 A”和“A 和 B”,除非有另外指出。

[0326] 术语“约”可以允许值或范围的可变程度,例如,在所规定的值或所规定的范围界限的 10% 内,在 5% 内,或在 1% 内。当给出连续值的范围或列举时,除非另作说明之外,该范围内的任意值或所给出的连续值之间的任意值。

[0327] BET 表面积 (BET SSA) 或气体吸收是表面积和镍金属粒子的多孔性的测量。BET 理论涉及固体表面上气体分子的吸收并且提供用于测量材料的比表面积的方法。参见,例如, Brunauer 等, J. Am. Chem. Soc. 60 :309 (1938)。被吸附气体的分子在受控的条件下在真空室内物理吸附到粒子表面上,包括任何孔或微晶的表面。例如, BET 比表面积 (BET SSA) 可以通过将样品在真空下在 105°C 脱气过夜之后使用 Tristar3000 氮吸附仪观测氮吸附测量。可以使用 0.05-0.3P/P<sub>0</sub> 的分压范围进行多点 BET 测量。吸附等高线通过作为引入至该室中的气体的体积的函数测量样品上方的气体的压力获得。吸附等高线的线性区域可以之后用于使用 BET 理论测定形成跨越可得的粒子表面积的单层所需的气体的体积,如通过以下公式描述的:

$$[0328] \quad \frac{1}{v[(P/P_0)-1]} = \frac{c-1}{v_m} \left( \frac{P}{P_0} \right) + \frac{1}{v_m c}$$

[0329] 其中 v 是气体的体积, P 是压力, P<sub>0</sub> 是饱和压力, v<sub>m</sub> 是形成单层所需的气体的体积, 而 c 是 BET 常数。关于压力作图,  $\phi (=P/P_0)$ , 并且体积允许由线的梯度和截距测定单层的体积。

[0330] 比率 BET SSA/C50 提供与微晶的几何结构无关的值。可以将对于一组样品获得的值与如这里定义的“镍活性”相关联, 并且发现活性与 BETSSA/C50 之间合理的线性相关性, 这如本文所论述。

[0331] “微晶”是局部晶体有序的粒子内的区域。每个活性镍粒子包含大量的微晶。

[0332] 如本文所使用的术语“微晶尺寸”是指可能不规则形状的微晶的平均直径。微晶尺寸可以作为微晶的直径测量,例如,沿微晶的主维度的直径,或作为微晶体积的立方根测量。微晶尺寸可以通过X射线衍射(XRD)分析使用本领域中可利用的程序和仪器测定。“平均微晶尺寸”或“平均微晶尺寸”是指对于如上定义微晶尺寸的分布的平均(均)值。平均微晶尺寸也可以定义为包含多个微晶的样品的平均体积的立方根,并且假设所有微晶具有相同的尺寸和形状。对于尺寸的分布,可以将平均尺寸定义为各个微晶体积的立方根的均值或各个微晶的体积的均值的立方根。

[0333] 术语“C10”是镍颗粒形式中微晶尺寸的度量,并且是指镍颗粒形式中最小的10%的微晶具有的最大直径(例如,以纳米计)。术语“C50”也是镍颗粒形式中微晶尺寸的测量,并且是指其中块状样品中50%的Ni微晶具有小于所述值的尺寸情况下的直径(尺寸)。C50值在本文也称为平均微晶尺寸(MCS)。术语“C90”也是镍颗粒形式中微晶尺寸的测量,并且是指其中块状样品中90%的镍微晶具有小于所述值的尺寸的直径(尺寸)。Cx是x%的用于微晶的样品具有更小尺寸时该微晶的尺寸。微晶尺寸可以使用X射线衍射(XRD)测量。

[0334] 如本文所使用的术语“微晶尺寸分布范围”是指表示定义为(C90-C10)/C50的微晶尺寸分布的统计值。

[0335] 本文作为术语使用的“表面微晶”是指包含在粒子内的微晶,但其中该微晶的一部分暴露于该粒子周围的环境,如含有配体的有机液体。为计算BET SSA/微晶尺寸比率,可以使用用于球体微晶的公式  $BETSSA/4\pi r(C50/2)^2$  和用于立方体微晶(立方体截面)的  $BETSSA/C50^2$ 。

[0336] 本文使用作为术语的表面微晶“边缘”是指微晶的不是平面表面的那些表面部分。

[0337] 虽然微晶的形状通常是不规则的,但是该形状可以通常描述为球体、立方体、四面体、八面体或平行六面体如针形或板形、棱柱或圆柱。Scherrer分析的大部分应用假设球体微晶形状。如果平均微晶形状由另一个分析已知,则对于Scherrer常数K可以选择合适的值。各向异性峰形状可以通过各向异性峰展宽识别,条件是微晶的维度为 $2x*2y*200z$ ,那么(h00)和(0k0)峰将比(001)峰更加展宽。此外,参见以下网站的讨论: [clays.org/journal/archive/volume%2047/47-6-742.pdf](http://clays.org/journal/archive/volume%2047/47-6-742.pdf),由M. Crosa等出版(1999),“Determination of Mean Crystallite Dimensions from X-Ray Diffraction Peak Profiles: A Comparative Analysis of Synthetic Hematites(由X-射线衍射峰曲线测定平均微晶维度:合成赤铁矿的比较分析)”,Clays and Clay Materials,47(6),742-747,以及其中所包含的参考文献,该参考文献和所引用的参考文献均通过引用以它们的全部内容结合在此。每单位质量微晶的平均数表达为每克镍形式的微晶的数目,并且陈述了在计算时关于微晶形状做出的任何假设。

[0338] 术语“D10”是镍颗粒形式中粒径的度量,并且是指镍颗粒形式中最小10%的镍粒子具有的最大直径(例如,以微米计)。

[0339] “Ni粒子”是离散的粒子或聚集的粒子,典型地在扫描电子显微照片中可见。

[0340] 如本文所使用的术语“粒径”是指可能不规则形状的粒子的平均直径。这种粒径可以通过用获自Malvern Instruments Ltd的Mastersizer2000粒径分析仪,使用

Hydro2000MU 附件和水作为分散剂的测量而测定,如本领域中所公知的。对于如上定义的粒径的布局的“平均粒径”或“中值粒径”是指平均值(中值)。对于低于 100-200 微米的尺寸,可以使用激光衍射技术测量平均粒径。

[0341] 本文可以使用如本领域中公知的用于化学基团的标准缩写,并且其在本领域的知识范围内;例如,Me= 甲基,Et= 乙基,i-Pr= 异丙基,Bu= 丁基,t-Bu= 叔丁基,Ph= 苯基,Bn= 苄基,Ac= 乙酰基,Bz= 苯甲酰基,等。

[0342] 该限制可以施加于任意所公开的种类或基团,其中其他以上公开的种类、基团或物种中的任意一种或多种可以从这种种类或组排除。

[0343] 如本文所使用的术语“室温”是指环境温度,其可以是,例如,约 16°C 至约 27°C。

[0344] “基本上球体”是指关于中心点基本上对称的粒子或微晶。例如,虽然从中心点至基本上球体粒子或微晶的表面的距离(半径)可以变化,但是这种变化不是如此大或如此可预测以使得基本上球体粒子或微晶的形状将更精确地定义为其其他几何形状(例如,作为立方体,而不是作为球体)。在一些实施方案中,基本上球体粒子或微晶可以具有变化约不超过约 25%,或不超过约 20%,或不超过约 15%,或不超过约 10%,或不超过约 5% 的半径。在一些实施方案中,基本上球体粒子或微晶可以是部分地球体。例如,基本上球体粒子或微晶可以是半球体,或是球体的四分之一。可以将基本上球体微晶耦合为粒子或另一个微晶,以使得基本上球体微晶是从粒子或其他微晶开始的部分的基本上球体的凸出。耦合至粒子或另一个微晶的部分地基本球体微晶可以因此为球体的约 25% 至约 95%,或球体的 25% 至 95% 之间的任意百分数。

[0345] Scherrer 方法(使用半最大全宽 FWHM 方法)给出厚度的均四次方根与均平方根值的比率。Stokes 和 Wilson 方法(使用积分宽度)确定垂直于反射平面测量的微晶厚度的体积平均。不同的方法给出微晶的总体积与它们在平行于反射平面的平面上的投影的总面积的比率。

[0346] 所有作为%或 ppm(百万分之一份)给出的值是指以重量计,除非另外详细地说明(例如,作为体积%)。换言之,数值百分比或百万分之若干份是以全部组合物的重量计的数值百分比或百万分之几份(除非有另作说明)。

[0347] 如本文所使用的,“基本上”是指大部分,或主要地,如至少约 80%,90%,95%,96%,97%,98%,99%,99.5%,99.9%,99.99%,99.999%,或至少约 99.9999%。

[0348] 以下实施例示例本发明的各方面。

[0349] 实施例 1:用于镍-配体配合物形成以及 Ni 和 S 含量的测定

[0350] 该实施例描述用于评价用于与含磷配体形成配合物的镍金属样品的活性的测定,以及确定多种碱式碳酸镍、氧化镍、镍金属等样品中镍和硫的含量的测定。

[0351] 为评价镍制备物用于产生氢氰化催化剂的适合性,将镍与含磷配体(例如,配体(V))在 3-戊烯腈(3PN)溶液中混合并保温数小时的时间,并且通过液相色谱(LC)测量溶液中可溶解的镍在下面描述的测定中随时间的水平。通常,目标是识别与含磷配体以适合用于在包括氢氰化催化剂的制造过程中使用的速率形成配合物的镍制备物。例如,合适的镍制备物形成足够的镍-配体配合物和/或在镍金属磷配体配合物形成测定中在不大于约 2 小时,不大于 1 小时,或不大于 30 分钟中达到平衡。优选地平衡在不大于 30 分钟中达到。

[0352] 镍-配体配合物形成测定程序

[0353] 对于与含磷配体形成镍金属配合物的测定,将镍金属在干燥的氮氛中处理。用于配合物形成的测定如下进行:反应器瓶装有 80 克的 3-戊烯腈(3PN)溶剂中的 5 重量%配体 V 溶液,3.2 克的镍金属(Ni(0)),以及 0.5 克的无水  $\text{ZnCl}_2$ 。将反应器瓶密封,从干燥箱移除,并且移动至实验室通风橱,在此将它放置在电磁搅拌板上。之后将反应瓶内的反应混合物加热至  $60^\circ\text{C}$ 。在一些测试中,将测定混合物加热至  $80^\circ\text{C}$ 。将反应混合物混合以保持含镍固体悬浮。将过滤的液体样品作为时间的函数取出并通过液相色谱分析可溶镍浓度。

[0354] 在一些测试中,使用来自 MetChem BNC(描述在表 1 中)的镍制备物作为对照,其中 MetChem 镍的活性被认为是 1.0 并且与配体 V 以更高速率形成可溶配合物的镍金属样品展现提高的镍活性。如果可溶镍(在与配体 V 的配合物中)以最小在  $60^\circ\text{C}$  至少 317ppm/hr 的速率或在  $80^\circ\text{C}$  至少 980ppm/hr 的速率形成,镍样品也被认为是最小活性的。

[0355] 采用用于催化剂-制备物测定中 Ni 溶解的经验速率方程以提供在以下反应中镍活性(与配体(V)成为可溶催化剂配合物的能力)的数值指示:

[0356]



[0357] 以下公式描述镍-配体(V)催化剂形成的速率:

$$r = a * k' * W_{\text{Ni}} * C_{\text{A}}^{a'} * C_{\text{B}}^b * [1 - C_{\text{C}} / (K_{\text{eq}} * C_{\text{A}} * C_{\text{B}})] * 2 * (C_{\text{A}} / C_{\text{A0}}) / [1 + (C_{\text{A}} / C_{\text{A0}})]$$

[0359] 其中:

[0360]  $a$  = 镍的活性

[0361]  $W_{\text{Ni}}$  = 镍的重量负载(镍的重量/溶液的重量)

[0362]  $k'$  = 阿雷尼乌斯(Arrhenius)速率常数:

$$[(\text{毫摩尔 Ni} / \text{升})^{0.5} / \text{hr}] = 1.539 \times 10^{10} \exp[-6832.1 / T(\text{K})]$$

[0364]  $C_{\text{A}}$  = 配体(V)的浓度(mmole/L)

[0365]  $C_{\text{A0}}$  = 配体(V)的初始浓度(mmole/L)

[0366]  $C_{\text{B}}$  =  $\text{ZnCl}_2$  的浓度(mmole/L)

[0367]  $a'$  = 关于配体(V)的反应级数 = 0

[0368]  $b$  = 关于  $\text{ZnCl}_2$  的反应级数 = 0.5

[0369]  $K_{\text{eq}}$  = 化学反应的平衡常数

$$[\text{升} / \text{mmole}] = \exp[11555 / T(\text{K}) - 35.231]$$

[0371]  $T$  = 以绝对温度计的温度。

[0372] 所假设的是 3-戊烯腈远远过量,所以其关于 3-戊烯腈溶解的速率的反应级数被认为是零。与镍的负载量的反应级数被认为是 1。

[0373] 速率常数  $k'$  对于在  $400^\circ\text{C}$  在纯氢下还原为镍的标准 MetChem BNC 定义。然而,为考虑到可以具有不同性质的镍的其他来源,使用称为镍溶解的活性的因子。该‘活性’数在如下具体条件下被选择为 1:对于在  $400^\circ\text{C}$  还原为镍的 MetChem BNC,在  $80^\circ\text{C}$  溶解在具有 0.8 的  $\text{ZnCl}_2$ /配体(V)摩尔比和 4 重量%镍负载量的催化剂-制备物溶液中,其中溶解速率为 980ppmNi/hr。原理上,对于给定镍,越高的活性,基本上上越高的速率常数。为了不用对于每种类型的镍分别测定速率常数,定义活性术语以消除该问题。

[0374] 应注意,如果在测定中采用重结晶配体(V),则所测量的镍活性高于如果采用萃取的(例如,再循环)配体(V)制备物的活性。活性上的差别为约 2 倍。

[0375] 硫含量测定程序

[0376] 碱式碳酸镍、氧化镍、镍金属和其他镍源中的硫含量通过燃烧与红外 (IR) 光谱分析、微电量分析或感应耦合等离子体 (ICP) 质谱法测量。

[0377] 对于燃烧 IR 检测,将 0.2-0.5g BNC/NiO/Ni 等样品称量至舟皿中,将舟皿放入至炉中,将样品在氧的蒸气中加热 (1350℃)。将燃烧气净化以移除湿气并扫至红外检测池中。将所检测的硫的量使用所储存的校正曲线和已知的样品重量转化为样品中的全部硫。将样品重复分析两次并且报告均值。检测限为约 20ppm。仪器不确定度为相对 5%或更好。

[0378] 微电量分析是比燃烧 IR 检测更灵敏的技术。微电量分析也使用形成物的燃烧和 SO<sub>2</sub> 的测量。用于微电量分析的样品重量通常为约 20-50mg。将样品在 1100℃引入至炉中。将燃烧气净化以移除水汽并在将气体引入至平衡色度滴定池之前冷却气体。硫通过所形成的 SO<sub>2</sub> 与 I<sub>3</sub> 形成 I<sup>-</sup> 和 SO<sub>4</sub> 的反应测定,并且由再次平衡比色皿 (cell) 所需的电荷计算。对于微电量分析的检测限可以是小于 1ppm,尽管引用了仅低至 1ppm 的水平,并且仪器不确定度为 5%以下。

[0379] 镍含量测定程序

[0380] 通过感应耦合等离子体光学发射光谱 (ICP-OES) 测定实施例 2-4 中描述的样品的镍含量,而实施例 5 和 6 中描述的样品的镍含量通过热重分析 (TGA) 测定。

[0381] 在 Perkin Elmer TGA4000 热重分析仪中通过将样品在流动速率为 40mL/ 分钟的氮气氛围中以 50℃ / 分钟的速率从 30 加热至 995℃,评价样品 (20-50mg) 的镍含量。水含量的特征在于第一加热事件 (第一重量损失) 和镍含量的特征在于在其中全部材料已经完全分解为 NiO 的 995℃观察到的最终总重量损失。

[0382] 除非有另外指出,下面提供用于多种镍金属制备物的分析数据 (例如,关于硫含量、BET、XRD 数据等) 用于具有薄 NiO 涂层的还原的钝化镍制备物。这种钝化因为所采用的分析技术进行过程中镍变得暴露于氧中而出现。所假设的是这种钝化 (即表面上 NiO 的量) 对分析结果具有可忽略的影响。

[0383] 碳酸盐含量

[0384] 使用由 Donald L. Pile 等在 Journal of Chemical Education, LA-UR-97-1384, “用于测定碳酸盐材料的 CO<sub>2</sub> 含量的精确方法 (A Precise Method for Determining the CO<sub>2</sub> Content of Carbonate Materials)”中描述的方法测定碳酸盐含量,该技术使用了一种简单装置,该简单装置被设计为测量由 BNC 样品和盐酸溶液的反应形成的 CO<sub>2</sub> 气体所产生的体积变化。

[0385] 实施例 2 :镍活性随 BNC 样品类型变化

[0386] 评价八个碱式碳酸镍 (BNC) 样品在制备 Ni 金属中的适用性。所测试的所有样品是商业产品,除了 BNC#5 之外,其根据上面描述的 BNC 沉淀程序制备。如下面描述的,由不同的 BNC 源制成的不同的颗粒镍金属制备物在与含磷配体的配合物形成上展现可变性。

[0387] 表 1 (上面的) 和表 2 提供关于 BNC 样品中痕量杂质的分析数据。除非有另外提及,所有百分比和百万分之一份 (ppm) 值是重量:重量 (w/w)。

[0388] 表 2 :用于本发明的 Ni 形成的制备的碱式碳酸镍评价的样品

[0389]

| BNC 序号 | C   | H   | N     | S     | Cl  | 镍     | CO <sub>3</sub> <sup>2-</sup> | Ni:C 重量比 | Ni:C 摩尔比 |
|--------|-----|-----|-------|-------|-----|-------|-------------------------------|----------|----------|
|        | %   | %   | %     | ppm   | ppm | %     | %                             |          |          |
| 1      | 3.9 | 3.3 | 0.09  | 212   | 13  | 42.08 | 19.5                          | 10.79    | 2.21     |
| 2      | 4.6 | 2   | 0.08  | 1902  | 3   | 50.71 | 23                            | 11.02    | 2.26     |
| 3      | 6.4 | 2.2 | 0.02  | 5     | 9   | 45.33 | 32                            | 7.08     | 1.45     |
| 4      | 4.8 | 2.4 | <0.02 | 7     | <1  | 46.19 | 24                            | 9.62     | 1.97     |
| 5      | 4.5 | 2.1 | <0.02 | 21000 | 7   | 51.57 | 22.5                          | 11.46    | 2.35     |
| 6      | 5.6 | 2.4 | <0.02 | 10    | 2   | 45.53 | 28                            | 8.13     | 1.66     |
| 7      | 3.3 | 3.3 | <0.02 | 9800  | 3   | 45.15 | 16.5                          | 13.68    | 2.80     |
| 8      | 4.5 | 2.7 | <0.02 | 4600  | 3   | 46.44 | 22.5                          | 10.32    | 2.11     |

[0390] 用于 Ni 粉末的制备的示例程序

[0391] 用于以上列出的 BNC 样品向 Ni 粉末的转化和那些 Ni 粉末用于与测试亚磷酸酯配体即配体 (V) 在有机液体 3PN 中的反应中的活性的评价, 可以使用以下程序。

[0392] 在还原步骤之前, 可以采用煅烧预处理, 如用空气流, 任选地包括水蒸气。将十五克的干燥固体 BNC 样品放置在可以在位于实验室通风橱中的电炉内加热的反应管内。煅烧可以在 300–400°C 温度范围内进行。图 1 显示性质在表 2 中给出的八个 BNC 样品序号 1–8 的煅烧预处理过程中的 CO<sub>2</sub> 损失。

[0393] 煅烧预处理不是必要的, 因为可以将 BNC 同时地煅烧, 同时将 BNC 中的镍还原。例如, 将由 MetChem (BNC 的美国销售商) 提供的在上面的表 2 中作为 BNC#1 列出的 BNC 的样品在不煅烧的情况下还原。将五十克的 BNC#1 材料在以 0.5 升 H<sub>2</sub>/ 分钟的流动速率的氢中在 400°C 还原四小时。还原在温度受控的管式炉中完成。将还原管取至干燥箱中并且将内含物转移至瓶中。所得到的粉末是磁性的, 从而指示通过还原产生了镍金属。

[0394] 将上面的表 2 中的 BNC 样品 #2–8 以相似的方式处理, 除了还采用煅烧预处理之外, 以提供用于如实施例 1 中描述的零价镍磷配体制备物评价的含 Ni 粉末。

[0395] 产物性质

[0396] 所发现的是, 一些 BNC 样品比其他样品更适合用于本发明的镍颗粒组合物的制备。本文和图中给出的数据示例在处理过程中和之后 BNC 样品的性质, 以显示何时特定样品将是镍活性的本发明的零价镍金属的颗粒形式。

[0397] 如上所述, 对 BNC 样品 2–8 进行煅烧, 但不将 BNC 样品 1 进行。然而, 将全部八个样品经由氢化还原。由八个还原 BNC 样品产生的镍制备物的特征在表 3 中给出。表 3 中的镍样品 1–8 由表 2 中列出的相应的 BNC 样品 1–8 制备。

[0398] 在表 3 中, “Ni 活性”意指通过从相应的 BNC 还原制备的 Ni 金属好于 BNC 样品 #1, 即由 MetChem BNC 经由一步还原法 (即, 不包括煅烧预处理) 获得的 Ni 粉末。样品 1 具有

刚好足以使得能够有效制备适合用作氢氰化催化剂使用的零价镍磷配体配合物的镍活性。有效制备是指镍粉末足够完全地并且以足够的速率反应,从而在经济上适合用于在进行工业规模的烯烃氢氰化反应,比如在 3PN 形成己二腈 (ADN) 的氢氰化中使用,己二腈 (ADN) 是一种在各种尼龙如尼龙 6 和尼龙 6,6 的制造中的重要中间体。

[0399] 表 3:镍样品性质

[0400]

| BNC 序号 | 活性 Ni | 平均 Ni 结晶尺寸 (nm) |
|--------|-------|-----------------|
| 1      | 是     | 31              |
| 2      | 是     | 21              |
| 3      | 否     | 80              |
| 4      | 否     | 40              |
| 5      | 是     | 28              |
| 6      | 否     | 47              |
| 7      | 是     | 27              |
| 8      | 是     | 21              |

[0401] 在表 3 中,标记为“是”的样品具有活性镍,而样品 3、4 和 6 不具有活性镍,这是通过包括可用于工业规模的烯烃氢氰化反应的催化的镍-磷配体配合物形成的测定来评定的。中值(平均)微晶尺寸与活性之间的关系也是从表 3 中的数据明显可见的。三个样品评价为用于零价镍二齿配体催化剂制备物的活性不足,即样品数目 3、4 和 6,它们具有八个样品测试中三个最大的平均微晶尺寸,这通过 XRD 测定。所有活性样品具有约 30nm 以下的平均微晶尺寸。

[0402] 实施例 3:BNC 物理和化学性质

[0403] 进一步评价实施例 1 中描述的“Ni 活性”样品 2、5、7 和 8,并且将它们与不具有足够的有效形成镍磷配体配合物并且具有比活性样品更大的微晶平均尺寸的活性镍样品 3、4 和 6 比较。

[0404] 分析程序—方法

[0405] TP-XRD 测量

[0406] 使用具有 Anton Paar HTK 加热台的 Siemens Bruker D5000 衍射计。将 BNC 样品作为干燥致密层安装在铂 (Pt) 箔上,该铂 (Pt) 箔自身附加至电加热 Pt 棒上。使用 4%  $H_2/N_2$  的气体流动。

[0407] 在室温的预加热扫描由原材料获得;这也允许将系统用  $H_2/N_2$  完全吹扫。在加热曲线之后,获得产物的室温扫描作为参考。

[0408] 使用以下测量条件。

[0409]

|        |                        |
|--------|------------------------|
| 衍射计    | Siemens/Bruker D5000D7 |
| X 射线管  | Cu LFF                 |
| 射线     | Cu K $\alpha$          |
| 生成器电压  | 40kV                   |
| 生成器电流  | 40mA                   |
| 衍射几何构造 | 反射 Bragg Brentano      |
| 可变发散狭缝 | 6mm 照射长度               |
| 抗散射缝   | 2mm 照射长度               |
| 接受狭缝   | 0.6mm                  |
| 一级索勒狭缝 | 2.3°                   |
| 次级索勒狭缝 | —                      |
| 检测器    | Scint                  |
| 单色仪    | 石墨单色器                  |
| 过滤器    | —                      |
| 预加热    |                        |
| 步长     | 0.05°                  |
| 每步的时间  | 2s                     |
| 扫描起始角度 | 5°                     |
| 扫描终止角度 | 90°                    |
| 样品形式   | 压缩的干燥粉末                |
| 样品负载   | 顶部压缩                   |
| 温度     | 室温                     |
| 温度变化速率 | —                      |

|      |                                                          |
|------|----------------------------------------------------------|
| 气氛   | 40cm <sup>3</sup> / 分钟 4% H <sub>2</sub> /N <sub>2</sub> |
| 加热过程 |                                                          |
| 步长   | 0.02°                                                    |
| 每步时间 | 3s                                                       |

[0410]

|        |                                                          |
|--------|----------------------------------------------------------|
| 扫描起始角度 | 38°                                                      |
| 扫描终止角度 | 106°                                                     |
| 样品形式   | 压缩的干燥粉末                                                  |
| 样品负载   | 顶部压缩                                                     |
| 温度     | 100℃, 之后 160-420℃, 间隔 20C                                |
| 温度变化速率 | 0.5C/s                                                   |
| 气氛     | 40cm <sup>3</sup> / 分钟 4% H <sub>2</sub> /N <sub>2</sub> |
| 后加热    |                                                          |
| 步长     | 0.02°                                                    |
| 每步的时间  | 2s                                                       |
| 扫描起始角度 | 30°                                                      |
| 扫描终止角度 | 108°                                                     |
| 样品形式   | 压缩的干燥粉末                                                  |
| 样品负载   | 顶部压缩                                                     |
| 温度     | 室温                                                       |
| 温度变化速率 | -                                                        |
| 气氛     | 40cm <sup>3</sup> / 分钟 4% H <sub>2</sub> /N <sub>2</sub> |

[0411] 仪器性质参数可以由 NIST 六硼化镧衍射图案测定。线形分析可以确定每个衍射峰中存在的另外的展宽。

[0412] 还原和微结构监控

[0413] 衍射图案使用 Wilton “LOSS” 软件分析, 其最优化包含对于一系列微晶尺寸计算

的一组峰形的模拟衍射图案的拟合。所获得的微晶尺寸值是体积 - 重量平均。数据使用“Williamson Hall”曲线进一步分析以分离来自如果存在时的晶格变形加宽的微晶尺寸加宽。立方金属结构中缺陷的存在可以通过 111 和 200 反射的线形的宽度比较而检查。

[0414] 反应进程可以由与 Ni 金属峰相关的面积并由如在低温衍射图案中观察到的未还原的 BNC 材料的图案计算。该 BNC 图案可以通过 LOSS 程序与模拟 Ni 峰和对应于 Pt 样品载体的模拟峰一起拟合。

[0415] TPR-MS 和 TPD-MS 测量

[0416] 使用可以如下的测试条件进行程序升温反应质谱 (TPR-MS) 和 / 或程序升温解吸反应质谱 (TPD-TPR MS) 研究：

[0417] 测试条件 TPD-MS (参见图 3B)：

[0418] Ar 平衡 ( $20\text{cm}^3\text{min}^{-1}$ , > 99% Ar, BOC)

[0419] 总流动速率 =  $20\text{cm}^3\text{min}^{-1}$

[0420] 内标 = Ar ( $m/z=36$ )

[0421] 催化剂质量 = 50-60mg

[0422] 速率 =  $15^\circ\text{C min}^{-1}$

[0423] 测试条件 TPR-MS (参见图 3C)：

[0424] 10%  $\text{H}_2$  ( $2\text{cm}^3\text{min}^{-1}$ , > 99%  $\text{H}_2$ , BOC)

[0425] Ar 平衡 ( $18\text{cm}^3\text{min}^{-1}$ , > 99% Ar, BOC)

[0426] 总流动速率 =  $20\text{cm}^3\text{min}^{-1}$

[0427] 内标 = Ar ( $m/z=36$ )

[0428] 催化剂质量 = 50-60mg

[0429] 速率 =  $15^\circ\text{C min}^{-1}$

[0430] 分析结果和讨论

[0431] 在表 2 中给出的八个 BNC 样品向镍金属粉末的转化过程中收集数据以评价哪一个 BNC 样品具有合适的或不适合的用于至零价镍 / 二齿亚磷酸酯配体配合物有效转化的性质。例如,这种数据可以提供另外的关于变量如微晶平均尺寸和 SSA (BET 和 LD) 如何影响镍制备物形成可溶零价镍 - 配体配合物的能力的信息。

[0432] 在 BNC 至 Ni 粉末的转化过程中,必须采用还原,但是煅烧是在还原步骤之前任选的。煅烧可以通过本领域中已知的通常方式,如在如上所述的流化床反应器、旋转炉等中进行。

[0433] 在八个 BNC 样品的每一个的煅烧过程中 (参见表 1、2 和 3) 并且在转化为颗粒 Ni 样品之后收集数据以评定产物作为活性 Ni 组合物的适用性。发现样品 2、5、7 和 8 为如本文所定义的适合用于与配体如与二齿亚磷酸酯配体形成的配合物的活性 Ni (表 3),而发现样品 3、4 和 6 是不适合的,并且不满足本文对于本发明的 Ni 粉末定义的关于 SSA 和微晶平均尺寸的结构 / 官能化标准。

[0434] 图 1 显示表 2 中列出的八个 BNC 样品的每一个在煅烧温度在氩气氛中在所指出的温度范围内的程序加热解吸扫描,其中通过质谱检测  $\text{CO}_2$ 。TPD (也称为 TDS) 包括加热样品的同时,样品被包含在真空中并且在真空中通过质量分析仪的方式同时检测残留气体。随着温度升高,特定吸附的物种将具有足够的逃逸能量并且将作为对于特定质量的压力升高

检测。

[0435] 图 1 显示在煅烧过程中无活性 BNC#3 释放大量的  $\text{CO}_2$ ，而活性 BNC 样品 5 和 7 在煅烧过程中释放最少量的  $\text{CO}_2$ 。由 BNC#2、5、7 和 8 制备的活性 Ni 样品也倾向于具有比由无活性 BNC 样品 #3、4 和 6 制造的无活性镍样品更小的微晶平均尺寸（例如，小于约 30nm）。这些数据表明更容易地煅烧的 BNC 样品至少在一些情况下可以产生具有好的活性和所需的结构特征的 Ni 颗粒形式。

[0436] 经由氢化的进一步处理示例活性 Ni 相对于无活性 Ni 的另外特征。这种氢化将 BNC（或者 NiO，条件是采用煅烧预处理）还原为 Ni 金属。

[0437] 图 2 和 3 显示分别在产生无活性 Ni 的前体的处理中和产生活性 Ni 的前体处理中观察到的完全不同的氢吸收曲线。

[0438] 如在图 2 中可以看出的，在还原后产生无活性 Ni 样品的表 2 的 BNC 样品 #3、4 和 6 展现不同尺寸的两个最大氢吸收的清楚图案，较小的在  $300^\circ$  附近的最大吸收并且较大的在  $400^\circ\text{C}$  附近的最大吸收。

[0439] 相反，图 3A 显示对于表 2 的在还原之后产生活性 Ni 样品的 BNC 样品 #2、5、7 和 8，氢吸收相对升高的温度的图。通过煅烧 BNC 样品 #2、5、7 和 8 的氢吸收图在约  $400\text{--}450^\circ\text{C}$  展现单个变宽的最大氢吸收。该图案不同于观察到两个吸收峰的图 3A 中对于煅烧 BNC 样品 #3、4 和 6 展现的氢吸收的图案。因此，在 BNC 对处理条件的响应与所制备的 Ni 的颗粒形式的活性之间存在相关性。

[0440] 外露层 BNC 样品 #1 是也用于制备具有下面的表 4 所示性质的 Ni1 的最低活性样品。如图 3A 中给出的，当将 BNC 样品 #1 还原时观察到双最大氢吸收，并且这种还原在比对于 BNC 样品 #2、5、7 和 8 观察到的最大温度稍微低的温度出现。对于 BNC#1 观察到的两个最大值也在大约相同的高度。

[0441] 在还原步骤之后，对所得到的含有 Ni 的金属产物进行分析，以对于各种样品检查微晶尺寸分布。例如，程序化升温的 X 射线衍射（TP-XRD）提供显示对于八个 BNC 产物的每一个的基于 Ni (111) 的 Ni 微晶尺寸分布的数据。

[0442] 图 4-11 显示分别通过 BNC 样品 #1-8 的氢还原获得的 Ni 金属颗粒形式的 TP-XRD 数据，如上面在表 2 中所述。温度轴显示在氢化过程中施加的升高温度的进行，微晶尺寸轴显示如这些数据中通过 XRD 测定的微晶尺寸，并且体积-%轴显示每块样品中的各种微晶尺寸等级的体积分布。样品计数对应于表 2 中给出那些。

[0443] 如所示的，活性样品 #2、5、7 和 8 一致地显示在整个处理中比无活性样品 #3、4 和 6 存在更小的微晶。被认为是最佳边际活性的样品 #1 比活性镍样品 #2、5、7 和 8 展现中心在约 30nm 的更大的微晶。样品 #2、5、7 和 8 全部一致地展现中心在约 20-25nm 的更小的微晶群，其中重要分数为 10nm 以下。相反，无活性样品 #3、4 和 6 都由显著大的微晶组成，平均约 40-50nm，具有小于约 20nm 的尺寸的非常小材料存在。应当记住的是这些数据是指微晶尺寸，而不是实际 Ni 粒子的尺寸，其在尺寸上为数微米至数十微米的级别。每个分立的 Ni 粒子由很多微晶组成。如本文所使用的，“尺寸”是平均直径。微晶是其中相邻的微晶不超过该有序，但是具有它们自己的内部有序的局部晶体有序区域。

[0444] 图 12 显示由 BNC#8 制备的镍样品中的微晶尺寸分布（CSD）。CSD 范围是微晶尺寸分布（CSD）的宽度，其中微晶尺寸通过 TP-XRD 获得并且 CSD 作为  $(\text{C90-C10})/\text{C50}$  计算，其

中  $C_x$  是  $x\%$  的用于微晶的样品具有更小的尺寸时该微晶的尺寸（例如， $C_{90}$  尺寸是 Ni 微晶的平均直径的长度（以纳米计），其中块状样品中 90% 的 Ni 微晶具有小于所述值的尺寸）。

[0445] 图 13 显示对于由表 2 的八个 BNC 样品制备的全部一组八个 Ni 粉末样品的微晶尺寸分布（CSD）范围数据。如显见的，这些样品基于微晶尺寸分布范围的数值又落入“活性”和“无活性”，即，“镍活性”和“无镍活性”的两个组。大于 1，或大于 1.5 的 CSD 范围通常是活性镍的指示。随着还原温度升高，CSD 变得更窄。约 300–400°C 的还原温度产生具有好的 CSD 范围的还原的镍制备物。在该研究中，所发现的是 BNC 预煅烧对 CSD 范围不具有主要的影响。

[0446] 图 14 显示  $C_{10}$ （以微米计的尺寸，在所述尺寸时 10% 的微晶具有小于所述值的尺寸）与样品的镍活性之间的关系。应注意这些数据是指微晶尺寸，而不是离散镍粒子的尺寸。再次显见的是图 14 所示的活性 Ni 样品相对无活性样品的分组反映在  $C_{10}$  值的分组中。本发明的 Ni 颗粒形式可以具有小于约 10nm 的  $C_{10}$  值。具有大于约 10nm 的  $C_{10}$  值的镍样品可以不是作为本文使用的术语的活性镍材料。如本文讨论的，还原温度可以影响微晶尺寸的分布。通常，约 300–400°C 的还原温度范围可以产生具有所需的  $C_{10}$  值的镍样品。

[0447] 图 15A–D 显示本发明的镍颗粒形式的各种样品的 SEM 照片。在粒子的物理结构上没有发现突出的特征，显示组合物的高度镍活性性质由物质的分子或大分子特征提供。不希望束缚于理论，本文的发明人相信该特征涉及镍粒子的表面上微晶边缘的可及性，因为据信边缘例如与溶液中的配体的反应性比平面微晶面更好。更高数目的表面微晶可以与可用于接近溶液中配体分子的微晶边缘的更高比例丰度相关联。

[0448] 实施例 4：BNC 样品和由其得到的 Ni 的进一步分析

[0449] 如下面讨论那样进一步评价所选择的 BNC 样品。

[0450] 用于 Ni 粉末的制造的一般步骤

[0451] 多种 BNC 样品作为用于镍制备物的原材料进行测试。对除了用以产生表 4 中的 Ni1 的 BNC 之外的 BNC 样品进行煅烧预处理，之后在所指定的温度用水蒸气还原。将至反应管的氢气体流量设定在 0.2 升 / 分钟（约一个大气），其中来自反应管的任何氢排放气体流动通过喷水口（bubbler）。之后将管式炉的温度以 10°C / 分钟的速率增加至 400°C 的最终温度，并且之后在 400°C 保持一小时，在其之后，允许反应管在氢流下冷却。在反应管温度落在 50°C 之下之后，将通往反应管的流转换为氮气以使氢从反应管排放。之后将反应管上的阀关闭以防止所得到的含镍固体暴露于空气中，并且将整个反应管转移至填充氮的干燥箱，在此将含镍固体排空至瓶中。该含镍固体含有镍金属，这通过它被吸引至磁体的观察所证实。这些含镍固体暴露于空气中的情况下可以减缓镍与配体（V）在 3PN 中的反应速率，和 / 或导致含镍固体燃烧。

[0452] 应注意，表 4 中的大部分 Ni1–Ni10 镍制备物由来自与如表 2 和 3 中所列出的那些相同的供应商的 BNC 样品获得，然而在来自这些供应商的 BNC 的组成上观察到显著的份额与份额之间，以及批次与批次之间的变化。因此，虽然表 4 中的 BNC 序号对应于表 2 和 3 中的 BNC 序号，并且显示相同的序号的 BNC 由相同的供应商获得，由相同的供应商获得的不同 BNC 批次通常具有不同的组成。

[0453] 使用与上面描述的那些相似的分析程序评价镍制备物。对于这些镍样品通过粒径分布分析测定  $D_{10}$  值。对于每一个 BNC 还原产物，通过本领域中可利用的两种方法，

BET SSA, 以及激光衍射 (LD) SSA 测定各个样品的比表面积 (SSA), 即, 每单位质量的表面积。激光衍射比表面积 (LDSSA) 和粒径分布 (PSD) 用来自 Malvern Instruments Ltd 的 Mastersizer2000 粒径分析仪, 使用 Hydro2000MU 附件和水作为分散剂进行测量。氮吸附 BET 比表面积 (BET SSA) 使用 Tristar3000 氮吸附仪器、在将样品在真空中于 105℃ 过夜脱气而测量。多点 BET 测量使用 0.05–0.3P/P<sub>0</sub> 的分压范围进行。

[0454] 将碱式碳酸镍的样品根据上面描述的程序处理, 并且评价 C50、C10、CSD 范围 (微晶尺寸分布范围 = (C90–C10)/C50)、LD 和 BET SSA 值, 以及在 C50 和 C10 尺寸的每克表面微晶的数目, 以及如上所述镍关于可溶催化剂形成的镍活性。将所处理的镍样品标记为 Ni1–Ni10。

[0455] 分析结果和讨论

[0456] 表 4 总结了对于制备的 Ni 样品 Ni1–Ni10 的数据。可以在表 4 中看出的, 在 BET SSA 与活性之间存在强相关性。具有大于 1m<sup>2</sup>/gm 但小于 10m<sup>2</sup>/gm 的 BET SSA 的样品 Ni1 在活性上与样品 Ni5 相当, 标记为 1 的对照活性, 并且由如上所述的 BNC 样品制备并基于活性选择的七个镍样品 Ni2、Ni3、Ni6、Ni7–Ni9 和 Ni10) 显示镍与二齿亚磷酸酯配体 (V) 的反应性 (“镍活性”, 参见图 17C) 与 BET SSA 之间的密切相关性。

[0457] 与配体 (V) 在 3PN 中的反应中的 Ni 活性强相关的另一个因素是微晶尺寸、数目或表面积。来自氢–还原的 BNC, 或煅烧和还原的 BNC 的镍金属的每个粒子是数个微米以上级别。每个镍粒子也可以形成为镍金属微晶的聚集体, 换言之, 如下面描述和讨论的尺寸的局部晶体有序的区域。

[0458] 图 16A 显示对于七个镍活性样品 (Ni1–Ni3、Ni6 和 Ni8–Ni10) 在镍活性与平均每克微晶数目之间的相关性, 基于微晶的形状粗略为球体的假设, 使用以下公式计算球体微晶的数目:

[0459] # 表面球体微晶 =  $BET / 4 \pi (C_x / 2)^2$ 。

[0460] 图 16B 显示对于七个镍活性样品 (Ni1–Ni3、Ni6 和 Ni8–Ni10) 在镍活性与平均每克微晶数目之间的相关性, 基于微晶是基本上正方形截面, 即, 是立方体或立方形的假设。使用以下公式计算立方形微晶的数目:

[0461] # 表面立方形微晶 =  $BET / (C_x)^2$ 。

[0462] 因为镍已知为在单质状态下通常是采取面心立方密堆积阵列, 所以微晶是立方形的假设可以是更准确的。图 16A 因此表示根据如上所述标准 Scherrer 分析的结果, 而图 16B 基于由据信是立方堆积的 Ni 原子所采取的微晶形状再计算结果。

[0463]

表 4: 具有微晶尺寸, SSA 值, 表面微晶的数目, 以及 BET SSA / C50 比率的镍样品

| 来自 BNC<br>的镍               | C50<br>nm | C10<br>nm | 微晶<br>范围 | C50 SA<br>m <sup>2</sup> | C10 SA<br>m <sup>2</sup> | LD SSA<br>m <sup>2</sup> /g | BET SSA<br>m <sup>2</sup> /g | 表面立方形<br>的数目<br>C50/gm Ni | 表面立方形<br>的数目<br>C10/gm Ni | BET SSA<br>/ C50<br>x 10 <sup>9</sup> m/gm | 活性    |
|----------------------------|-----------|-----------|----------|--------------------------|--------------------------|-----------------------------|------------------------------|---------------------------|---------------------------|--------------------------------------------|-------|
| Ni1(BNC #1)<br>400C,<br>一步 | 28        | 19        | 0.6      | 7.84E-16                 | 3.61E-16                 | 0.123                       | 1.90                         | 2.42E+15                  | 5.26E+15                  | 0.07                                       | 1.09  |
| Ni2(BNC #1)<br>300C,<br>一步 | 19        | 11        | 1.14     | 3.61E-16                 | 1.21E-16                 | 0.123                       | 1.90                         | 5.26E+15                  | 1.57E+16                  | 0.10                                       | 2.00  |
| Ni3(BNC #2)<br>程序运行 13     | 26.5      | 9         | 2.02     | 7.02E-16                 | 8.10E-17                 | 1.320                       | 30.20                        | 4.30E+16                  | 3.73E+17                  | 1.14                                       | 10.20 |
| Ni4(BNC #3)<br>400C,<br>一步 | 44.5      | 40.5      | 0.37     | 1.98E-15                 | 1.64E-15                 | NA                          | NA                           | NA                        | NA                        | NA                                         | 0.06  |
| Ni5(BNC #3)<br>300C,<br>两步 | 30        | 16        | 0.9      | 9.00E-16                 | 2.56E-16                 | NA                          | NA                           | NA                        | NA                        | NA                                         | 1     |

[0464]

| 来自 BNC<br>的镍                | C50<br>nm | C10<br>nm | 微晶<br>范围 | C50 SA<br>m <sup>2</sup> | C10 SA<br>m <sup>2</sup> | LD SSA<br>m <sup>2</sup> /g | BET SSA<br>m <sup>2</sup> /g | 表面立方形<br>的数目<br>C50/gm Ni | 表面立方形<br>的数目<br>C10/gm Ni | BET SSA<br>/ C50<br>x 10 <sup>9</sup> m/gm | 活性   |
|-----------------------------|-----------|-----------|----------|--------------------------|--------------------------|-----------------------------|------------------------------|---------------------------|---------------------------|--------------------------------------------|------|
| Ni6(BNC #7)<br>化学程序运行<br>14 | 31        | 12        | 2.06     | 9.61E-16                 | 1.44E-16                 | 0.607                       | 12.90                        | 1.34E+16                  | 8.96E+16                  | 0.42                                       | 3.00 |
| Ni7                         | NA        | NA        | NA       | NA                       | NA                       | 0.469                       | 15                           | NA                        | NA                        | NA                                         | 6.29 |
| Ni8(BNC #8)<br>程序运行 12      | 35.5      | 12.5      | 1.75     | 1.26E-15                 | 1.56E-16                 | 0.832                       | 18.10                        | 1.44E+16                  | 1.16E+17                  | 0.51                                       | 3.35 |
| Ni9(BNC #8)<br>程序运行 16      | 32.5      | 12        | 2.06     | 1.06E-15                 | 1.44E-16                 | 0.808                       | 20.50                        | 1.94E+16                  | 1.42E+17                  | 0.63                                       | 5.24 |
| Ni10<br>(BNC #8)<br>400C 两步 | 29        | 10        | 1.63     | 8.41E-16                 | 1.00E-16                 | 0.707                       | 16.59                        | 1.97E+16                  | 1.66E+17                  | 0.57                                       | 5.40 |

[0465] 提供 BET SSA/C50(表 4) 的计算用于与镍活性比较。可以看出的是至少约 0.07x10<sup>9</sup> 或至少约 0.1x10<sup>9</sup>m/gm 的 BET SSA/C50 的比率提供 1 的最小的镍活性。更高的该

比率的值与更高的镍活性相关,并且最高的镍活性与  $0.5-1.0 \times 10^9 \text{m/gm}$  范围内的 BET SSA/C50 比率相关。

[0466] 图 17A 是显示 BET SSA 与 LD SSA 的相关性的图,而图 17B 是对于镍样品 Ni1、Ni3、Ni6-Ni8 和 Ni9 的 BET SSA 相对 D10 的图。图 17C 示例 BET SSA 与镍有效地与二齿亚磷酸酯配体 (V) 形成配合物的活性的密切相关性。

[0467] 图 18 图示了平均微晶尺寸 (MCS=C50) 相对如本文定义的镍活性,以及 C10 相对如本文定义的镍活性。对于这些计算,假设的是微晶的几何结构是基本上正方形界面,即立方体或立方形状。还注意到的是 BETSSA 与 Ni 的激光衍射 SSA 线性相关,参见图 17A。

[0468] 如图 18 所示,小于约 30nm 的平均微晶尺寸 (C50) 和小于约 20nm 的 C10 值通常与 1 以上的镍活性相关。为了获得更高的镍活性值,小的平均微晶尺寸并且尤其是小 C10 值是高度相关的。如可以在表 4 中看出的,达到约 10nm 的 C10 值提供具有更高镍活性的样品。图 19 显示镍样品的尺寸不大于 C10 值的表面微晶的数目与该样品的镍活性之间的相关性。

[0469] 原始 C50 值与镍活性之间的相关性表现为较弱。分别具有 44.5 和 30nm 的 C50 值,以及分别 40.5 和 16nm 的 C10 值的对照样品 Ni7 和 Ni8 显示最低镍活性。具有 28nm 的 C50 和 19nm 的 C10 的样品 Ni1 具有稍微更高的镍活性。在更大幅度的镍活性,C10 值稳定地变得更小,但 C50 值相对是常数。图 17C 显示对于相同的镍样品 BET SSA 与镍活性的相关性。对于七个样品 Ni1-Ni3、Ni6、Ni8、Ni9 和 Ni10 在增加的 BET SSA 与镍活性之间观察到相关性。

[0470] 这些数据显示镍活性通过更低的 C10 值,更大的 BET SSA 值,更大的每克表面微晶数目,以及更大的具有 D10 以下尺寸的粒子数目而增加。

[0471] 在表 4 中,对于七个活性样品 Ni1-Ni3、Ni5-Ni6 和 Ni9-Ni10 的每一个计算 BET SSA 除以 C50 的比率。该比率可以看作是将 SSA 对于所研究的范围内的微晶尺寸归一化。显然的是在 SSA/C50 比率与镍活性之间存在强相关性,以使得 BET SSA/C50 的比率为不小于约  $0.07 \times 10^9 \text{m/gm}$ ,或至少  $0.1 \times 10^9 \text{m/gm}$ ,或至少约  $0.4 \times 10^9 \text{m/gm}$  的镍金属颗粒组合物是具有好的活性的镍颗粒形式的指示。具有非常好的活性的镍颗粒形式可以具有高达约  $1.0 \times 10^9 \text{m/gm}$  的 BET SSA/C50 比率。它们应当被制备成具有更高的 BET SSA/C50 值的样品预期具有还更高的作为本文使用的术语的镍活性,即,关于与含磷配体在有机介质中形成可溶零价镍催化剂配合物的活性。

[0472] 图 20 使用表 4 中对于每个具有至少 1 的如本文定义的活性的镍样品给出的数据,图示了镍活性与 BET SSA/C50 之间的强相关性。

[0473] 同样,发现通过 BET 和 LD 方法测定的 SSA 值具有约 23.46 的基本上恒定的比率。因此,可以使用大于约  $(0.1/23.46) \times 10^9 \text{m/gm} = 0.0043 \times 10^9 = 4.3 \times 10^6$  的 LD SSA/C50 的比率来指示本发明的镍组合物,所述镍组合物具有适合用于与二齿镍-亚磷酸酯零价配合物的有效催化剂制备物的镍活性。

[0474] 实施例 5:不适合用于制备活性镍的镍前体

[0475] 分析按从各种商业源接收的镍和氧化镍样品,以如实施例 1 中描述确定它们的硫含量,以及它们与配体 (V) 形成配合物的活性。

[0476] 在这种分析之后,将 10 克的这些商业源的镍金属和氧化镍装载至流化床反应器中,在氮流下加热至  $400^\circ\text{C}$  达 1h 并且在  $400^\circ\text{C}$  用  $\text{N}_2$  中的 20%  $\text{H}_2$  还原 2h。之后将所得到的还

原镍粉末转移至 N<sub>2</sub> 吹扫的手套箱中, 并且使用实施例 1 中描述的测定再次分析与配体 (V) 的配合物形成, 平均微晶尺寸 (MSD) 和 BET 表面积。

[0477] 结果在表 5 和 6 中给出。

[0478]

表 5: 商业 NiO(样品 C)和 Ni 粉末(样品 A、B 和 D)

| 供应商代码        | 组成*                  | Ni <sup>a</sup> 中的<br>ppm S | Ni 的 BET SSA <sup>b</sup> ,<br>m <sup>2</sup> /g | Ni MCS <sup>c</sup> ,<br>nm | 活性还原 Ni | 活性未还原的 Ni <sup>a</sup> |
|--------------|----------------------|-----------------------------|--------------------------------------------------|-----------------------------|---------|------------------------|
| A (Ni)       | 99% Ni               | 1                           | 0.33 <sup>a</sup>                                | 102                         | 0.01    | 0                      |
| B (Ni)       | 98-99% Ni            | 1                           | 1.63 <sup>a</sup>                                | -                           | 0.51    | 0.01                   |
| C (NiO)      |                      | 110                         | 10.2                                             | 35.6                        | 0.48    | 0.48                   |
| D (Ni / NiO) | 30-90% Ni;<br>余量 NiO | 200                         | 53.60 <sup>a</sup>                               | -                           | 0.24    | 0.03                   |

\*组成来自供应商提供的材料安全性数据表;  
<sup>a</sup>数据是对于按从供应商接收的镍材料;  
<sup>b</sup>BET SSA 是上面更详细地描述的镍粒子表面积测量;  
<sup>c</sup>MCS 是上面更详细地描述的平均微晶尺寸(C50)。

[0479]

表 6: 商业碱式碳酸镍,  $\text{Ni}(\text{CO}_3)_x(\text{OH})_y(\text{H}_2\text{O})_z$

| BNC 供应商 <sup>a</sup> | BNC 组成 <sup>b</sup> |       |                   |                 |                           | 还原 Ni 性质   |                            |                        |      |
|----------------------|---------------------|-------|-------------------|-----------------|---------------------------|------------|----------------------------|------------------------|------|
|                      | %CO <sub>3</sub>    | %Ni   | %H <sub>2</sub> O | ppm S           | S/Ni 比率 x10 <sup>-4</sup> | Ni 中 ppm S | BET SSA, m <sup>2</sup> /g | Ni MCS <sup>c</sup> nm | 活性   |
| BNC #1               | 19.50               | 42.08 | 30.27             | 212             | 9.22                      | -          | 2.50                       | 28                     | 1.00 |
| BNC #2               | 21.89               | 43.83 | 21.29             | 400             | 16.7                      | 400        | 11.00                      | 25                     | 0.22 |
| BNC #2               | 20.78               | 41.64 | 25.23             | 300             | 13.2                      | 200        | 12.70                      | 15                     | 1.98 |
| BNC #2               | 22.70               | 50.01 | 11.18             | 400             | 14.6                      | 500        | 11.40                      | 19                     | 0.91 |
| BNC #2               | 26.06               | 40.17 | 25.27             | 300             | 13.7                      | 700        | 11.80                      | 31                     | 0.23 |
| BNC #2               | 33.75               | 49.1  | 10.90             | 400             | 14.9                      | 700        | 10.00                      | 82                     | 0.39 |
| BNC #3               | 32.00               | 45.33 | 19.49             | 5               | 0.20                      | -          | -                          | 34                     | 0.07 |
| BNC#4                | 24.51               | 46.16 | 21.91             | 7               | 0.28                      | -          | 0.80                       | 32                     | 0.05 |
| BNC #6               | 28.00               | 45.53 | 21.45             | 10              | 0.40                      | -          | -                          | 41                     | 0.50 |
| BNC# 11              | 26.28               | 47.26 | 13.97             | nd <sup>d</sup> | -                         | -          | -                          | -                      | 0.50 |

<sup>a</sup> 对应于表 2-4 中列出的相同的 BNC 供应商的 BNC 供应商序号; BNC #11 是 BNC 的新供应商;

<sup>b</sup> 对于按从供应商收到的样品的数据;

<sup>c</sup> MCS 是上面更详细地描述的平均微晶尺寸(C50);

<sup>d</sup> nd: 未检测。

[0480] 应注意 BNC 样品 #1 是 MetChem BNC。在 400℃还原之后,该 MetChem BNC 产生具有 1.00 的相对活性的镍金属制备物。由 MetChem BNC 产生的镍金属具有在 60℃为 317ppm/

hr 并且在 80°C 为 980ppm/hr 的初始溶解速率 (4% 镍负载)。

[0481] 实施例 6 :用于制备活性镍的合适的前体和方法

[0482] A. 由含有硫杂质的各种商业镍原材料制备活性镍

[0483] 检查各种可商购的镍原材料如碱式碳酸镍和甲酸镍的性质以评价哪个性质与好的镍 - 配体配合物形成相关联。

[0484] a) 碱式碳酸镍 (BNC) : $\text{Ni}(\text{CO}_3)_x(\text{OH})_y(\text{H}_2\text{O})_z(\text{SO}_4)_q$ 。

[0485] 分析来自各种商业源的碱式碳酸镍 (BNC ; $\text{Ni}(\text{CO}_3)_x(\text{OH})_y(\text{H}_2\text{O})_z(\text{SO}_4)_q$ ) BNC 通过将十克的 BNC 样品装入至流化床反应器中,将反应器在氮流下加热至 400°C 历时 1h 并且将样品在 400°C 用  $\text{N}_2$  中的 20%  $\text{H}_2$  还原 2h。之后将所得到的还原镍粉末转移至  $\text{N}_2$  吹扫的手套箱中并且使用实施例 1-4 中描述的镍 - 配体配合物形成以及其他测定进行评价。结果在表 7a 中给出。

[0486]

表 7a: 用于制备活性镍-配体催化剂的 BNC 源的性质

| BNC 供应商 | BNC 组成 <sup>a</sup> |       |                   |       |                              | Ni 组成 |                                             | 还原 Ni 性质                      |               |       |
|---------|---------------------|-------|-------------------|-------|------------------------------|-------|---------------------------------------------|-------------------------------|---------------|-------|
|         | %CO <sub>3</sub>    | %Ni   | %H <sub>2</sub> O | ppm S | S/Ni 比率<br>x10 <sup>-4</sup> | ppm S | 通过 XRD 的<br>%Ni <sub>3</sub> S <sub>2</sub> | BET SSA,<br>m <sup>2</sup> /g | Ni MCS,<br>nm | 活性    |
| BNC #8  | 22.39               | 47.74 | 17.18             | 2505  | 96                           | 5500  | 0.90                                        | 4.70                          | 50            | 7.96  |
| BNC #8  | 24.57               | 46.25 | 17.90             | 3162  | 125                          | 5300  | 0.80                                        | 4.30                          | 38            | 8.66  |
| BNC #8  | 23.44               | 47.3  | 17.52             | 3797  | 147                          | 8200  | 2.30                                        | 4.60                          | 48            | 10.11 |
| BNC #8  | 22.19               | 47.15 | 18.24             | 4674  | 181                          | 8600  | 3.10                                        | 3.45                          | 51            | 6.31  |
| BNC #7  | 16.75               | 40.97 | 27.31             | 18760 | 838                          | 26800 | 13.50                                       | 12.90                         | 31            | 9.00  |
| BNC #2  | 16.66               | 44.49 | 18.15             | 23930 | 985                          | 33700 | 12.50                                       | 9.20                          | 42            | 16.34 |

<sup>a</sup>对于按从供应商收到的样品的数据。

[0487] 表 7a 说明镍金属形成镍 - 磷配体配合物的能力涉及镍 (或用于制备镍金属的 BNC) 中硫的含量。

[0488] b) 甲酸镍二水合物 (NF) : $\text{Ni}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$

[0489] 通过将十克的这些 NF 样品装入至流化床反应器中并将样品在氮流下在不存在氢的情况下加热至 400℃ 历时 2h, 分析来自两个商业源的甲酸镍二水合物 ( $\text{Ni}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ , 称为 ‘NF’) 的组成。之后将所得到的镍粉末转移至  $\text{N}_2$  吹扫的手套箱中, 并且使用实施例 1-4 中描述的镍-配体配合物形成和其他测定进行评价。表 7b 提供结果。

[0490] 表 7b : 用于制备活性镍-配体催化剂的 NF 源的组成

[0491]

| NF 供应商 | NF 组成 <sup>a</sup> |                   |       |                          | 活性   |
|--------|--------------------|-------------------|-------|--------------------------|------|
|        | %Ni                | %H <sub>2</sub> O | ppm S | S/Ni 比率 $\times 10^{-4}$ |      |
| NF #1  | 32.12              | 21.88             | 575   | 32.8                     | 1.97 |
| NF #2  | 31.33              | 20.15             | 1300  | 75.9                     | 6.86 |

[0492] <sup>a</sup> 对于按从供应商收到的样品的数据。

[0493] 表 7b 中给出的结果指示也可以由含有硫杂质 (作为硫酸根离子) 的商业甲酸镍二水合物在不进行镍金属的还原 (例如, 没有氢还原) 的情况下热分解直接而制备活性镍。对于移除硫酸根离子杂质的方法, 参见 N. Minkova, M. Krusteva, V. Valiseva, D. Trendafelov, Communications of the Department of Chemistry, 第 222-228 页, 第 13 卷, 第 12 期, 1980。

[0494] 甲酸镍的使用与需要用氢的还原步骤以获得适合用于配体催化剂制备物的镍材料的商业 BNC 或 NiO 粉末的使用形成对比。

[0495] c) 用于通过从含有硫酸根杂质的 BNC 移除硫而制备去活的 Ni 的方法

[0496] 硫 (硫酸根离子) 从最初适合用于制备活性镍的 BNC 的移除产生不适合用于制备活性镍的 BNC。

[0497] 硫移除通过用 2.5% 碳酸钠溶液 (10 份碳酸盐溶液 / 1 份 BNC) 在 90℃ 洗涤含有痕量的硫酸根离子的 BNC 达 2h 完成。在将混合物冷却至环境温度之后, 将所得到的脱硫的 BNC 使用真空抽吸过滤至纸上并在空气中在 80℃ 在烘箱中干燥 20h。之后使用实施例 1 中描述的方法分析样品中硫、 $\text{CO}_3$ 、镍和水的含量。

[0498] 将十克的“脱硫的”BNC 样品装入至流化床反应器中, 在氮流下加热至 400℃ 达 1h 并在 400℃ 用  $\text{N}_2$  中的 20%  $\text{H}_2$  还原 2h。之后将所得到的还原镍粉末转移至  $\text{N}_2$  吹扫的手套箱中并使用实施例 1-4 中描述的镍-配体配合物形成和其他测定进行评价。

[0499] 表 7c 显示硫移除之前和之后 BNC#8 的组成。如所给出的, 当将 BNC 中的硫含量减少时, Ni 的活性显著地降低。

[0500]

表 7c: BNC#8 的组成及其在 S 移除之前和之后相应的 Ni 活性

| BNC 供应商                               | BNC 组合物 <sup>a</sup> |       |                   |       |                              | Ni 组合物 |                                             | 还原 Ni 性质                      |               |      |
|---------------------------------------|----------------------|-------|-------------------|-------|------------------------------|--------|---------------------------------------------|-------------------------------|---------------|------|
|                                       | %CO <sub>3</sub>     | %Ni   | %H <sub>2</sub> O | ppm S | S/Ni 比率<br>x10 <sup>-4</sup> | ppm S  | 通过 XRD 的<br>%Ni <sub>3</sub> S <sub>2</sub> | BET SSA,<br>m <sup>2</sup> /g | Ni MCS,<br>nm | 活性   |
| BNC #8,<br>按收到<br>BNC #8,<br>在 S 移除之后 | 24.57                | 46.25 | 17.90             | 3162  | 125                          | 5300   | 0.80                                        | 4.30                          | 38            | 8.66 |
|                                       | 20.17                | 53.90 | 10.10             | 698   | 23.7                         | 1100   | 0.36                                        | 2.20                          | 43            | 0.03 |

<sup>a</sup>对于按从供应商收到的样品的数据。

- [0501] B. 用硫酸镍溶液制备活性镍的方法 – 商业碱式碳酸镍 (BNC) 的掺杂
- [0502] 将商业 BNC 用各种 NiSO<sub>4</sub> 的 1M 盐水溶液处理,该处理通过将 BNC 与盐以按重量计

1 : 5 的比率混合并将混合物在室温于空气中搅拌 15 分钟。之后将金属粉末使用真空抽吸过滤至纸上并且在空气中在 80℃ 在烘箱中干燥 20h。之后使用实施例 1 中描述的方法分析样品中硫、CO<sub>3</sub>、镍和水的含量。

[0503] 将干燥粉末的十克样品用钵和研杵缓慢地研磨以分散固体,将样品装入至流化床反应器中,之后在氮流下在 1h 内加热至 400℃ 并且在 400℃ 用 N<sub>2</sub> 气中 20% H<sub>2</sub> 还原 2h。之后将所得到的还原镍粉末转移至 N<sub>2</sub> 吹扫的手套箱中,并使用实施例 1-4 中描述的测定评价镍 - 配体催化剂制备物活性以及组成、BET SSA 和 MCS。

[0504] 在以下表 8 中给出的结果显示 BNC 用硫酸镍的处理提高了与含磷配体活性配合的镍的形成。

[0505]

表 8: BNC 样品用 1M 硫酸镍溶液的处理

| BNC 样品                            | BNC 组成           |       |                   |       |                           | 还原 Ni 组成 |                                             | 还原 Ni 性质                      |               |       |
|-----------------------------------|------------------|-------|-------------------|-------|---------------------------|----------|---------------------------------------------|-------------------------------|---------------|-------|
|                                   | %CO <sub>3</sub> | %Ni   | %H <sub>2</sub> O | ppm S | S/Ni 比率 x10 <sup>-4</sup> | ppm S    | 通过 XRD 的<br>%Ni <sub>3</sub> S <sub>2</sub> | BET SSA,<br>m <sup>2</sup> /g | Ni MCS,<br>nm | 活性    |
| BNC #2<br>+ 1M NiSO <sub>4</sub>  | 15.97            | 47.83 | 14.79             | 34000 | 1301                      | 53000    | 18.00                                       | 10.9                          | 42            | 17.03 |
| BNC #2<br>+ 1M NiSO <sub>4</sub>  | 18.30            | 46.08 | 15.87             | 32000 | 1271                      | 66000    | 21.50                                       | 12.9                          | 92            | 19.53 |
| BNC #11<br>+ 1M NiSO <sub>4</sub> | 19.32            | 48.4  | 14.02             | 9880  | 373.6                     | 33000    | 8.60                                        | 16.6                          | 31            | 10.42 |
| BNC #4<br>+ 1M NiSO <sub>4</sub>  | 20.66            | 46.6  | 18.49             | 12775 | 501.8                     | 31200    | 13.10                                       | 2.6                           | 66.5          | 6.36  |

[0506] 进行另外的实验以优化结合至 BNC 样品中的硫酸盐。将可商购的碱式碳酸镍 (BNC#11) 加入至一系列 0.01-1M 硫酸镍溶液。BNC 与 NiSO<sub>4</sub> 比率为约 5。将 BNC 固体在硫

酸镍溶液中制浆并搅拌约 15-30 分钟。进行另外的实施例,其中使用水代替硫酸镍溶液。之后将所得到的固体从溶液过滤并在真空下在 80℃干燥过夜。之后将固体在 400℃在马弗炉中在空气下煅烧以制备氧化镍。

[0507] 之后将氧化镍用 30% 氢在如前所述的流动反应器条件下还原以给出还原镍。将镍在不暴露至空气的情况下转移至镍催化剂制备物装备中。通过实施例 1 中描述的镍-配体配合物形成测定测量镍相对时间的溶解,以测定镍溶解的活性。如在下表中指出的,随着硫酸镍浓度从 0.01M 升高至 0.05M,镍活性从 1.4 跳跃至大于 8。

[0508] 表 9 :BNC 用硫酸镍的处理

[0509]

| BNC 样品                         | Ni 中 % S (wt % ) | Ni 活性 |
|--------------------------------|------------------|-------|
| BNC#11                         | 0.0%             | 0.5   |
| BNC#11, 水洗的                    | 0.12%            | 0.5   |
| BNC#11+0.01M NiSO <sub>4</sub> | 0.30%            | 1.4   |
| BNC#11+0.05M NiSO <sub>4</sub> | 0.88%            | 8.2   |
| BNC#11+0.10M NiSO <sub>4</sub> | 1.37%            | 7.5   |
| BNC#11+1.00M NiSO <sub>4</sub> | 2.60%            | 8.7   |

[0510] C. 通过 BNC 的硫酸镍掺杂制备的活性镍随时间并且经过配体形成的数个循环保持活性

[0511] 可商购的 BNC (BNC#11) 通过使用硫酸镍掺杂有硫。将 BNC-硫酸镍混合物在 400℃用氮中的 10-30% 氢煅烧并还原。使用实施例 1 中描述的镍-催化剂制备物测定,测试所得到的镍的溶解和配合物形成。在首先用配体溶解镍之后,将溶解的镍-配体催化剂倾析,留下未溶解的 / 未反应的镍。再次对未溶解的镍测试其溶解和与配体形成配合物的活性。将这重复总共 4 次以检查活性的变化并确定在一次或多次溶解之后在活性上是否存在减少。原材料中硫的量为基于镍的 2.6 重量%。

[0512] 表 10 :硫的存在改善镍配合物形成

[0513]

| BNC #11 样品                     | 开始溶解时的镍(g) | 活性   |
|--------------------------------|------------|------|
| BNC #11                        | 3.20       | 0.5  |
| BNC #11+ 2.6% S                | 3.22       | 8.71 |
| BNC #11+ 2.6% S<br>– 第一次配合物形成  | 3.01       | 8.55 |
| BNC #11 + 2.6% S<br>– 第二次更新    | 2.81       | 7.00 |
| BNC #11 + 2.6% S<br>– 第三次配合物形成 | 2.60       | 8.57 |
| BNC #11+ 2.6% S<br>– 第四次配合物形成  | 2.40       | 7.10 |

[0514] D. 用于通过商业 NiO (样品 C) 或涂布 NiO 的 (钝化的) 镍 (样品 D) 的掺杂由 NiSO<sub>4</sub> 溶液制备活性镍的方法

[0515] 将预先评定为无活性 (参见实施例 5) 的可商购的 NiO 或涂布 NiO 的镍样品与 1M NiSO<sub>4</sub> 水溶液以重量计 1 : 5 的比率混合并且在室温在空气中搅拌 15 分钟。之后使用真空抽吸将粉末过滤至纸上并且在空气中、80℃在烘箱中干燥 20h。将所得到的粉末 (~ 10g) 用钵和研杵轻轻地研磨以分散固体。之后将研磨的粉末装入至流化床反应器中, 在氮流下加热至 400℃并且用 20% H<sub>2</sub> 在 N<sub>2</sub> 中在 400℃直接还原 2h。之后将所得到的还原镍粉末转移至 N<sub>2</sub> 吹扫的手套箱中并如实施例 1 中所述评价镍 - 配体催化剂制备物活性。

[0516] 表 11 : 低活性镍源通过 NiSO<sub>4</sub> 处理改善

[0517]

| NiO 样品                   | Ni 组成 |                                             | 还原 Ni 性质                      |               | 活性    |
|--------------------------|-------|---------------------------------------------|-------------------------------|---------------|-------|
|                          | ppm S | 通过 XRD 的<br>%Ni <sub>3</sub> S <sub>2</sub> | BET SSA,<br>m <sup>2</sup> /g | Ni MCS,<br>nm |       |
| C + 1M NiSO <sub>4</sub> | 7155  | 2.90                                        | 11.20                         | 31            | 6.74  |
| D + 1M NiSO <sub>4</sub> | 25000 | 7.4                                         | 24.70                         | 39.0          | 11.32 |

[0518] E. 通过碱式碳酸镍和其后来的氧化镍的单质硫掺杂制备活性镍的方法

[0519] 测试可商购的 BNC#1 以评价硫 (例如, 而不是硫酸盐) 是否可以激活其中的镍以提高与含磷配体的配合物形成。

[0520] 测试 BNC#1 的三个等分试样 (#1A、#1B 和 #1C)。将约 35g 的 BNC#1A 与 0.16g 的单质硫 (基于镍的 1 重量%) 混合。将混合物在 400℃在马弗炉中在空气下煅烧为氧化镍。将氧化镍 / 硫粉末在 400℃用氮气混合物中的 30% 氢还原 2 小时。在实施例 1 中描述的标

准催化剂制备物条件下评价还原镍的活性。

[0521] 将另一个BNC样品(BNC#1B)首先煅烧以形成氧化镍。之后将氧化镍用1%单质硫(基于镍)掺杂并在400°C用30%氢在氮气混合物中进一步还原2小时。

[0522] 最终,将第三BNC#1C样品煅烧并在400°C使用上述条件在没有任何硫加入的情况下还原。在实施例1中描述的镍-配体配合物形成测定下测量所有还原镍样品的活性。

[0523] 具有硫的MetChem镍的活性是不掺杂有单质硫的镍的6倍高。

[0524] 表12:使用单质硫活化镍

| [0525] | BNC #1 样品                    | 最终的镍中的% S (wt %) | 活性  |
|--------|------------------------------|------------------|-----|
|        | BNC #1A+ 1% 单质 S             | 待测               | 5.8 |
|        | BNC #1B → 氧化镍,<br>之后+ 1%单质 S | 0.95%            | 6.1 |
|        | BNC #1C (没有加入硫)              | 0.12%            | 1.3 |

[0526] F. 通过用单质硫掺杂商业源的氧化镍而活化镍的方法:产物镍的比较操作和无效果实例

[0527] 将各种商业氧化镍的二十克样品与约0.16g的单质硫(基于镍的1重量%)混合并在400°C在10-30% H<sub>2</sub>/N<sub>2</sub>的流动下还原数小时直至材料完全被还原。之后将还原镍溶解成实施例1中描述的镍-配体配合物形成测定混合物,并且测定溶解物的活性。

[0528] 将20g氧化镍样品用10-30% H<sub>2</sub>/N<sub>2</sub>在400°C分别还原数小时以获得未用硫处理的还原镍。

[0529] 使用催化剂制备物测定测定镍产物的活性。

[0530] 表13:氧化镍用硫的外理提高了还原的镍活性

[0531]

| 氧化镍样品            | % S (wt %) | 表面积 (m <sup>2</sup> /g) |      | 活性   |
|------------------|------------|-------------------------|------|------|
|                  |            | 氧化镍                     | 镍    |      |
| NiO 样品 E         | 0.12%      | 4.8                     | 待测   | 1.31 |
| NiO 样品 E+ 1% S   | 0.95%      | 4.8                     | 2.8  | 6.07 |
| NiO 样品 F         | 0.17%      | 52.7                    | 待测   | 1.27 |
| NiO 样品 F+ 1% S   | 待测(tbd)    | 52.7                    | 5.14 | 8.04 |
| NiO 样品 F+ 1.6% S | 1.62%      | 52.7                    | 5.14 | 9.01 |
| NiO 样品 G         | 0.05%      | 0.77                    | 待测   | 0.10 |
| NiO 样品 G+ 1% S   | 0.5%       | 0.77                    | 1.47 | 2.96 |
| NiO 样品 H         | 0.05%      | 81.2                    | 待测   | 0.54 |
| NiO 样品 H+ 1% S   | 1.04%      | 81.2                    | 1.4  | 4.63 |
| NiO 样品 I         | 0.22%      | 7.6                     | 待测   | 3.35 |
| NiO 样品 I+ 1% S   | 0.74%      | 7.6                     | 4.0  | 6.96 |
| NiO 样品 J         | 0.16%      | 99.2                    | 待测   | 2.57 |
| NiO 样品 J+ 1% S   | 1.05%      | 99.2                    | 3.4  | 5.23 |

[0532] G. 镍的活性与还原镍的 BET 表面积相关

[0533] 实施例 6F 显示大约 1% 单质硫加入至氧化镍样品, 之后还原, 使得这些样品在催化剂-制备溶解测定中得到镍活性相比于其没有加入任何硫时的基准活性得到了提高。然而, 将表 13 中的所有数据关于 BET 表面积相对于活性作图, 这并没有对这些氧化镍样品提供有意义的相关性, 可能因为这些样品具有不同的硫含量和还原条件。

[0534] 然而, 如果将镍的还原条件和硫浓度保持为大约恒定, 则存在镍的活性与镍 BET 表面积之间有意义的相关性。因此, 将具有相似硫含量 (在该情况下 ~ 1%) 的氧化镍样品在相似的条件还原 (在这种情况下, 还原在 400°C 进行 2 小时)。图 21 显示这些镍样品的 BET 表面积与镍配合物形成活性相关。硫负载的程度一定程度上依赖于氧化镍的初始表面积。如果硫负载不恒定, 则活性将不与 BET 表面积良好相关, 因为硫含量在促进镍的活性中发挥主要作用, 而 BET SSA 发挥次要作用。

[0535] H. 还原温度影响单质硫掺杂镍的活性

[0536] 氧化镍样品 F 掺杂有 ~ 1% 单质硫 (基于镍) 并且在从 200 变化至 500°C 的温度还原。还原时间为 4 小时。所使用的氢的量为用于完成氧化镍的还原所需化学计量量的大约 20 倍。即使硫的量在所有这些情况下应当是相同的, 所观察的活性也是所使用的温度的函数。活性经过最优值, 其中在 300°C 的还原温度观察到最高值。下表显示温度的效果。

[0537] 表 14: 还原温度影响镍金属活性

[0538]

| 样品                | 温度 (°C) | % S (镍的重量%) | 活性   |
|-------------------|---------|-------------|------|
| NiO 样品 F (无 S 加入) | 400     | 0.17%       | 1.3  |
| NiO 样品 F+1% S     | 200     | 0.808       | 5.5  |
| NiO 样品 F+1% S     | 250     | 0.954       | 8.7  |
| NiO 样品 F+1% S     | 300     | 1.039       | 11.3 |
| NiO 样品 F+1% S     | 350     | 0.968       | 9.0  |
| NiO 样品 F+1% S     | 400     | 1.035       | 7.0  |
| NiO 样品 F+1% S     | 450     | 0.941       | 5.5  |
| NiO 样品 F+1% S     | 500     | 1.005       | 3.2  |

[0539] I. 用固体硫酸镍或硫化镍加入至商业碱式碳酸镍 (BNC) 中以制备镍的方法

[0540] 使用钵和研杵将商业 BNC 样品 (BNC#2) 与  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  或  $\text{Ni}_3\text{S}_2$  在空气中混合。之后将所得到的粉末 (~ 10g) 装入至流化床反应器中, 在氮流下加热至 400°C 历时 1h (对于 NiO 没有保留时间) 并且在 400°C 用  $\text{N}_2$  中的 20%  $\text{H}_2$  还原 2h。之后将所得到的还原镍粉末转移至  $\text{N}_2$  吹扫的手套箱中并且在实施例 1 中描述的镍-配体配合物形成测定中评价。

[0541] 表 15: 可以通过将各种形式的硫 (硫酸盐、硫化物) 加入至固体形式的 BNC 中以制备活性镍

[0542]

| 样品                                                      | BNC/NiO 组合物     |       |                        | Ni 性质 |       |
|---------------------------------------------------------|-----------------|-------|------------------------|-------|-------|
|                                                         | % $\text{CO}_3$ | %Ni   | % $\text{H}_2\text{O}$ | ppm S | 活性    |
| BNC #2 + 8.7% $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ | 27.68           | 46.77 | 13.52                  | 15413 | 15.76 |
| BNC #2 + 3.5% $\text{Ni}_3\text{S}_2$                   | 32.25           | 48.01 | 12.19                  | 18755 | 20.91 |

[0543] J. 在不进行热处理的情况下通过还原镍的硫掺杂制备活性镍的方法

[0544] 将约 20g 的氧化镍 (样品 E) 在 400°C 用 30%  $\text{H}_2/\text{N}_2$  还原数个小时, 直至将氧化物完全还原为镍。将约 2.5 重量% (基于镍) 的单质硫加入至还原镍中。之后通过在镍催化剂制备物测定中溶解, 测试产物的活性。还原相似的氧化镍并且测试在不存在硫的情况下金属的活性。

[0545] 将氧化镍的第二源与硫混合并且在实施例 1 中描述的镍-配体配合物形成测定中评价。

[0546] 表 16: 还原镍的硫活化

[0547]

| 样品                      | % S(wt%) | 表面积  | 活性  |
|-------------------------|----------|------|-----|
| NiO( 样品 E)              | 0.12%    | 待测   | 1.3 |
| NiO( 样品 E)+3.7% S       | 待测       | 待测   | 1.9 |
| NiO( 样品 F)= > Ni        | 0.17%    | 52.7 | 1.3 |
| NiO( 样品 F)= > Ni+2.5% S | 待测       | 52.7 | 4.3 |

[0548] 在另一个实验中,通过 NiO( 样品 F) 在 400℃的还原制备约 3.2g 的镍。将还原镍金属粉末在催化剂制备物测定中测试,其中将约 150-500ppm 的单质硫(基于催化剂制备物测定的总重量)直接加入至使用实施例 1 中描述程序的催化剂制备物测定混合物。

[0549] 表 17 :硫向镍催化剂制备混合物的直接加入

[0550]

| 样品                      | 催化剂制备物中的 S 量 (ppm) | 活性  |
|-------------------------|--------------------|-----|
| NiO( 样品 F)= > Ni        | 0                  | 0.5 |
| NiO( 样品 F)= > Ni+0.4% S | 150                | 2.8 |
| NiO( 样品 F)= > Ni+0.6% S | 250                | 3.1 |
| NiO( 样品 F)= > Ni+1.2% S | 500                | 4.0 |

[0551] 在另一个实验中,将 BNC#11 和 NiO( 样品 F) 在 400℃还原。将约 3.2g 的还原镍在镍催化剂制备物测定中测试。将硫酸镍的形式中约 10-150ppm 当量硫加入至实施例 1 中描述的催化剂制备物测定混合物中。

[0552] 表 18 :硫酸镍向镍催化剂制备混合物的加入

[0553]

| 样品                        | 得自 NiSO <sub>4</sub> 的当量 S (ppm) | 活性  |
|---------------------------|----------------------------------|-----|
| NiO( 样品 F)= > Ni          | 0                                | 0.5 |
| NiO( 样品 F)= > Ni+10ppm S  | 10                               | 0.7 |
| NiO( 样品 F)= > Ni+50ppm S  | 50                               | 1.3 |
| NiO( 样品 F)= > Ni+150ppm S | 150                              | 1.5 |
| BNC#11 → Ni               | 0                                | 0.5 |
| BNC#11 → Ni+150ppm S      | 150                              | 2.0 |

[0554] 在另一个实验中,将单质硫直接加入至含有镍金属的镍催化剂制备混合物。之后

将混合物加热至 60℃ 并且如实施例 1 中描述地进行测定程序。

[0555] 表 19 : 向镍 - 配体催化剂制备反应混合物的单质硫加入

|        | 样品                                   | 活性  |
|--------|--------------------------------------|-----|
| [0556] | Ni D + 基于 Ni 的 12%S <sub>8</sub>     | 1.1 |
|        | 再使用的 NiD + 基于 Ni 的 12%S <sub>8</sub> | 3   |

[0557] 应注意在表 5 中, 当不加入硫源时, Ni D 具有仅约 0.24 的活性。

[0558] K. 通过在镍 - 配体催化剂制备之前将单质硫 S<sub>8</sub> 与未还原的涂布 NiO 的 Ni 预混合并加热以提高镍活性的方法

[0559] 将单质硫与商业涂布 NiO 的 Ni 或钝化的 Ni 在烧瓶中、在戊烯腈溶液中混合或者纯粹作为固体混合物。将混合物搅拌, 同时在 110℃ 加热 24h。之后在实施例 1 中描述的镍 - 配体配合物形成测定中评价所得到的粉末 / 浆液。

[0560] 表 20 : 向镍 - 配体催化剂制备反应混合物的单质硫加入

[0561]

| 样品                                                    | 活性   |
|-------------------------------------------------------|------|
| 未还原的 NiB + 基于 3PN 中的 Ni 的 11%S <sub>8</sub>           | 0.92 |
| 未还原的 NiB + 基于 Ni 的 11%S <sub>8</sub> (固体混合物)          | 1.73 |
| 得自钝化 Ni 的 BNC #12 + 基于 Ni 的 12%S <sub>8</sub> (固体混合物) | 0.84 |

[0562] 还应注意的是, 如上面的表 5 中给出的, 未还原的镍样品 B 具有 0.01 的活性。

[0563] L. 通过羰基系镍的 S 掺杂制备活性镍

[0564] 将基于羰基系镍样品用硫处理, 所述处理或者通过用硫酸镍直接掺杂它们并热处理而进行, 或者通过用单质硫强制硫化处理而进行。

[0565] 在前一种情况下, 将样品镍 A 用 1M NiSO<sub>4</sub> 在搅拌下处理约 15-30 分钟。将溶液过滤以保持装载有硫酸镍的镍。之后将这些固体在真空下在 80℃ 干燥并且之后在 400℃ 进一步煅烧和还原。在还原形式中, 镍样品具有 0.49m<sup>2</sup>/g 的 BET 表面积。

[0566] 在首先溶解 / 形成配合物之后, 使用相同的镍催化剂制备混合物中的未溶解的镍连续进行四次加入溶解 / 形成配合物。

[0567] 表 21 : NiSO<sub>4</sub> 处理改进镍配合物形成

[0568]

| 镍样品 A                                    | % S (wt %) | 活性   |
|------------------------------------------|------------|------|
| Ni A                                     | 0.006      | 0.15 |
| Ni + 1 M. NiSO <sub>4</sub>              | 0.354      | 0.78 |
| Ni A+ 1 M. NiSO <sub>4</sub><br>第一次配合物形成 | 0.354      | 2.23 |
| Ni + 1 M. NiSO <sub>4</sub><br>第二次配合物形成  | 0.354      | 1.04 |
| Ni A+ 1 M. NiSO <sub>4</sub><br>第三次配合物形成 | 0.354      | 0.95 |
| Ni + 1 M. NiSO <sub>4</sub><br>第四次配合物形成  | 0.354      | 1.02 |

[0569] 将商业镍 K 和 L(原样)的样品在含有选择量的硫的己二腈(ADN)溶液在 110-120℃ 搅拌 24-48 小时。在表 21 中给出这些镍样品的活性。

[0570] 表 22 :硫处理提高了镍催化剂活性

[0571]

| Ni 样品         | 活性   |
|---------------|------|
| K             | 0    |
| K+1.25% S/ADN | 0.14 |
| K+31.3% S/ADN | 0.58 |
| L             | 0    |
| L+1.25% S/ADN | 0.12 |
| L+31.3% S/ADN | 0.78 |

[0572] 以下陈述意图描述本发明的一些方面。

[0573] 描述本发明的特征的陈述

[0574] 1. 一种产生镍氢氰化催化剂的方法,所述方法包括:

[0575] (a) 在来自镍金属的镍原子与一种或多种含磷配体形成配合物之前或过程中使镍金属与硫源接触从而形成所述镍氢氰化催化剂;或

[0576] (b) 将镍原材料与硫源接触,由所述镍原材料和所述硫源的混合物产生镍金属,并且将所述镍金属与一种或多种含磷配体接触,从而在来自所述镍金属的镍原子与一种或多种含磷配体之间形成配合物。

[0577] 2. 陈述 1 所述的方法,所述方法还包括在将所述镍金属或所述镍原材料与所述硫

源接触之前确定所述镍金属或所述镍原材料的硫含量。

[0578] 3. 陈述 2 所述的方法, 其中所述镍金属或所述镍原材料的硫含量使用红外 (IR) 光谱分析、微电量分析、感应耦合等离子体 (ICP) 质谱法或它们的组合测定。

[0579] 4. 陈述 2 或 3 所述的方法, 其中如果所述镍金属或所述镍原材料的硫含量为相对于所述镍金属或所述镍原材料的重量小于 0.2 重量%至 0.8 重量%, 则将所述镍金属或所述镍原材料与所述硫源接触。

[0580] 5. 陈述 2-4 中任一项所述的方法, 其中如果所述镍金属或所述镍原材料的硫含量相对于所述镍金属或所述镍原材料的重量小于 0.4 重量%, 则将所述镍金属或所述镍原材料与所述硫源接触。

[0581] 6. 陈述 1-5 中任一项所述的方法, 其中所述硫源选自由以下各项组成的组: 单质硫、含硫气体、含硫盐、含硫离子以及它们的组合。

[0582] 7. 陈述 1-6 中任一项所述的方法, 其中所述硫源是液体、固体、气体或这些物理形式的组合。

[0583] 8. 陈述 1-7 中任一项所述的方法, 其中所述硫源包括硫酸盐、亚硫酸盐、硫化物、次硫酸盐、硫代硫酸盐、三氧化硫、二氧化硫、一氧化硫、卤化硫, 以及它们的组合。

[0584] 9. 陈述 1-8 中任一项所述的方法, 其中所述硫源选自由以下各项组成的组: 硫的聚合物、硫的聚合链的混合物、环状硫、硫的一种或多种同素异形体, 以及它们的组合。

[0585] 10. 陈述 1-9 中任一项所述的方法, 其中所述硫源选自由以下各项组成的组: 硫化氢、硫酸镍、亚硫酸镍、硫化镍、连二亚硫酸镍、硫代硫酸镍、三氧化硫、二氧化硫、一氧化硫、二氯化二硫、二氯化硫、四氯化硫、一氯五氟化硫、十氟化二硫、六氟化硫、四氟化硫、三氟化硫以及它们的组合。

[0586] 11. 陈述 1-10 中任一项所述的方法, 其中所述硫源是含硫镍盐。

[0587] 12. 陈述 1-11 中任一项所述的方法, 其中所述硫源是至少 95%至 99.9%不含硅、钠、钾、钙、镁、磷、铝、铜、钨、汞、铁以及它们的组合。

[0588] 13. 陈述 1-12 中任一项所述的方法, 其中当所述镍金属或所述镍原材料是溶液或固体颗粒形式时, 所述硫源与所述镍金属或所述镍原材料接触。

[0589] 14. 陈述 1-13 中任一项所述的方法, 其中在所述镍金属或所述镍原材料在液体有机介质中或气体流中的悬浮之前或过程中, 所述硫源与所述镍金属或所述镍原材料接触。

[0590] 15. 陈述 1-14 中任一项所述的方法, 其中所述镍金属和 / 或所述镍原材料是至少 95%至 99.9%不含硅、钠、钾、钙、镁、磷、铝、铜、钨、汞、铁以及它们的组合。

[0591] 16. 陈述 1-15 中任一项所述的方法, 其中所述镍原材料是碱式碳酸镍、碳酸镍、碳酸氢镍、草酸镍、甲酸镍、方酸镍、氢氧化镍、氧化镍、镍盐或它们的组合。

[0592] 17. 陈述 1-16 中任一项所述的方法, 其中在煅烧所述镍原材料之前或之后, 将所述镍原材料与所述硫源接触。

[0593] 18. 陈述 1-17 中任一项所述的方法, 其中所述镍原材料或所述镍金属在还原成零价颗粒镍之前与所述硫源接触。

[0594] 19. 陈述 1-18 中任一项所述的方法, 其中还原在 200°C至 400°C持续约 3 至约 5 小时。

[0595] 20. 陈述 1-19 中任一项所述的方法, 其中在所述镍金属的还原之后或在所述镍原

材料至零价镍的还原之后,将所述镍金属或所述镍原材料与所述硫源接触。

[0596] 21. 陈述 1-20 中任一项所述的方法,其中约 0.1 重量%至约 50 重量%的重量百分比的硫与所述镍金属或所述镍原材料接触,其中所述硫重量百分比相对于所述镍金属或所述镍原材料中镍的总重量。

[0597] 22. 陈述 1-21 中任一项所述的方法,其中约 0.2 重量%至约 15 重量%的重量百分比的硫与所述镍金属或所述镍原材料接触,其中所述硫重量百分比相对于所述镍金属或所述镍原材料中镍的总重量。

[0598] 23. 陈述 1-22 中任一项所述的方法,其中约 0.4 重量%至约 12 重量%的重量百分比的硫与所述镍金属或所述镍原材料接触,其中所述硫重量百分比相对于所述镍金属或所述镍原材料中镍的总重量。

[0599] 24. 陈述 1-23 中任一项所述的方法,其中所述方法产生硫与镍的原子比为约 0.003 至约 1.8 的镍金属颗粒。

[0600] 25. 陈述 1-24 中任一项所述的方法,其中所述方法产生硫与镍的原子比为约 0.01 至约 0.2 的镍金属颗粒。

[0601] 26. 陈述 1-25 中任一项所述的方法,其中所述方法产生硫与镍的原子比为约 0.003 至约 0.05 的镍金属颗粒。

[0602] 27. 陈述 1-26 中任一项所述的方法,其中当将约 4% 镍在约 60℃至 80℃在有机腈溶剂中与每摩尔含磷配体约 0.5 至 2.5 摩尔路易斯酸混合时,配合物形成的平衡在约 2 小时内达到。

[0603] 28. 陈述 1-27 中任一项所述的方法,其中当将约 4% 镍在约 60℃至 80℃在有机腈溶剂中与每摩尔含磷配体约 0.5 至 2.5 摩尔路易斯酸混合时,配合物形成的平衡在约 30 分钟内达到。

[0604] 29. 陈述 1-28 中任一项所述的方法,其中在配合物形成过程中存在路易斯酸。

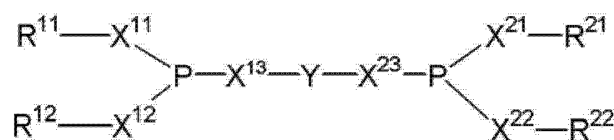
[0605] 30. 陈述 29 所述的方法,其中所述路易斯酸选自由以下各项组成的组:氯化锌、氯化亚铁,或它们的组合。

[0606] 31. 陈述 1-30 中任一项所述的方法,其中配合物形成出现在有机腈溶剂中。

[0607] 32. 陈述 31 所述的方法,其中所述有机腈溶剂是戊烯腈。

[0608] 33. 陈述 1-32 中任一项所述的方法、其中所述磷配体中的一种或多种是式 (III) 的配体:

[0609]



式(III)

[0610] 其中:

[0611]  $\text{X}^{11}$ 、 $\text{X}^{12}$ 、 $\text{X}^{13}$ 、 $\text{X}^{21}$ 、 $\text{X}^{22}$  和  $\text{X}^{23}$  独立地表示氧或单个直接键;

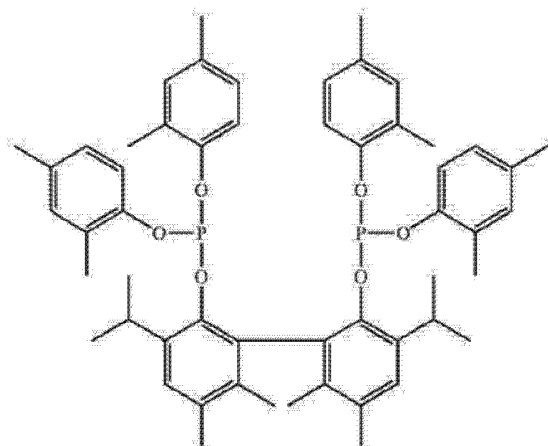
[0612]  $\text{R}^{11}$  和  $\text{R}^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团;

[0613]  $\text{R}^{21}$  和  $\text{R}^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团;并且 Y 表示桥连

基。

[0614] 34. 陈述 1-33 中任一项所述的方法,其中所述磷配体中的一种或多种是配体(V):

[0615]



配体(V)。

[0616] 35. 陈述 1-34 中任一项所述的方法,其中由在非-含氧气氛下混合的来自所述镍金属的镍原子与一种或多种含磷配体之间形成配合物。

[0617] 36. 陈述 1-35 中任一项所述的方法,其中在来自所述镍金属的镍原子与一种或多种含磷配体之间形成的配合物催化烯烃的氢氰化。

[0618] 37. 陈述 36 所述的方法,其中所述烯烃是戊烯腈。

[0619] 38. 一种催化剂制备混合物,所述催化剂制备混合物包含镍金属、一种或多种含磷配体和约 0.001 重量%至约 15 重量%硫,其中所述硫重量百分比相对于所述混合物中镍的总重量。

[0620] 39. 陈述 37 所述的催化剂制备混合物,其中所述混合物在有机腈溶剂中。

[0621] 40. 陈述 39 所述的催化剂制备混合物,其中所述溶剂是戊烯腈。

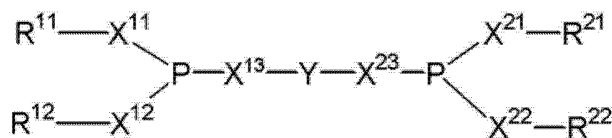
[0622] 41. 陈述 38-40 中任一项所述的催化剂制备混合物,所述催化剂制备混合物还包含路易斯酸。

[0623] 42. 陈述 41 所述的催化剂制备混合物,其中所述路易斯酸选自由以下各项组成的组:氯化锌、氯化亚铁,或它们的组合。

[0624] 43. 陈述 42 所述的催化剂制备混合物,其中所述路易斯酸是氯化锌。

[0625] 44. 陈述 38-43 中任一项所述的催化剂制备混合物,其中所述磷配体中的一种或多种是式 (III) 的配体:

[0626]



式(III)

[0627] 其中,

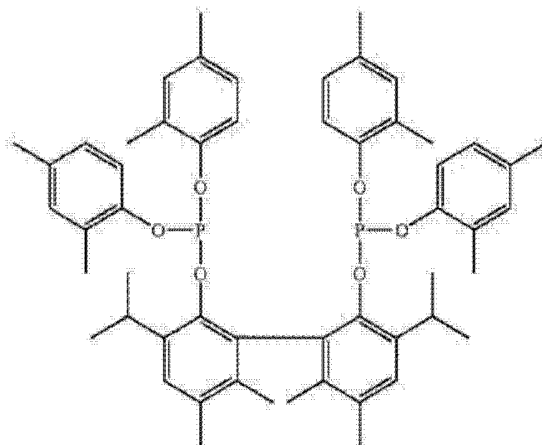
[0628]  $X^{11}$ 、 $X^{12}$ 、 $X^{13}$ 、 $X^{21}$ 、 $X^{22}$  和  $X^{23}$  独立地表示氧或单个直接键；

[0629]  $R^{11}$  和  $R^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团；

[0630]  $R^{21}$  和  $R^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团；并且 Y 表示桥连基。

[0631] 45. 陈述 38-44 中任一项所述的催化剂制备混合物，其中所述磷配体中的一种或多种是配体 (V)；

[0632]



配体(V)。

[0633] 46. 陈述 38-45 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含约 2 至约 8 重量%的重量百分比的所述一种或多种含磷配体。

[0634] 47. 陈述 38-46 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含约 4.75 至约 5.75 重量%的重量百分比的所述一种或多种含磷配体，

[0635] 48. 陈述 38-47 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含约 5.25 重量%的重量百分比的所述一种或多种含磷配体。

[0636] 49. 陈述 38-48 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含约 1 至约 7 重量%的镍重量百分比。

[0637] 50. 陈述 38-49 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含约 4 至约 5 重量%的镍重量百分比。

[0638] 51. 陈述 42-50 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含约 0.5 至约 2.5 的锌与含磷配体的摩尔比。

[0639] 52. 陈述 42-51 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含约 0.70 至约 0.80 的锌与含磷配体的摩尔比。

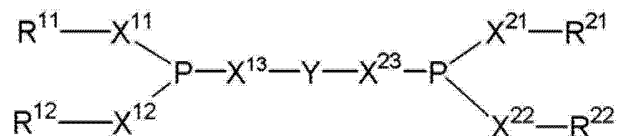
[0640] 53. 陈述 38-52 中任一项所述的催化剂制备混合物，所述催化剂制备混合物包含相对于所述混合物中镍的总重量为约 0.01 重量%至约 12 重量%硫。

[0641] 54. 一种在镍原子与一种或多种含磷配体之间形成的配合物，所述配合物包含约 0.00001 重量%至约 15 重量%硫，其中所述硫重量百分比相对于所述配合物中镍的总重量。

[0642] 55. 陈述 54 所述的配合物，所述配合物包含约 0.0001 重量%至约 2 重量%硫。

[0643] 56. 陈述 54 或 55 所述的配合物, 其中所述磷配体中的一种或多种是式 (III) 的配体:

[0644]



式(III)

[0645] 其中,

[0646]  $X^{11}$ 、 $X^{12}$ 、 $X^{13}$ 、 $X^{21}$ 、 $X^{22}$  和  $X^{23}$  独立地表示氧或单个直接键;

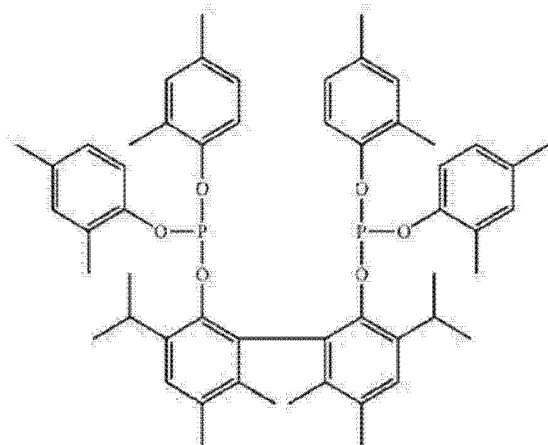
[0647]  $R^{11}$  和  $R^{12}$  独立地表示相同的或不同的、单个或桥连的有机基团;

[0648]  $R^{21}$  和  $R^{22}$  独立地表示相同的或不同的、单个或桥连的有机基团; 并且

[0649] Y 表示桥连基。

[0650] 57. 陈述 54-56 中任一项所述的配合物, 其中所述磷配体中的一种或多种是配体 (V):

[0651]



配体(V)。

[0652] 58. 陈述 54-57 中任一项所述的配合物, 其中所述配合物在有机腈溶剂中。

[0653] 59. 陈述 54-58 中任一项所述的配合物, 其中所述配合物在戊烯腈溶剂中。

[0654] 60. 一种包含镍微晶的镍颗粒形式, 其中所述镍颗粒形式具有选自由以下各项组成的组中的至少两种性质:

[0655] 镍颗粒形式具有至少约  $1\text{m}^2/\text{gm}$  的 BET 比表面积;

[0656] 至少 10% 的所述镍微晶具有小于约 20nm 的尺寸 (C10);

[0657] 镍微晶具有不大于约 100nm 的平均微晶尺寸;

[0658] 镍颗粒形式具有不小于  $0.07 \times 10^9 \text{m}^2/\text{gm}$  的 BET 比表面积 / C50 的比率;

[0659] 镍微晶尺寸分布范围为大于约 1.0;

[0660] 镍颗粒形式平均具有每克镍至少约  $10^{15}$  个表面微晶;

[0661] 所述形式的至少 10% 的所述粒子具有不大于约  $6\mu\text{m}$  的尺寸 (D10);

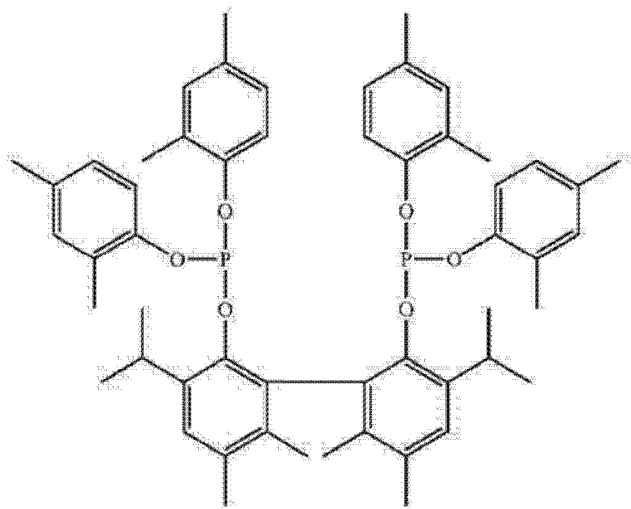
[0662] 镍颗粒形式具有至少约  $0.4\text{m}^2/\text{gm}$  的激光衍射比表面积;

[0663] 镍颗粒形式具有约  $0.3 \times 10^6 \text{m}^2/\text{gm}$  至约  $10.0 \times 10^6 \text{m}^2/\text{gm}$  的 BET 比表面积与 D10 的比率；

[0664] 平均存在每克镍至少约  $10^{16}$  个小于或等于尺寸 C10 的表面微晶；以及

[0665] 当将约 4 至 5 重量%的所述镍颗粒形式与含有大约 5.25 重量%配体 (V) 和大约 6300ppm  $\text{ZnCl}_2$  的 3-戊烯腈混合时，镍颗粒形式与配体 (V) 在约 2 小时内形成配合物；其中配体 (V) 具有下式：

[0666]



[0667] 61. 陈述 60 所述的镍颗粒形式，具有以上组中所述性质的至少三个。

[0668] 62. 陈述 60 或 61 所述的镍颗粒形式，具有以上组中所述性质的至少四个。

[0669] 63. 陈述 60-62 中任一项所述的镍颗粒形式，其中所述镍颗粒形式具有至少约  $2 \text{m}^2/\text{g}$  的 BET 比表面积。

[0670] 64. 陈述 60-63 中任一项所述的镍颗粒形式，其中所述镍颗粒形式具有至少约  $4 \text{m}^2/\text{g}$  的 BET 比表面积。

[0671] 65. 陈述 60-64 中任一项所述的镍颗粒形式，其中所述镍颗粒形式具有至少  $10 \text{m}^2/\text{g}$  的 BET 比表面积。

[0672] 66. 陈述 60-65 中任一项所述的镍颗粒形式，其中所述 BET SSA/C50 的比率为至少约  $0.1 \times 10^9 \text{m}^2/\text{gm}$ 。

[0673] 67. 陈述 60-66 中任一项所述的镍颗粒形式，其中所述平均微晶尺寸为不大于约 70nm。

[0674] 68. 陈述 60-67 中任一项所述的镍颗粒形式，其中所述平均微晶尺寸为不大于约 50nm。

[0675] 69. 陈述 60-68 中任一项所述的镍颗粒形式，其中所述平均微晶尺寸为不大于约 30nm。

[0676] 70. 陈述 60-69 中任一项所述的镍颗粒形式，其中所述 BET SSA/C50 的比率为至少约  $0.4 \times 10^9 \text{m}^2/\text{gm}$ 。

[0677] 71. 陈述 60-70 中任一项所述的镍颗粒形式，其中激光衍射 LD SSA/C50 的比率为至少约  $4.3 \times 10^6$ 。

[0678] 72. 陈述 60-71 中任一项所述的镍颗粒形式，其中所述激光衍射 LD SSA/C50 的比

率为至少约  $10^7$ 。

[0679] 73. 陈述 60-72 中任一项所述的镍颗粒形式,其中至少 10%的所述微晶具有小于约 10nm 的尺寸 (C10)。

[0680] 74. 陈述 60-73 中任一项所述的镍颗粒形式,所述镍颗粒形式具有不大于约 20-25nm 的平均微晶尺寸。

[0681] 75. 陈述 60-74 中任一项所述的镍颗粒形式,所述镍颗粒形式具有大于 1.5 的镍微晶尺寸分布范围。

[0682] 76. 陈述 60-75 中任一项所述的镍颗粒形式,其中所述镍颗粒形式平均具有每克镍至少约  $2 \times 10^{15}$  个表面微晶。

[0683] 77. 陈述 60-76 中任一项所述的镍颗粒形式,其中所述镍颗粒形式平均具有每克镍至少约  $5 \times 10^{15}$  个表面微晶。

[0684] 78. 陈述 60-77 中任一项所述的镍颗粒形式,其中所述镍颗粒形式平均具有每克镍至少约  $1 \times 10^{16}$  个表面微晶。

[0685] 79. 陈述 60-78 中任一项所述的镍颗粒形式,其中所述每克镍的表面微晶是对于基本上球体微晶或基本上立方微晶计算的。

[0686] 80. 陈述 60-79 中任一项所述的镍颗粒形式,其中平均每克存在:对于立方微晶计算的每克镍至少约  $2 \times 10^{15}$  个表面微晶,或对于基本上球体微晶计算的每克镍至少约  $10^{15}$  个的表面微晶,或同时存在这两种情况。

[0687] 81. 陈述 60-80 中任一项所述的镍颗粒形式,其中所述至少 10%的所述粒子具有不大于约  $4 \mu\text{m}$  的直径 (D10)。

[0688] 82. 陈述 60-81 中任一项所述的镍颗粒形式,其中 BET 比表面积与激光衍射比表面积的比率为 20 至 30 之间。

[0689] 83. 陈述 60-82 中任一项所述的镍颗粒形式,其中 BET 比表面积与 D10 的比率为 3 至  $5\text{m}^2/\text{gm}/\mu\text{m}$  或约  $0.5 \times 10^6\text{m}/\text{gm}$  至约  $5 \times 10^6\text{m}/\text{g}$ 。

[0690] 84. 陈述 60-83 中任一项所述的镍颗粒形式,其中平均存在每克镍至少约  $10^{16}$  个尺寸 C10 以下的表面微晶。

[0691] 85. 陈述 60-84 中任一项所述的镍颗粒形式,其中平均存在每克镍至少约  $5 \times 10^{16}$  个尺寸 C10 以下的表面微晶;或者其中平均存在每克镍至少约  $10^{17}$  个尺寸 C10 以下的表面微晶。

[0692] 86. 陈述 60-85 中任一项所述的镍颗粒形式,其中所述镍颗粒形式基本上是零价镍。

[0693] 87. 陈述 60-86 中任一项所述的镍颗粒形式,其中所述镍颗粒形式通过镍原材料的还原产生。

[0694] 88. 陈述 60-87 中任一项所述的镍颗粒形式,其中所述镍颗粒形式通过碱式碳酸镍的还原产生,其中所述碱式碳酸镍少于相对于所述碱式碳酸镍中镍量的碳酸盐摩尔当量。

[0695] 89. 陈述 60-88 中任一项所述的镍颗粒形式,其中所述镍颗粒形式通过碱式碳酸镍的还原产生,其中所述碱式碳酸镍具有小于约 1 的  $\text{NiCO}_3 : \text{Ni}(\text{OH})_2$  的摩尔比。

[0696] 90. 陈述 60-89 中任一项所述的镍颗粒形式,其中所述镍颗粒形式通过碱式碳酸

镍的还原产生,其中所述碱式碳酸镍具有至少 6 : 1,或至少 7 : 1,或至少 8 : 1,或至少 9 : 1,或至少 10 : 1 的 Ni : C 的质量比。

[0697] 91. 陈述 60-90 中任一项所述的镍颗粒形式,其中所述镍颗粒形式通过碱式碳酸镍的还原产生,其中所述碱式碳酸镍具有 6 : 1 至约 20 : 1 的 Ni : C 的质量比。

[0698] 92. 陈述 60-91 中任一项所述的镍颗粒形式,其中所述镍颗粒形式已经从 Ni (II) 还原成零价镍。

[0699] 93. 陈述 60-92 中任一项所述的镍颗粒形式,其中所述镍颗粒形式已经用氢从 Ni (II) 还原成零价镍。

[0700] 94. 陈述 60-93 中任一项所述的镍颗粒形式,其中所述镍颗粒形式已经在 250-400°C 从 Ni (II) 还原成零价镍。

[0701] 95. 陈述 60-94 中任一项所述的镍颗粒形式,其中所述镍颗粒形式基本上不含其他金属。

[0702] 96. 陈述 60-95 中任一项所述的镍颗粒形式,其中所述镍颗粒形式基本上不含铝、铜、钨、锌和 / 或铁。

[0703] 97. 陈述 60-96 中任一项所述的镍颗粒形式,其中所述镍颗粒形式基本上不含碱金属和 / 或碱土金属。

[0704] 98. 陈述 60-97 中任一项所述的镍颗粒形式,其中所述镍颗粒形式基本上不含阴离子。

[0705] 99. 陈述 60-98 中任一项所述的镍颗粒形式,其中所述镍颗粒形式基本上不含碳酸盐、氢氧化物和 / 或氧。

[0706] 100. 陈述 60-99 中任一项所述的镍颗粒形式,所述镍颗粒形式包含相对于所述混合物中镍的总重量为约 0.01 重量%至约 12 重量%硫。

[0707] 101. 陈述 60-100 中任一项所述的镍颗粒形式,所述镍颗粒形式包含相对于所述混合物中镍的总重量为约 0.1 重量%至约 2 重量%硫。

[0708] 102. 陈述 60-101 中任一项所述的镍颗粒形式,所述镍颗粒形式包含相对于所述混合物中镍的总重量为约 0.2 重量%至约 2 重量%硫。

[0709] 103. 陈述 60-102 中任一项所述的镍颗粒形式,所述镍颗粒形式包含相对于所述混合物中镍的总重量为约 0.4 重量%至约 1 重量%硫。

[0710] 104. 一种配合物,所述配合物包含一种或多种含磷配体和来自陈述 60-103 中任一项所述的镍颗粒形式的镍原子。

[0711] 105. 陈述 104 所述的配合物,所述配合物具有氢氰化催化活性。

[0712] 106. 陈述 104 或 105 所述的配合物,所述配合物具有用于氢氰化包含至少一个 C = C 键的化合物的催化活性。

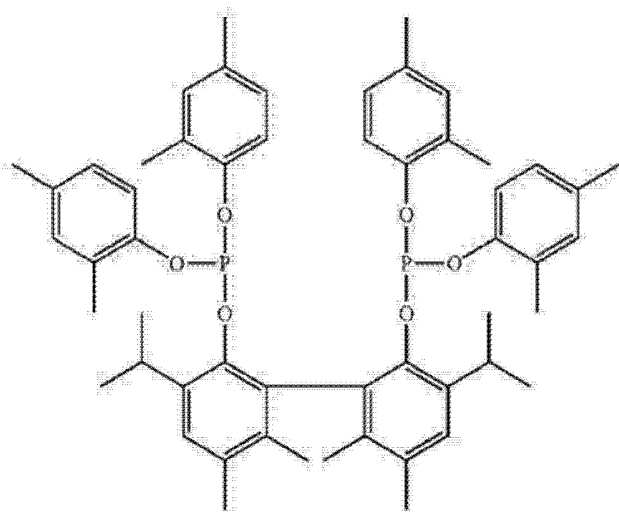
[0713] 107. 一种有机液体溶液,所述有机液体溶液包含一种或多种含磷配体和通过所述一种或多种含磷配体配合而溶解的镍原子,其中所述镍原子来自陈述 60-103 中任一项所述的镍颗粒形式。

[0714] 108. 陈述 107 所述的溶液,所述溶液还包含一种或多种戊烯腈。

[0715] 109. 陈述 107 或 108 所述的溶液,所述溶液还包含路易斯酸。

[0716] 110. 陈述 109 所述的溶液,其中所述路易斯酸是氯化锌。

- [0717] 111. 陈述 107-110 中任一项所述的溶液,所述溶液具有氢氰化催化活性。
- [0718] 112. 陈述 107-111 中任一项所述的溶液,所述溶液具有用于氢氰化包含至少一个  $C=C$  键的化合物的催化活性。
- [0719] 113. 一种制备具有催化活性的零价镍配合物的方法,所述方法包括将包含一种或多种含磷配体和陈述 60-103 中任一项所述的镍颗粒形式的有机液体溶液混合。
- [0720] 114. 陈述 113 所述的方法,其中所述有机液体溶液还包含路易斯酸。
- [0721] 115. 陈述 113 或 114 所述的方法,其中所述有机液体溶液还包含一种或多种腈。
- [0722] 116. 陈述 113-115 中任一项所述的方法,其中至少所述一种腈是单腈。
- [0723] 117. 陈述 113-116 中任一项所述的方法,其中所述有机液体溶液包含一种或多种戊烯腈。
- [0724] 118. 一种用于氢氰化具有至少一个  $C=C$  键化合物的方法,所述方法包括将所述化合物与  $HC \equiv N$  在包含具有一种或多种含磷配体的零价镍配合物的催化剂的存在下接触,其中所述配合物的镍组分得自陈述 60-103 中任一项所述的镍颗粒形式。
- [0725] 119. 陈述 118 所述的方法,其中一种或多种含磷配体包括亚磷酸酯配体。
- [0726] 120. 陈述 118 或 119 所述的方法,其中一种或多种含磷配体包括二齿亚磷酸酯配体。
- [0727] 121. 陈述 120 所述的方法,其中所述二齿亚磷酸酯配体是配体 (V) :
- [0728]



配体(V)。

- [0729] 122. 一种识别碱式碳酸镍测试样品是否将产生具有与一种或多种含磷配体形成配合物的镍原子的镍颗粒形式的方法,所述方法包括 :
- [0730] (a) 煅烧碱式碳酸镍测试样品 ;和
- [0731] (b) 观察所述测试样品与对照碱式碳酸镍样品相比是放出更多还是更少二氧化碳 ;
- [0732] 其中当所述碱式碳酸镍测试样品比所述对照碱式碳酸镍放出更少二氧化碳时,所述碱式碳酸镍测试样品将产生具有在约 2 小时内基本上与一种或多种含磷配体形成配合物的镍原子的活性镍颗粒形式 ;并且

[0733] 其中所述对照碱性镍将产生具有在约 2 小时内基本上不与一种或多种含磷配体形成配合物的镍原子的镍颗粒形式。

[0734] 123. 一种识别镍测试样品是否将产生具有与一种或多种含磷配体形成配合物的镍原子的镍颗粒形式的方法,所述方法包括:

[0735] (a) 将所述镍测试样品用氢还原;和

[0736] (b) 观察所述镍测试样品在还原过程中是否在约 350℃至 450℃之间展现单个氢吸收峰;

[0737] 其中当所述镍测试样品在还原过程中在约 350℃至 450℃之间展现单个氢吸收峰时,所述镍测试样品将产生具有在约 2 小时内基本上与一种或多种含磷配体形成配合物的镍原子的活性镍颗粒形式。

[0738] 124. 陈述 123 所述的方法,其中所述镍测试样品是碱式碳酸镍、氧化镍、氢氧化镍,或它们的混合物。

[0739] 125. 陈述 123 或 124 所述的方法,所述方法还包括在活性镍颗粒形式的镍原子与一种或多种含磷配体之间形成配合物以产生氢氰化催化剂。

[0740] 126. 一种避免浪费的方法,所述方法包括:

[0741] (a) 煅烧碱式碳酸镍测试样品;和

[0742] (b) 观察所述测试样品与对照碱式碳酸镍样品相比是放出更多还是更少二氧化碳;

[0743] 其中当所述碱式碳酸镍测试样品比所述对照碱式碳酸镍放出更多二氧化碳时,所述碱式碳酸镍测试样品将不产生具有在约 2 小时内基本上不与一种或多种含磷配体形成配合物的镍原子的活性镍颗粒形式;并且

[0744] 其中,在还原之后,所述对照碱式碳酸镍产生具有在有机腈溶剂中混合之后约 2 小时内基本上不与一种或多种含磷配体形成配合物的镍原子的镍制备物。

[0745] 127. 陈述 126 所述的方法,其中通过识别比所述对照碱式碳酸镍放出更多二氧化碳的碱式碳酸镍测试样品,并且不使用由其获得所述碱式碳酸镍测试样品的碱式碳酸镍来制备用于在氢氰化催化剂中使用的镍颗粒形式,从而避免浪费。

[0746] 128. 陈述 126 或 127 所述的方法,其中通过识别比所述对照碱式碳酸镍放出更多二氧化碳的碱式碳酸镍测试样品,并且通过不使用由其获得所述碱式碳酸镍测试样品的碱式碳酸镍来制备镍制备物,从而避免浪费,因为所述镍制备物与一种或多种含磷配体在有机腈溶剂中混合之后约 2 小时内将不与所述一种或多种含磷配体形成配合物。

[0747] 129. 一种避免浪费的方法,所述方法包括:

[0748] (a) 将含镍测试样品还原;和

[0749] (b) 观察所述镍测试样品在还原过程中是否在约 350℃至 450℃之间展现单个氢吸收峰;

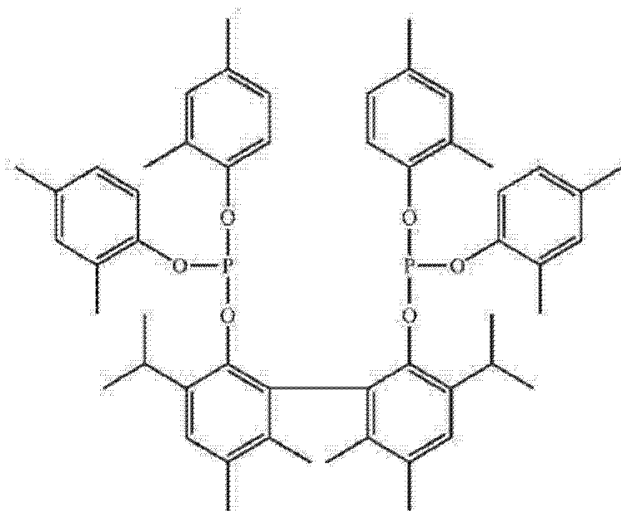
[0750] 其中当所述镍测试样品在还原过程中在约 300℃至 450℃之间展现两个氢吸收峰时,所述镍测试样品将不产生具有基本上在与一种或多种含磷配体混合之后约 2 小时内与所述一种或多种含磷配体产生配合物的镍原子的镍颗粒形式。

[0751] 130. 陈述 129 所述的方法,其中通过识别在还原过程中在约 300℃至 450℃之间展现两个氢吸收峰的一种或多种镍测试样品,并且不使用由其获得所述一种或多种镍测试样

品的镍源来产生氢氰化催化剂,从而避免浪费。

[0752] 131. 陈述 122-130 中任一项所述的方法,其中所述一种或多种含磷配体是配体(V) :

[0753]



配体(V)。

[0754] 以上方面在不丧失一般性的情况下给出,并且不对于任何所要求保护的发明给出限制。应当明白的是本公开不限于所描述的特定方面,因为这些可以变化。还应当明白的是本文使用的术语仅用于描述特定方面的目的,并且不意图是限定,因为本公开的范围将仅由所附权利要求限定。

[0755] 在本文已经宽泛地并且一般地描述了本发明。落入一般公开内的较窄物种和亚组的每一个也形成本发明的一部分。这包括具有从一般类型去除任意对象的附带条件或否定限制的本发明的一般说明,而与排除的对象是否具体地在本文陈述无关。本领域技术人员在阅读本公开之后将明白的是,本文描述和示出的每个单独的方面具有分离的要素和特征,这些要素和特征可以容易地从任意其他数个实施例的特征分离或与任意其他数个实施例的特征组合而不脱离本公开的范围或精神。在本发明的特征或方面用马库什组描述的情况下,本领域技术人员将明白本发明也从而以任意马库什组的单独的成员或成员的亚组描述。任何所述方法可以按照所述的情景的顺序进行,或者以逻辑上可能的任何其他顺序进行。

[0756] 本说明书中叙述的所有出版物和专利通过引用结合在此,好像将每个单独的出版物或专利详细地并分别地指出通过引用结合,并且它们通过引用结合在此以公开和描述与所引用的出版物相关的方法和/或材料。申请人保留将来自这些所应用的专利或出版物的任何和所有材料和信息物理结合至本说明书中的权利。任何出版物的引用针对其在申请日之前的公开并且不应被解释为承认本公开没有资格通过在先公开的方式比这些公开居先。此外,所提供的公开日可以不同于可能需要独立地确认的实际公开日。本文引用的或提到的所有专利和出版物也指示了本发明所属领域的技术人员的技术水平。

[0757] 以下权利要求描述本发明的另外的方面。

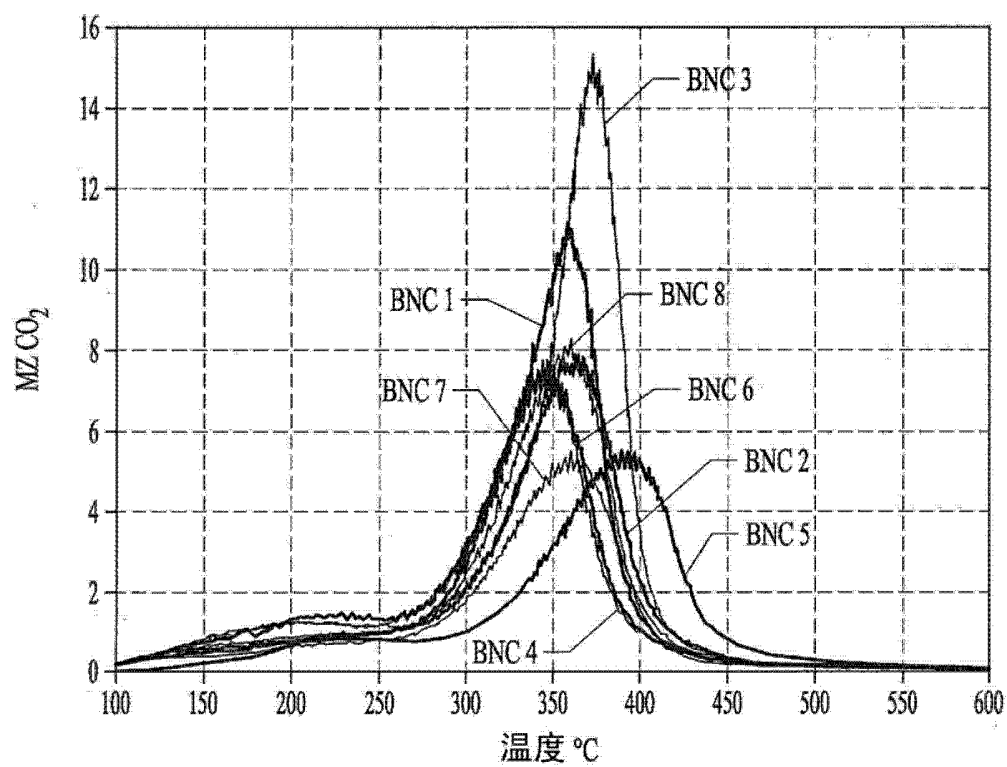


图 1

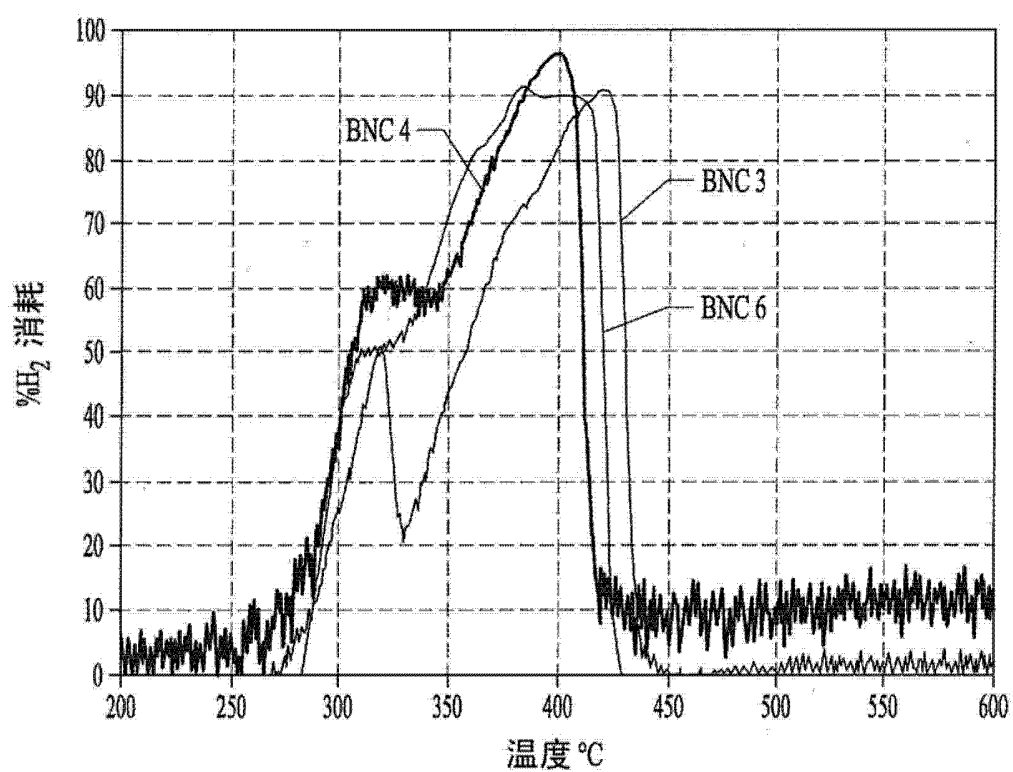


图 2

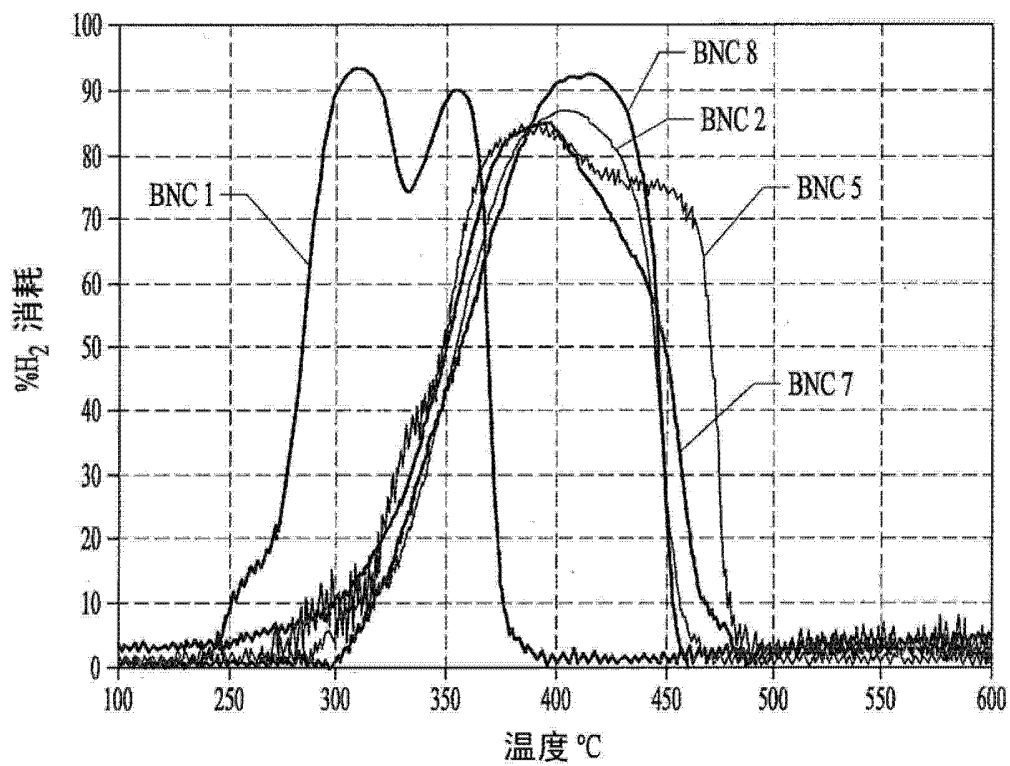


图 3A

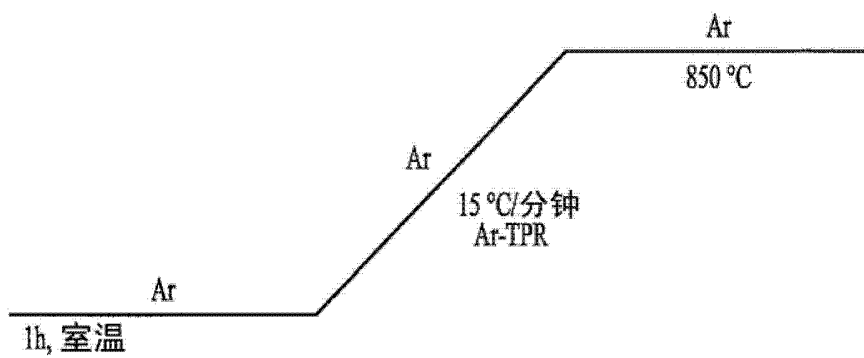


图 3B

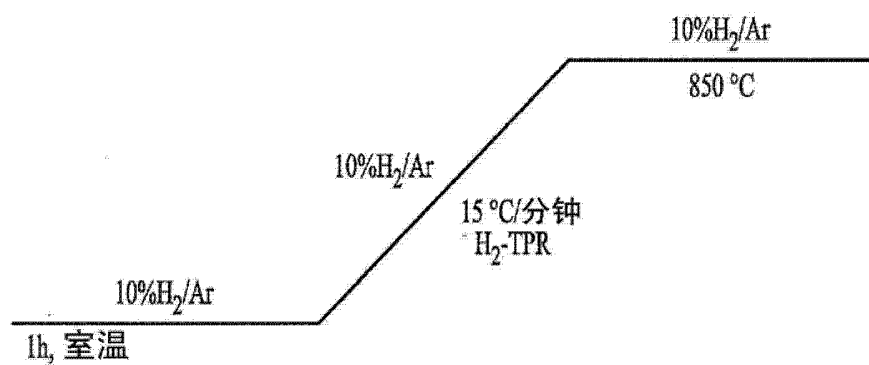


图 3C

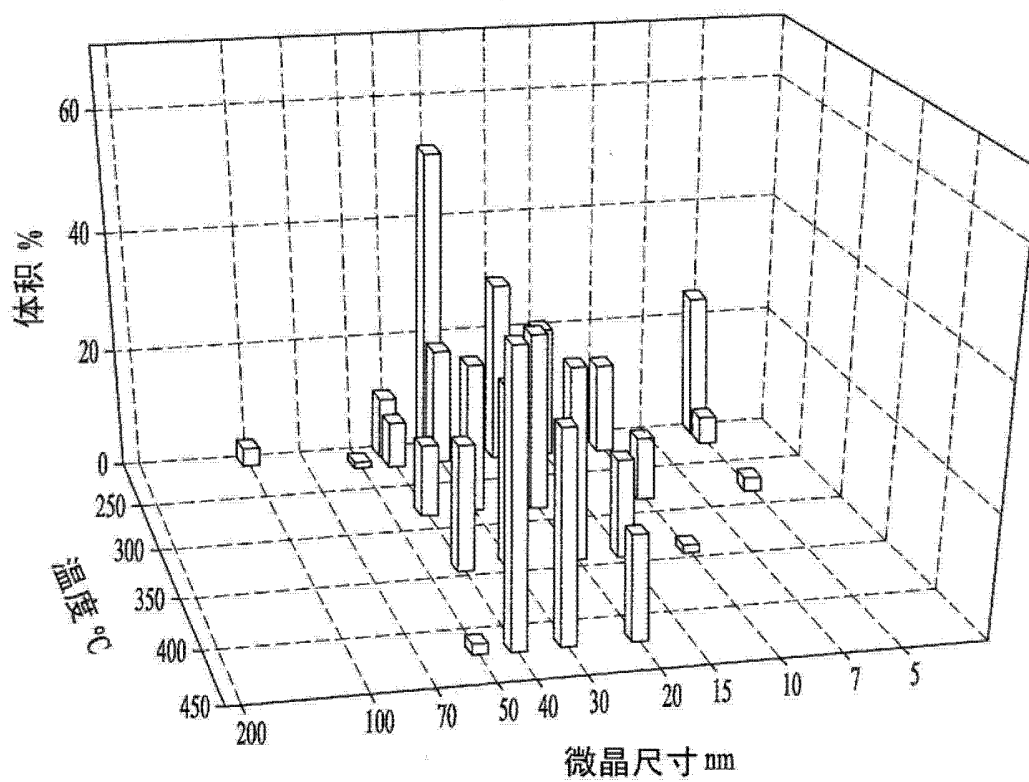


图 4

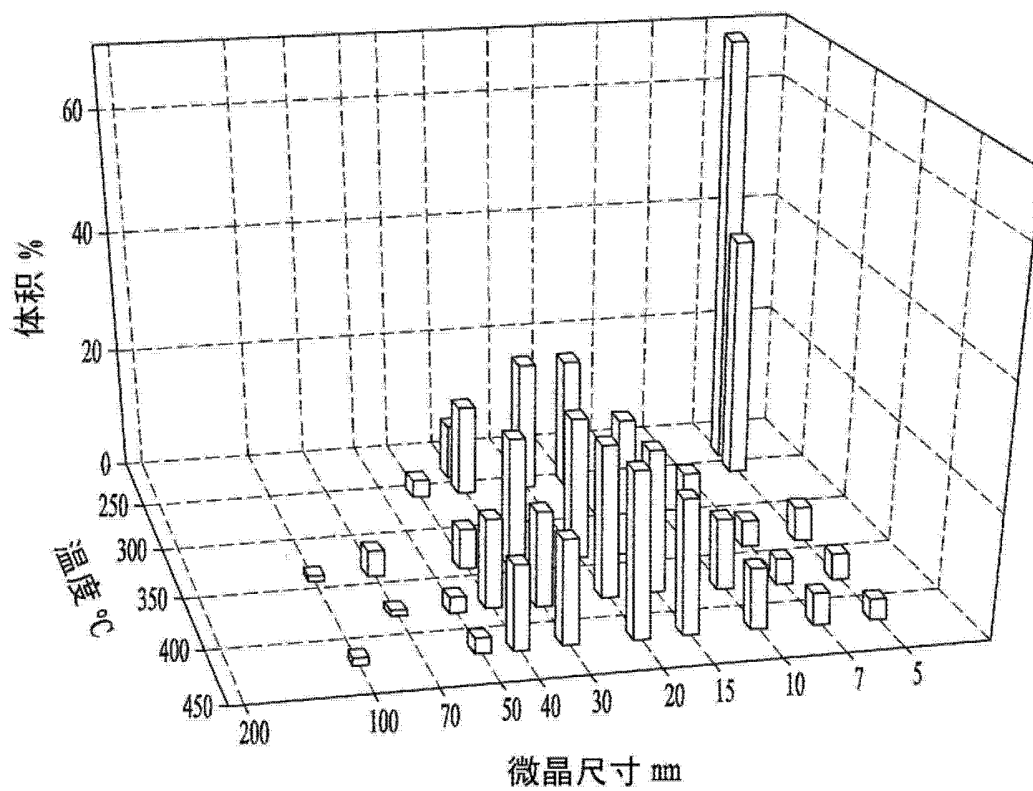


图 5

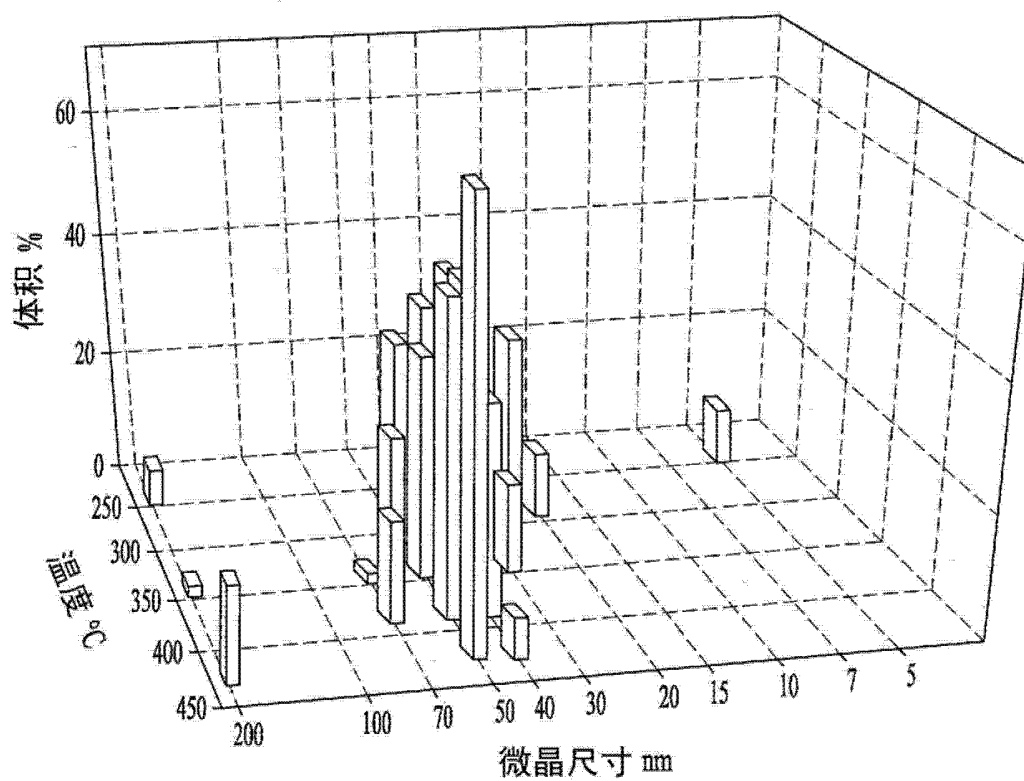


图 6

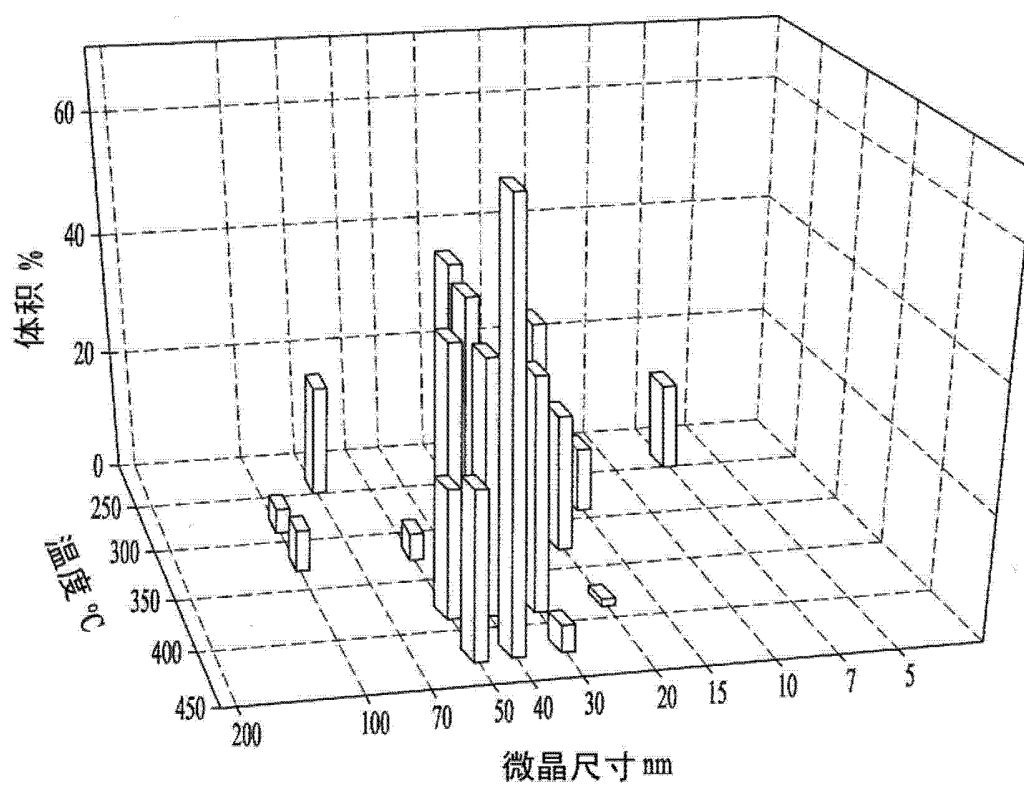


图 7

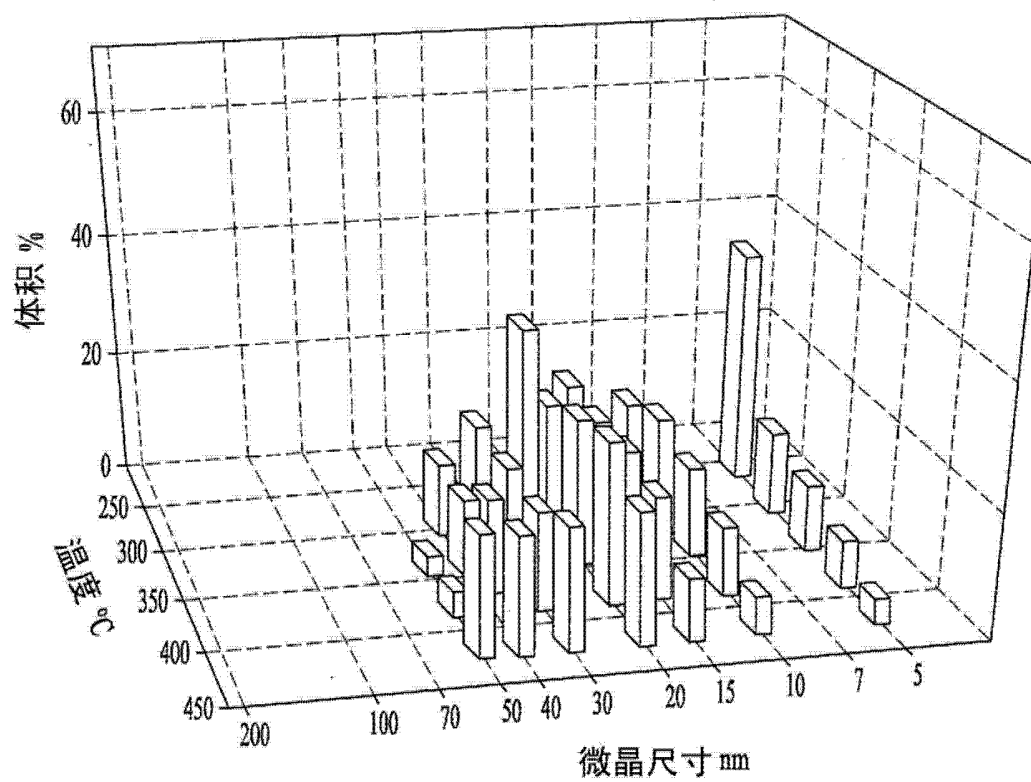


图 8

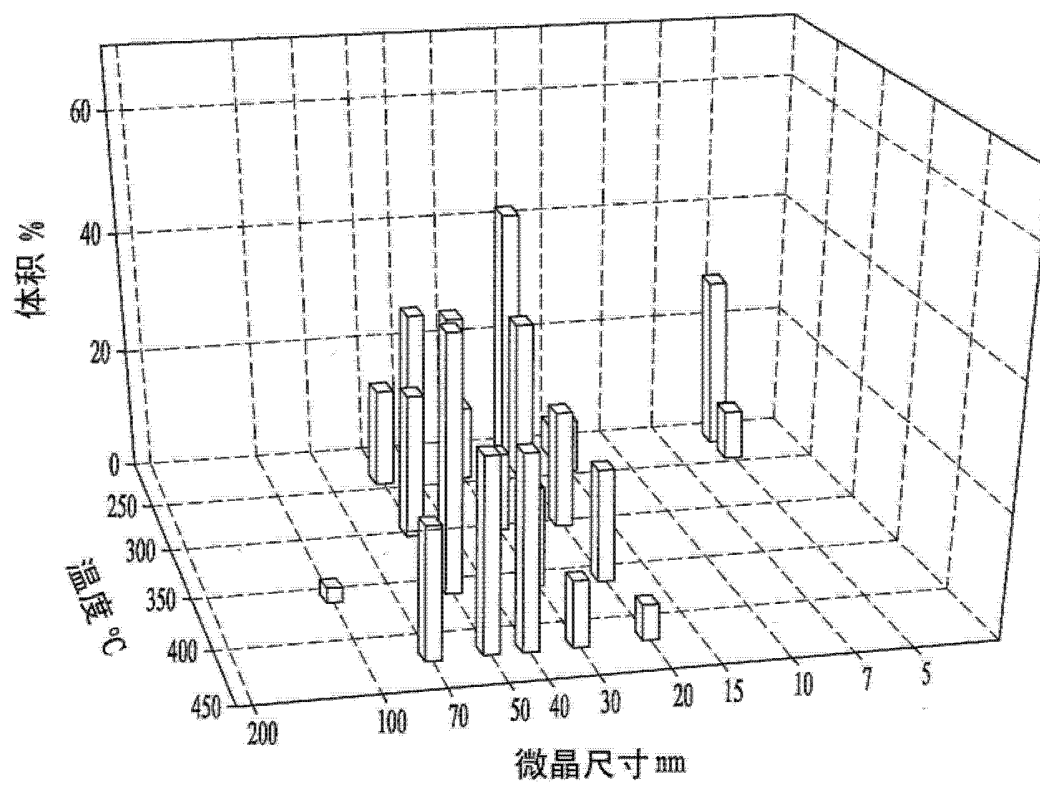


图 9

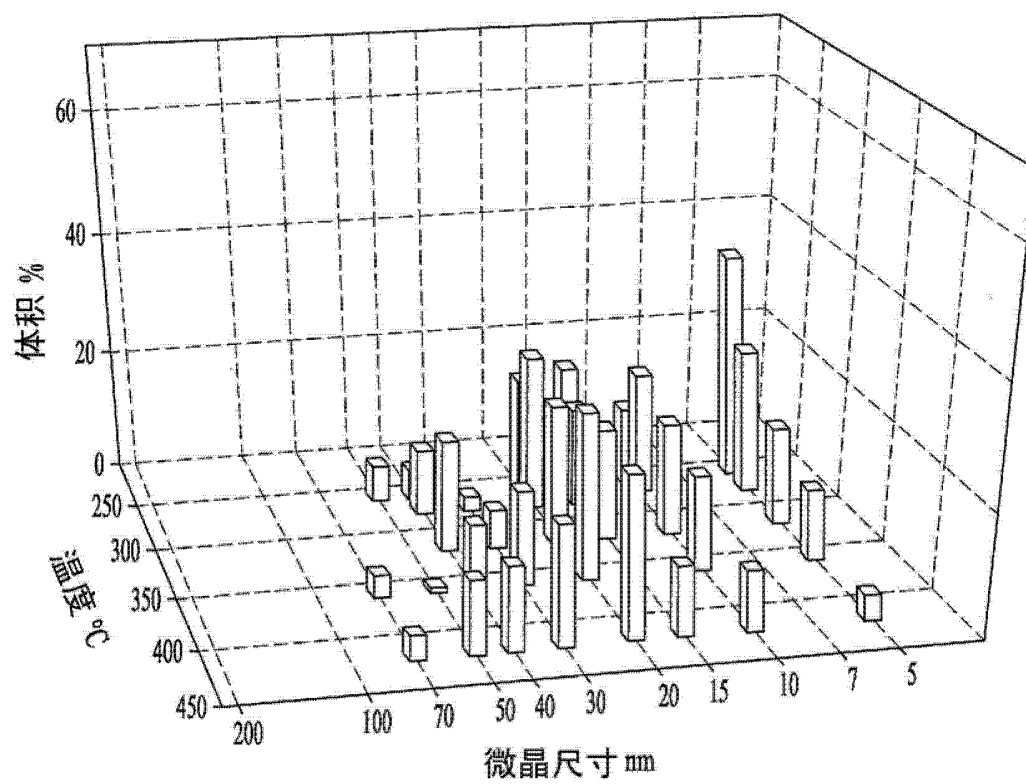


图 10

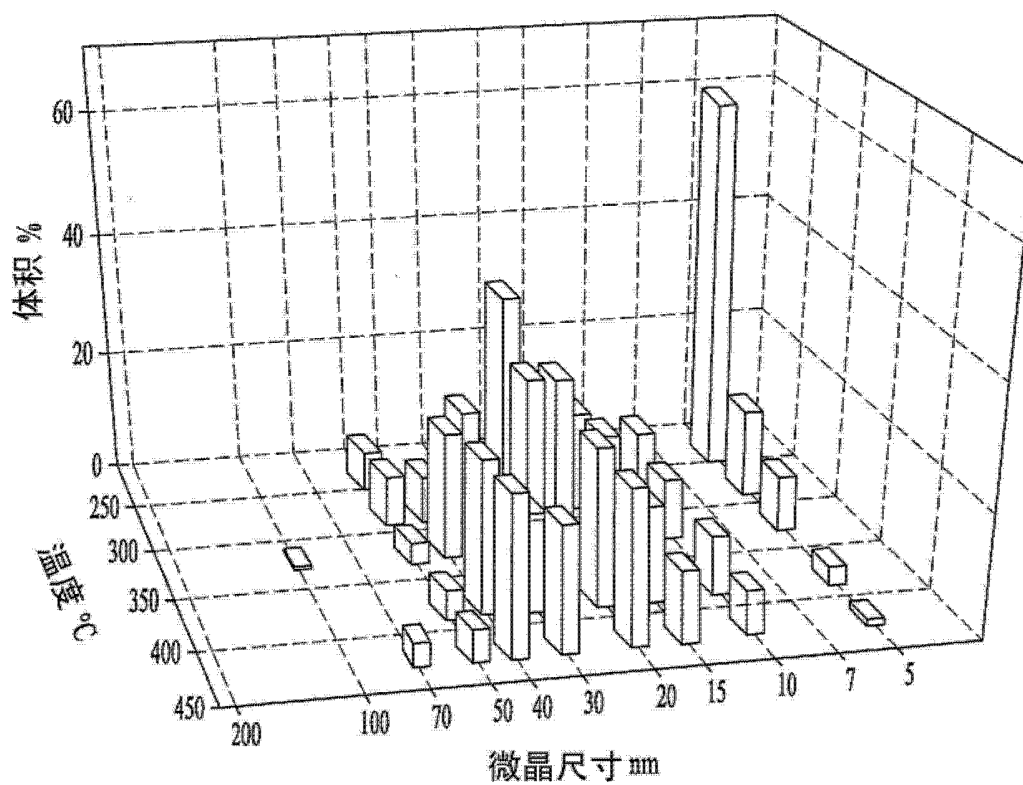


图 11

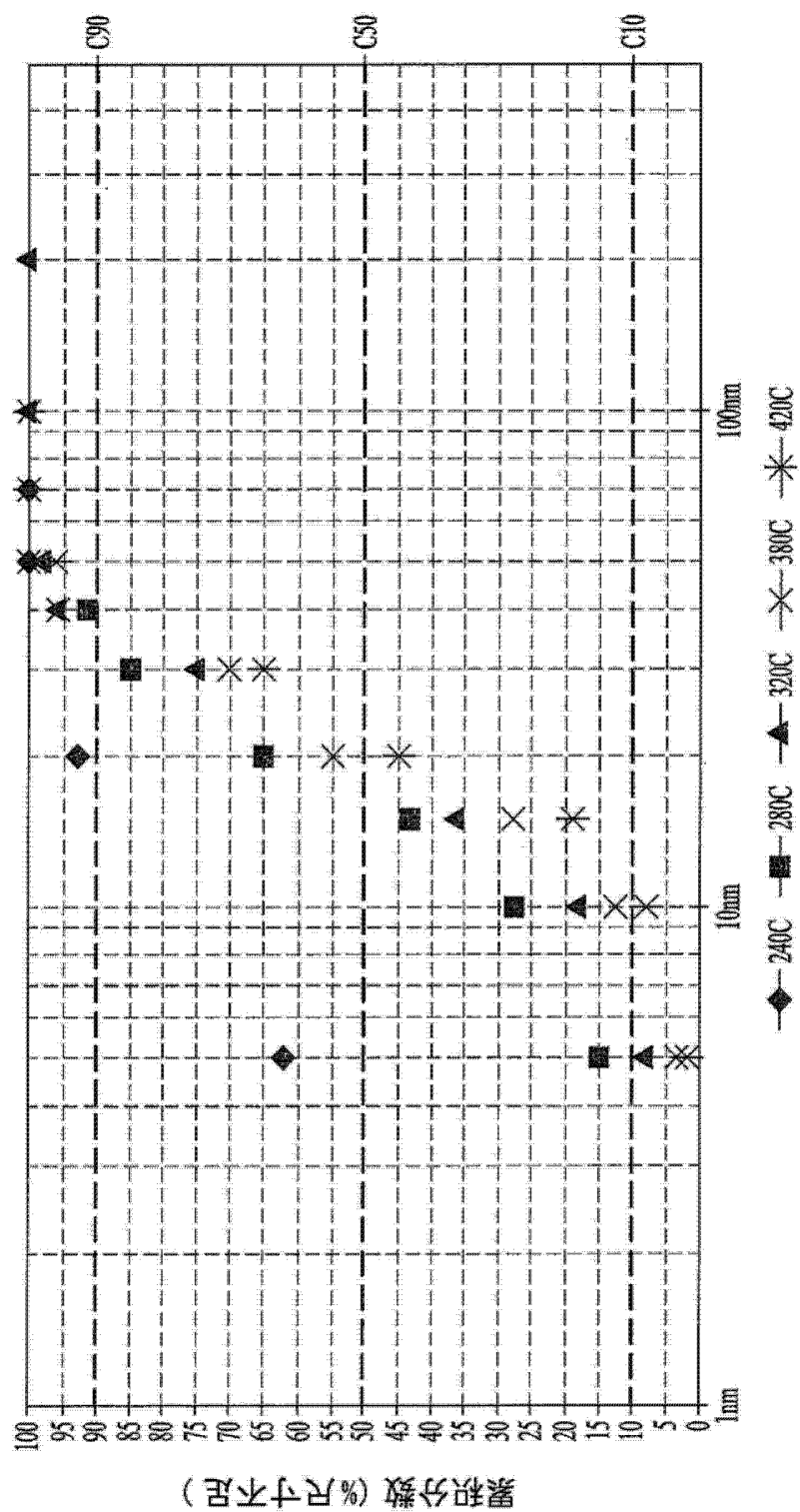


图 12

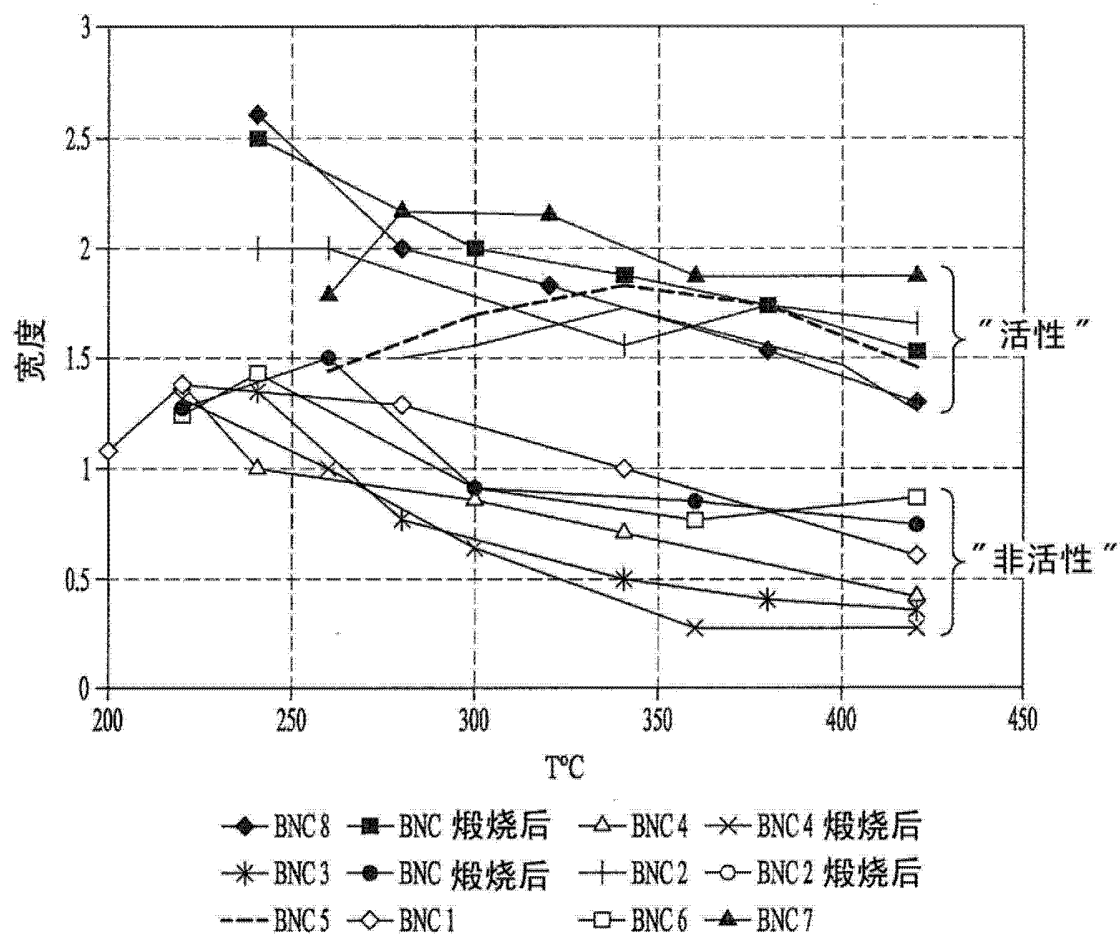


图 13

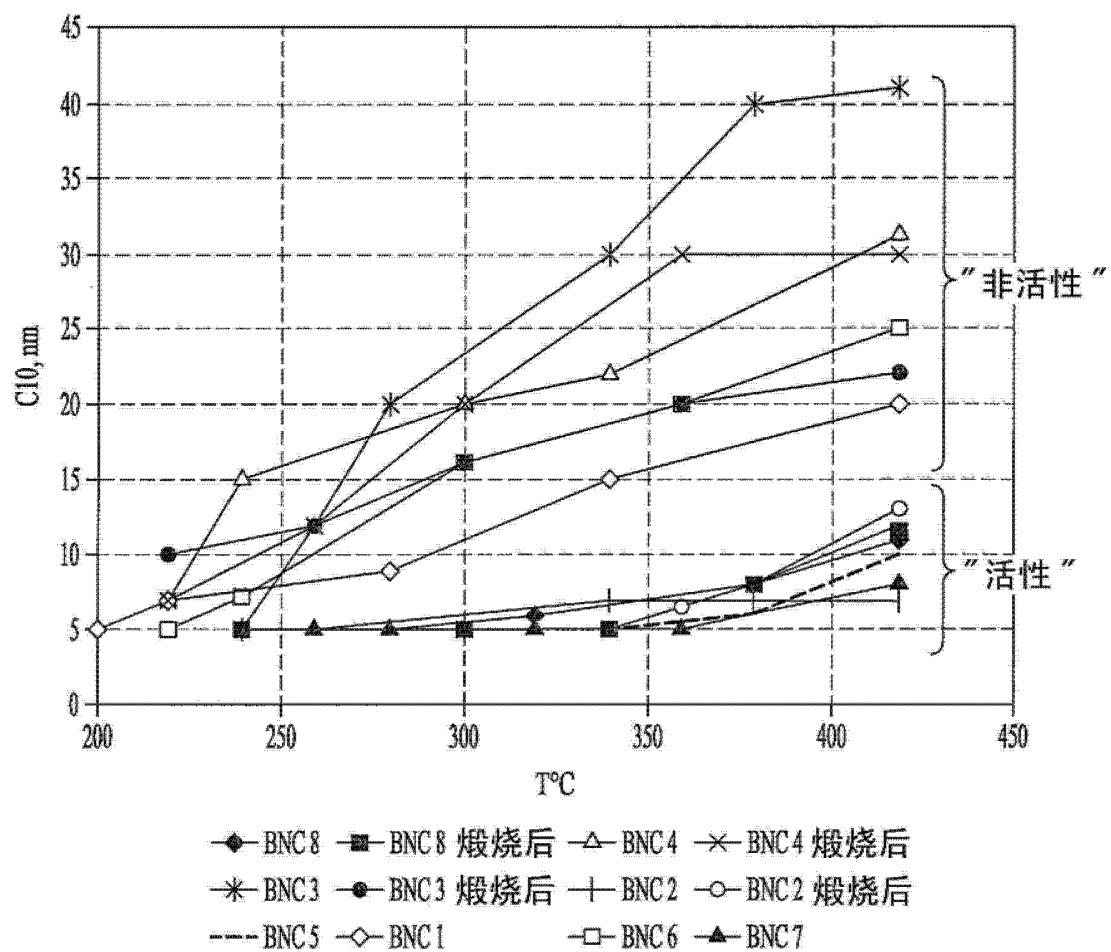


图 14

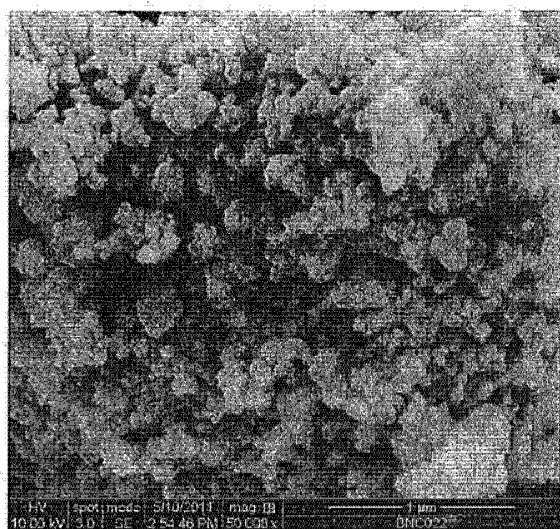


图 15A

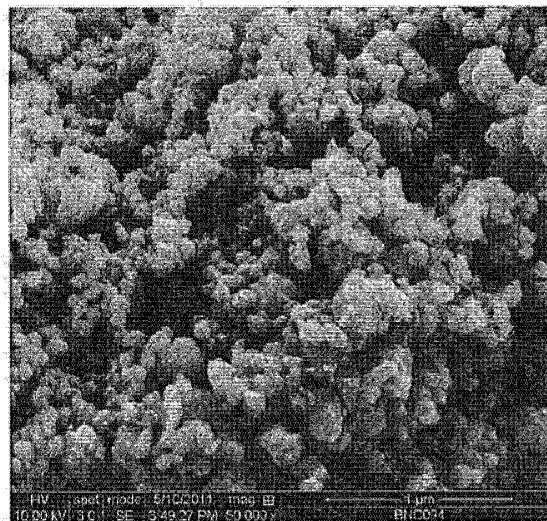


图 15B

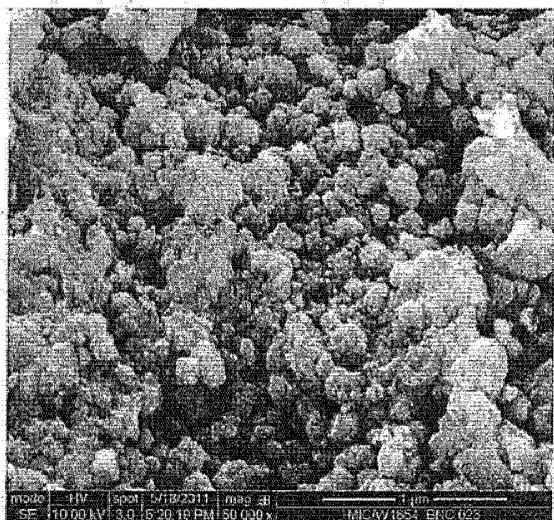


图 15C

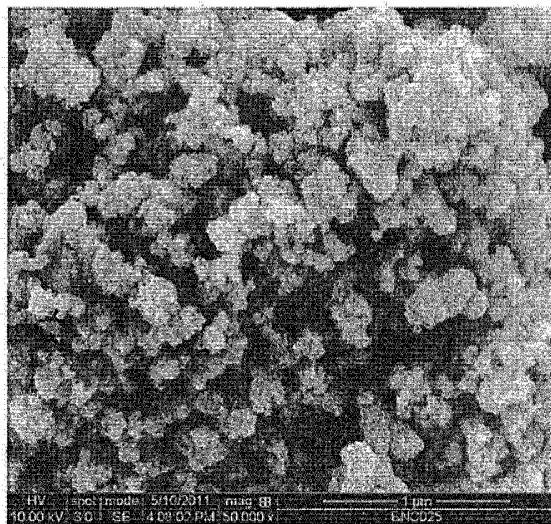


图 15D

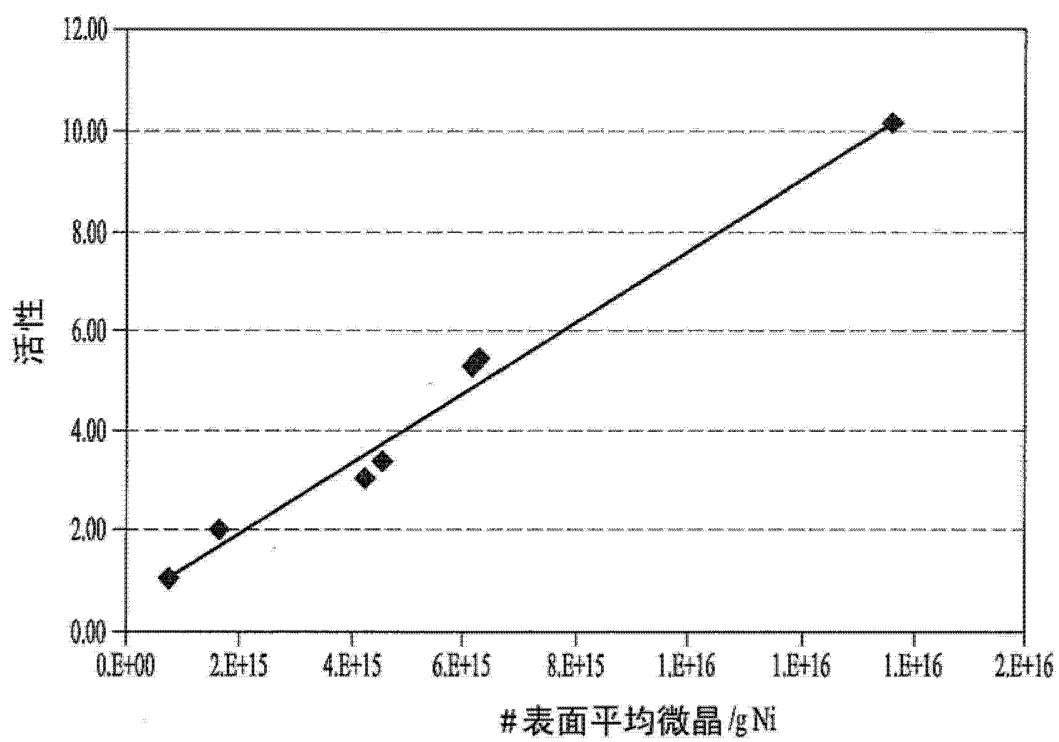


图 16A

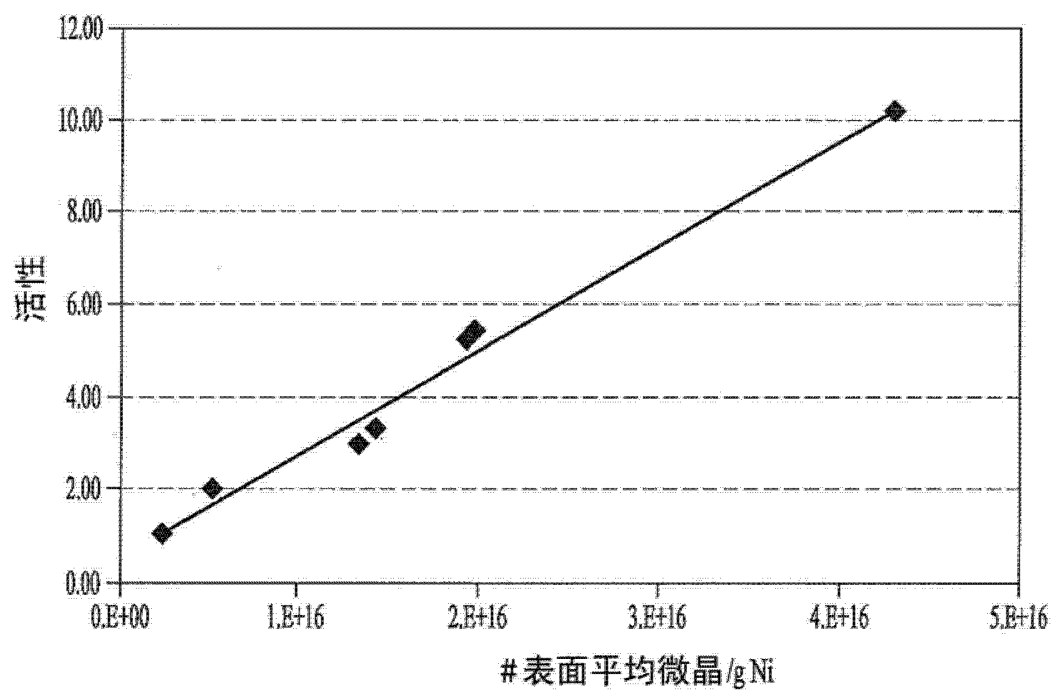


图 16B

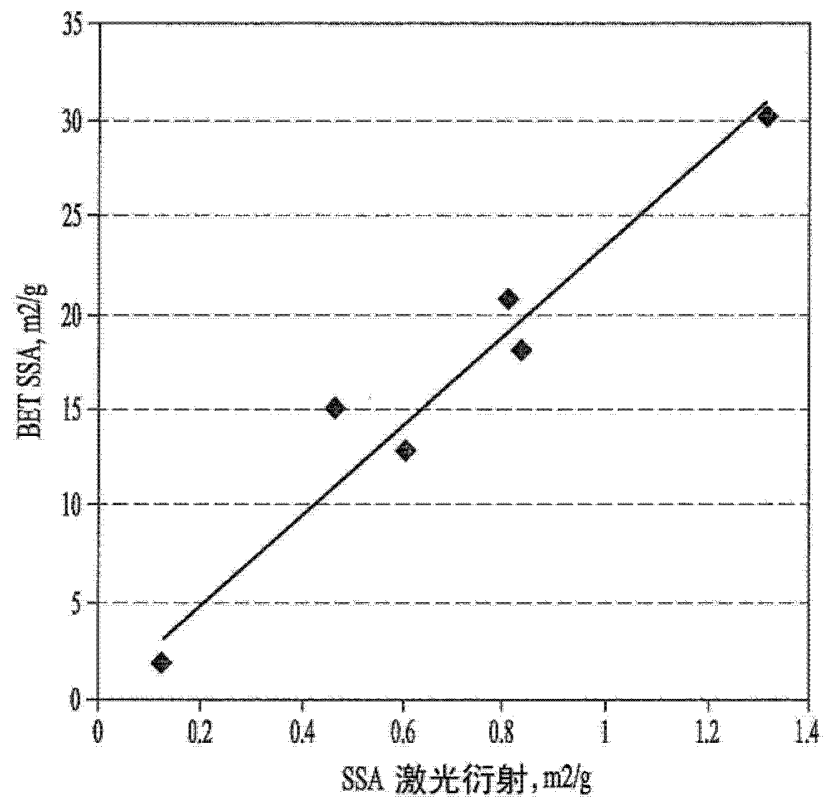


图 17A

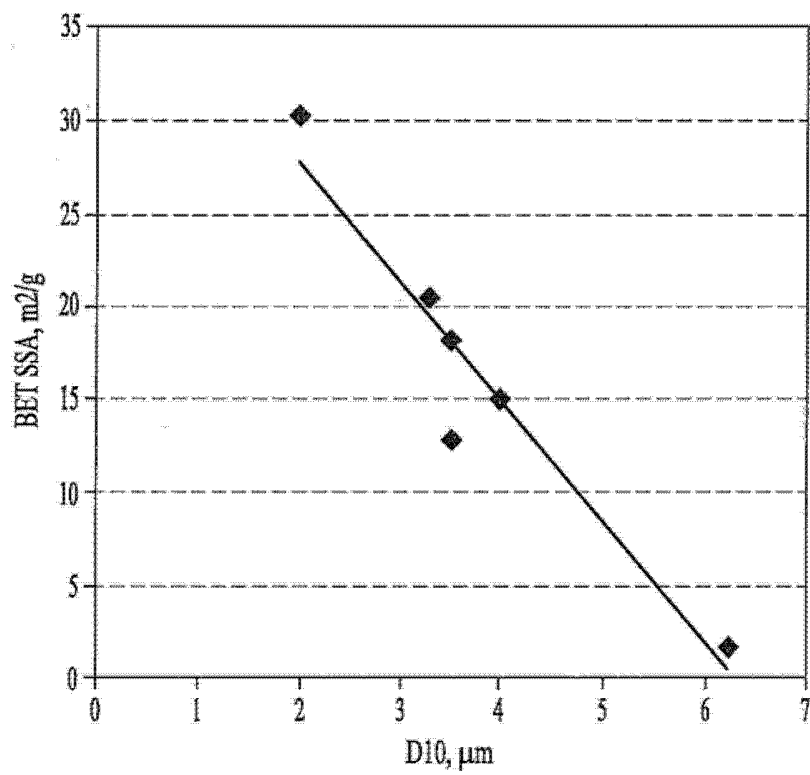


图 17B

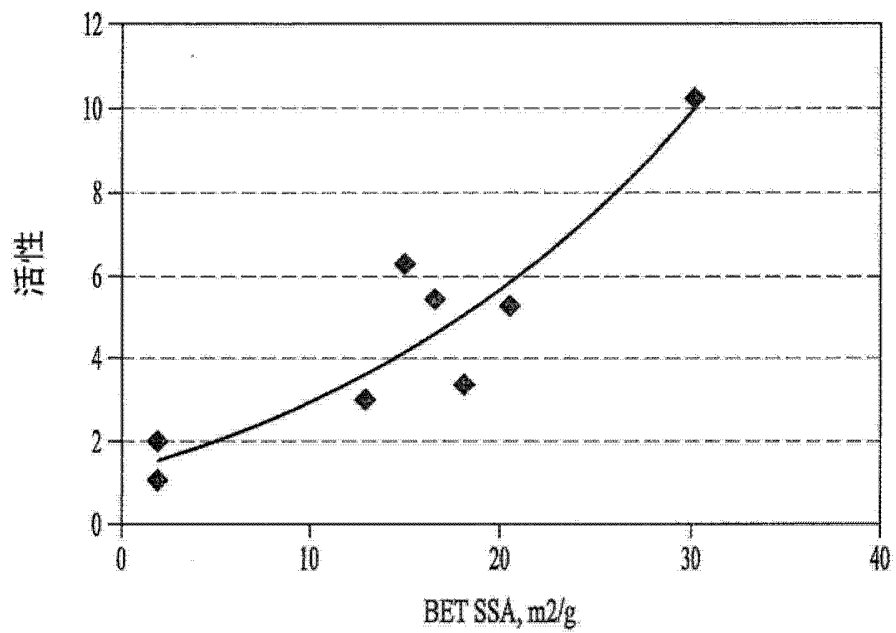


图 17C

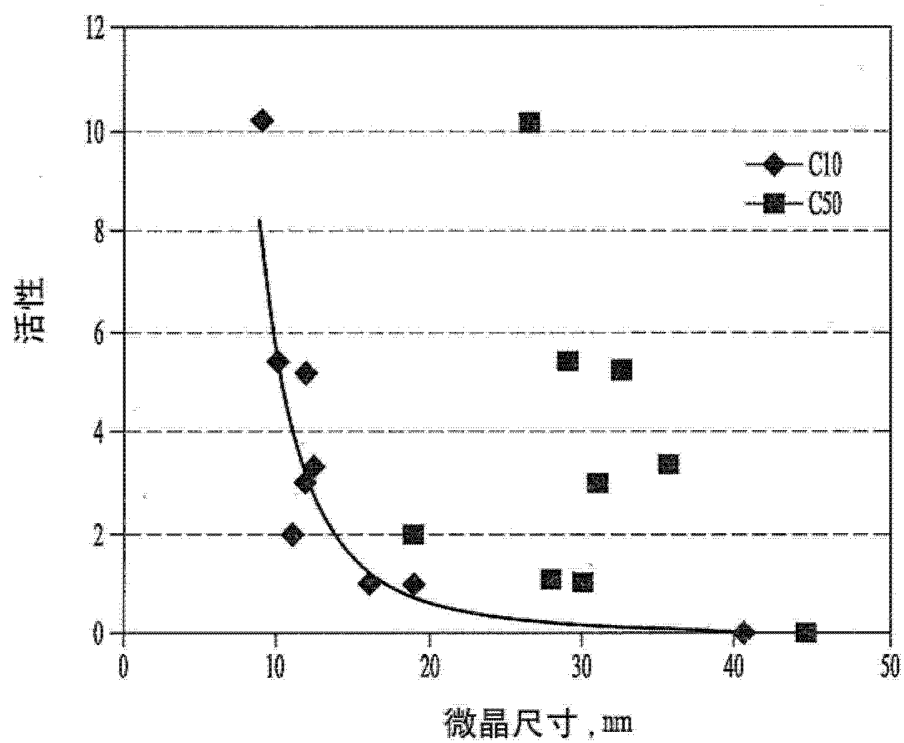


图 18

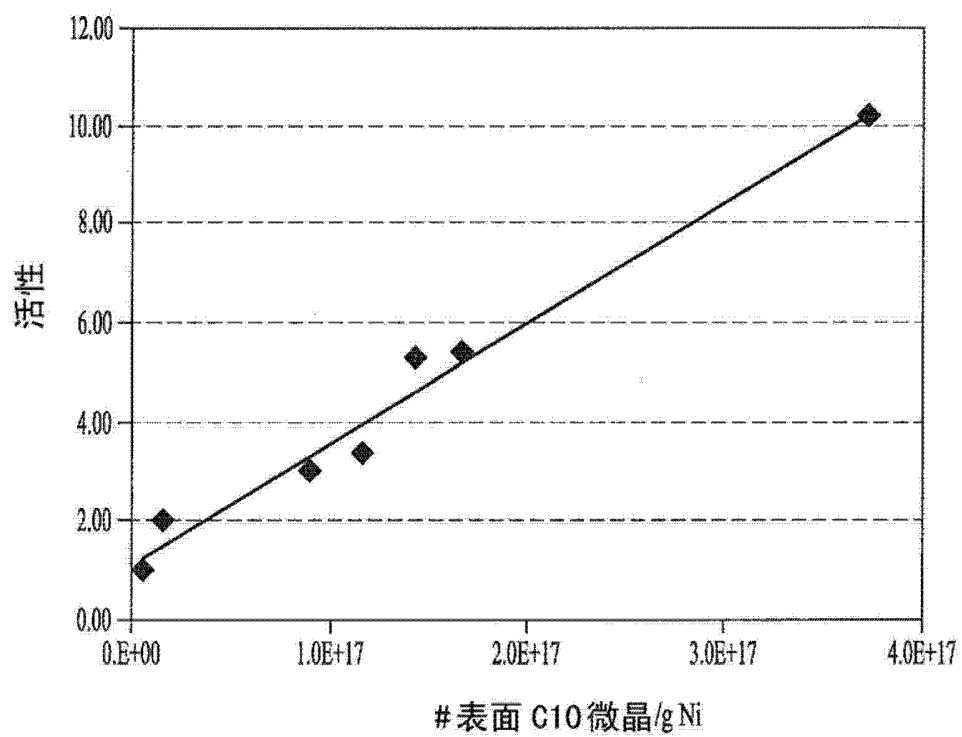


图 19

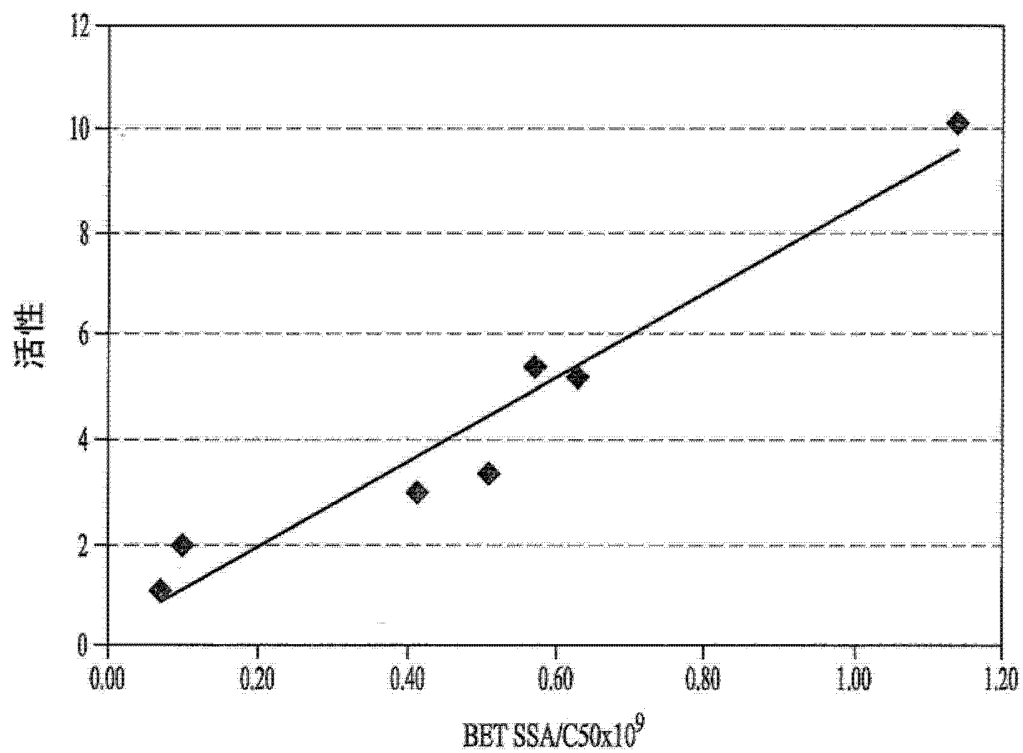


图 20

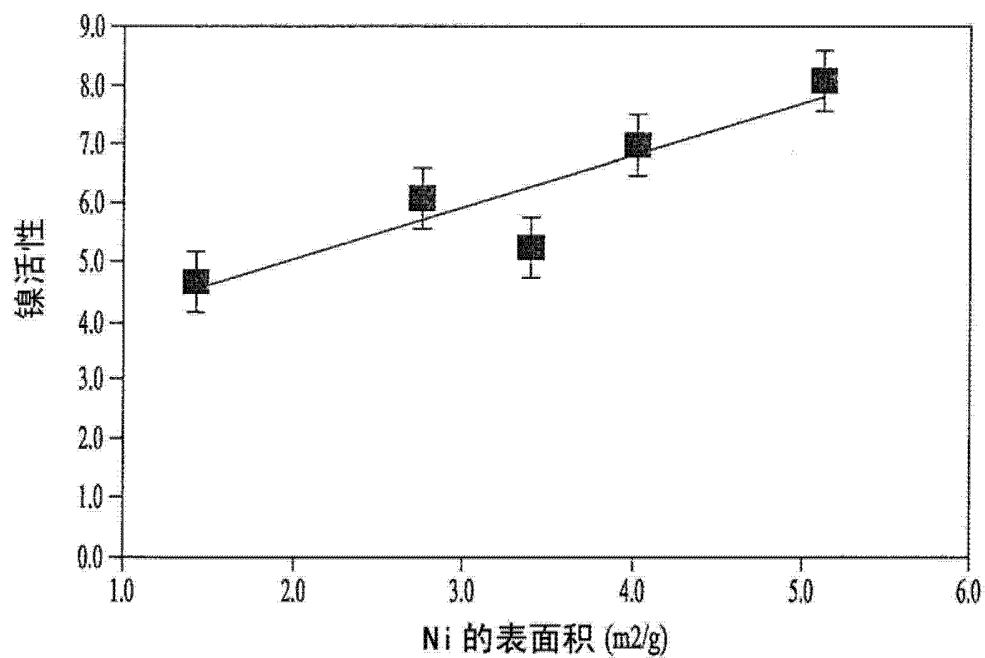


图 21