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(54) Title: METAL UTILIZATION IN SUPPORTED, METAL-CONTAINING CATALYSTS

(57) Abstract: Generally, the present invention relates to improvements in metal utilization in supported, metal-containing catalysts. For example, the present invention relates to methods for directing and/or controlling metal deposition onto surfaces of porous substrates. The present invention also relates to methods for preparing catalysts in which a first metal is deposited onto a support (e.g., a porous carbon support) to provide one or more regions of a first metal at the surface of the support, and a second metal is deposited at the surface of the one or more regions of the first metal. Generally, the electropositivity of the first metal (e.g., copper or iron) is greater than the electropositivity of the second metal (e.g., a noble metal such as platinum) and the second metal is deposited at the surface of the one or more regions of the first metal by displacement of the first metal. The present invention further relates to treated substrates, catalyst precursor structures and catalysts prepared by these methods. The invention further relates to use of catalysts prepared as detailed herein in catalytic oxidation reactions, such as oxidation of a substrate selected from the group consisting of N-(phosphonomethyl)iminodiacetic acid or a salt thereof, formaldehyde, and/or formic acid.

METAL UTILIZATION IN SUPPORTED, METAL-CONTAINING CATALYSTS

FIELD OF THE INVENTION

[0001] Generally, the present invention relates to improvements in metal utilization in supported, metal-containing catalysts. For example, the present invention relates to methods for directing and/or controlling metal deposition onto surfaces of porous substrates. More particularly, some embodiments of the present invention relate to methods for treating porous substrates (e.g., porous carbon substrates or porous metal substrates) to provide treated substrates having one or more desirable properties (e.g., a reduced surface area attributable to pores having a nominal diameter within a predefined range) that may be utilized as supports for metal-containing catalysts.

[0002] The present invention also relates to methods for preparing catalysts in which a first metal is deposited onto a support (e.g., a porous carbon support) to provide one or more regions of a first metal at the surface of the support, and a second metal is deposited at the surface of the one or more regions of the first metal. Generally, the electropositivity of the first metal (e.g., copper or iron) is greater than the electropositivity of the second metal (e.g., a noble metal such as platinum) and the second metal is deposited at the surface of the one or more regions of the first metal by displacement of the first metal.

[0003] The present invention further relates to treated substrates, catalyst precursor structures and catalysts prepared by these methods.

[0004] The invention further relates to use of catalysts prepared as detailed herein in catalytic oxidation reactions, such

as oxidation of a substrate selected from the group consisting of N-(phosphonomethyl)iminodiacetic acid or a salt thereof, formaldehyde, and/or formic acid.

BACKGROUND OF THE INVENTION

[0005] N-(phosphonomethyl)glycine (known in the agricultural chemical industry as glyphosate) is described in Franz, U.S. Patent No. 3,799,758. Glyphosate and its salts are conveniently applied as a post-emergent herbicide in aqueous formulations. It is a highly effective and commercially important broad-spectrum herbicide useful in killing or controlling the growth of a wide variety of plants, including germinating seeds, emerging seedlings, maturing and established woody and herbaceous vegetation, and aquatic plants.

[0006] Various methods for producing glyphosate are known in the art, including various methods utilizing carbon-supported noble metal-containing catalysts. See, for example, U.S. Patent No. 6,417,133 to Ebner et al. and Wan et al. International Publication No. WO 2006/031938. Generally, these methods include the liquid phase oxidative cleavage of N-(phosphonomethyl)iminodiacetic acid (i.e., PMIDA) in the presence of a carbon-supported noble metal-containing catalyst. Along with glyphosate product, various by-products may form, such as formaldehyde, formic acid (which is formed by the oxidation of the formaldehyde by-product); aminomethylphosphonic acid (AMPA) and methyl aminomethylphosphonic acid (MAMPA), which are formed by the oxidation of N-(phosphonomethyl)glycine; and iminodiacetic acid (IDA), which is formed by the de-phosphonomethylation of PMIDA. These by-products may reduce glyphosate yield (e.g., AMPA and/or MAMPA) and may introduce toxicity issues (e.g., formaldehyde). Thus, significant by-product formation is preferably avoided.

[0007] It is generally known in the art including, for example, as described in Ebner et al. U.S. 6,417,133 and by Wan et al. in International Publication No. WO 2006/031938, that carbon primarily catalyzes the oxidation of PMIDA to glyphosate and the noble metal primarily catalyzes the oxidation of by-product formaldehyde to carbon dioxide, and water. The catalysts of Ebner et al. U.S. 6,417,133 and Wan et al.
WO 2006/031938 have proven to be highly advantageous and effective catalysts for the oxidation of PMIDA to glyphosate and the oxidation of by-products formaldehyde and formic acid to carbon dioxide and water without excessive leaching of noble metal from the carbon support. These catalysts are also effective in the operation of a continuous process for the production of glyphosate by oxidation of PMIDA. Even though these catalysts are effective in PMIDA oxidation and are generally resistant to noble metal leaching under PMIDA oxidation conditions, there exist opportunities for improvement.

[0008] For example, the distribution and/or size of the pores of the porous substrates utilized in noble metal-containing catalysts may impact catalyst performance and metal utilization. Methods to introduce compounds (i.e., pore blocking compounds) within pores of substrates to modify metal deposition are known in the art. See, for example, U.S. Patent No. 5,439,859 to Durante et al.

[0009] One object of the present invention is development of catalysts effective for the oxidation of PMIDA, formaldehyde, and/or formic acid that more efficiently utilize the costly noble metal, and methods for their preparation. More efficient metal usage may provide catalysts more active than conventional catalysts. Another object of the present invention is development of methods for preparing effective catalysts that require a

reduced proportion of costly noble metal as compared to conventional catalysts, while still exhibiting suitable activity.

SUMMARY OF THE INVENTION

[0010] This invention provides catalysts and methods for preparing catalysts that are useful in heterogeneous oxidation reactions, including the preparation of glyphosate by the oxidation of PMIDA.

[0011] Briefly, therefore, the present invention is directed to oxidation catalysts comprising a particulate carbon support, a first metal, and a second metal, the support having at its surface particles comprising the first metal and the second metal.

[0012] In at least one embodiment, the second metal distribution within at least one of the particles as characterized by energy dispersive x-ray (EDX) line scan analysis as described in Protocol B produces a second metal signal that varies by no more than about 25% across a scanning region having a dimension that is at least about 70% of the largest dimension of the at least one particle. In a further embodiment, the second metal distribution within at least one of the particles as characterized by EDX line scan analysis as described in Protocol B produces a second metal signal that varies by no more than about 20% across a scanning region having a dimension that is at least about 60% of the largest dimension of the at least one particle. In another embodiment, the second metal distribution within at least one of the particles as characterized by EDX line scan analysis as described in Protocol B produces a second metal signal that varies by no more than about 15% across a scanning region having a dimension that is at least about 50% of the largest dimension of the at least one particle.

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[0012.1] Thus, in a first aspect, the present invention provides a process for oxidizing a substrate selected from the group consisting of N-(phosphonomethyl) iminodiacetic acid or a salt thereof, formaldehyde, and formic acid, the process comprising:

contacting the substrate with an oxidizing agent in the presence of an oxidation catalyst comprising a particulate carbon support, a first metal, and a second metal, the support having at its surface particles comprising the first metal and the second metal, wherein:

the second metal distribution within at least one of said particles as characterized by EDX line scan analysis produces a second metal signal that varies by no more than about 25% across a scanning region having a dimension that is at least about 70% of the largest dimension of the at least one particle.

[0012.2] In a second aspect, the present invention provides an oxidation catalyst comprising a particulate carbon support, a first metal, and platinum, the support having at its surface particles comprising the first metal and platinum, wherein the first metal is selected from the group consisting of cobalt, copper, iron, and combinations thereof, and:

the platinum distribution within at least one of said first metal and platinum-containing particles as characterized by EDX line scan analysis produces a platinum signal that varies by no more than about 25% across a scanning region having a dimension that is at least about 70% of the largest dimension of the at least one particle and wherein first metal and platinum-containing particles at the surface of the carbon support comprise a core comprising the first metal and a shell at least partially surrounding the core and comprising platinum, the shell having a thickness of no more than three platinum atoms.

[0012.3] In a third aspect, the present invention provides a process for oxidizing a substrate selected from the group consisting of N-(phosphonomethyl) iminodiacetic acid or a salt thereof, formaldehyde, and formic acid, the process comprising:

contacting the substrate with an oxidizing agent in the presence of an oxidation catalyst comprising a first metal, a noble metal, and a porous carbon support, the catalyst comprising one or more first metal regions at the surface of the carbon support and one or more noble metal regions at the surface of the one or more first metal regions, wherein the first metal has an electropositivity greater than the electropositivity of the noble metal,

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wherein the oxidation catalyst is prepared by a process comprising contacting the carbon support having one or more first metal regions at its surface with a noble metal deposition bath comprising ions of the noble metal, thereby depositing the noble metal by displacement of the first metal from one or more of said regions, preferably, the weight ratio of the noble metal to the first metal being at least about 0.25:1.

[0012.4] In a fourth aspect, the present invention provides a process for oxidizing a substrate selected from the group consisting of N-(phosphonomethyl) iminodiacetic acid or a salt thereof, formaldehyde, and formic acid, the process comprising:

contacting the substrate with an oxidizing agent in the presence of an oxidation catalyst comprising a particulate carbon support, a first metal, and a noble metal, the support having at its surface metal particles comprising the first metal and the noble metal, wherein:

the metal particles comprise a core comprising the first metal and a shell at least partially surrounding the core and comprising the noble metal, wherein at least about 70% of the noble metal is present within the particle shell.

[0012.5] In a fifth aspect, the present invention provides a process for oxidizing a substrate selected from the group consisting of N-(phosphonomethyl) iminodiacetic acid or a salt thereof, formaldehyde, and formic acid, the process comprising:

contacting the substrate with an oxidizing agent in the presence of an oxidation catalyst comprising a particulate carbon support, platinum, and copper, the support having at its surface metal particles comprising platinum and copper, wherein the atom percent of the platinum at the surface of the particles is at least about 40%.

[0012.6] In a sixth aspect, the present invention provides an oxidation catalyst comprising a particulate carbon support, platinum, and copper, the support having at its surface metal particles comprising platinum and copper, wherein the atom percent of platinum at the surface of the particles is at least about 40% and wherein metal particles comprising platinum and copper at the surface of the carbon support comprise a core comprising copper and a shell at least partially surrounding the core and comprising platinum, the shell having a thickness of no more than three platinum atoms.

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[0012.7] In preferred embodiments of the first and second aspect of the invention, the process or catalyst is characterized in that:

(a) EDX line scan analysis is conducted in accordance with Protocol B;

(b) the second metal signal or platinum signal varies by no more than about 20% across the scanning region;

(c) the second metal signal or platinum signal varies by no more than about 20% across a scanning region having a dimension that is at least about 60% of the largest dimension of the at least one particle, preferably the second metal signal or platinum signal varies by no more than about 15% across the scanning region;

(d) the second metal signal or platinum signal varies by no more than about 15% across a scanning region having a dimension that is at least about 50% of the largest dimension of the at least one particle, preferably the second metal signal or platinum signal varies by no more than about 10% across the scanning region;

(e) the atomic ratio of second metal or platinum to first metal of the at least one particle is less than 1:1;

(f) the at least one particle has a largest dimension of at least about 6 nm;

(g) the at least one particle constitutes at least about 1% of the metal particles at the surface of the carbon support;

(h) the first metal distribution of the at least one metal particle as characterized by EDX line scan analysis produces a first metal signal, the ratio of the maximum first metal signal to the maximum second metal signal across the scanning region being at least about 1.5:1.

[0012.8] In preferred embodiments of the first, third and forth aspect of the invention, the process or catalyst is characterized in that:

(a) the first metal is selected from the group consisting of vanadium, tungsten, molybdenum, gold, osmium, iridium, tantalum, palladium, ruthenium, antimony, bismuth, arsenic, mercury, silver, copper, titanium, tin, lead, germanium, zirconium, cerium, nickel, cobalt, iron, chromium, zinc, manganese, aluminum, beryllium, magnesium, lithium, barium, cesium, and combinations thereof;

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(b) the first metal is selected from the group consisting of copper, tin, nickel, cobalt, and combinations thereof;
(c) the first metal is selected from the group consisting of cobalt, copper, iron, and combinations thereof;
(d) the first metal is copper, or the first metal is iron, or the first metal is cobalt;
(e) the first metal or copper constitutes at least about 1% by weight of the catalyst, or the first metal or copper constitutes from about 1% to about 10% by weight of the catalyst;
(f) the second metal is a noble metal, preferably the noble metal is selected from the group consisting of platinum, palladium, ruthenium, rhodium, iridium, silver, osmium, gold, and combinations thereof, more preferably the noble metal comprises platinum, palladium, or platinum and palladium, or the noble metal is platinum.

[0012.9] In preferred embodiments of the invention, the process or catalyst is characterized in that:
(a) the second metal, noble metal, or platinum constitutes at least about 1% by weight of the catalyst;
(b) the second metal, noble metal, or platinum constitutes less than about 8% by weight of the catalyst;
(c) the second metal, noble metal, or platinum constitutes from about 3% to about 6% by weight of the catalyst, or the second metal, noble metal, or platinum constitutes from about 1% to about 5% by weight of the catalyst;
(d) the substrate is N-(phosphonomethyl) iminodiacetic acid or a salt thereof, preferably said oxidation catalyst is effective for oxidation of byproduct formaldehyde and/or formic acid produced in the oxidation of N-(phosphonomethyl) iminodiacetic acid or a salt thereof.

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[0013] The present invention is also directed to an oxidation catalyst comprising a particulate carbon support, copper, and platinum, the support having at its surface particles comprising copper and platinum. The platinum distribution within at least 70% (number basis) of the particles as characterized by EDX line scan analysis as described in Protocol B produces a platinum signal that varies by no more than about 25% across a scanning region having a dimension that is at least about 70% of the largest dimension of said particles.

[0014] The present invention is further directed to an oxidation catalyst comprising a particulate carbon support, a first metal, and a noble metal, the support having at its surface metal particles comprising the first metal and the noble metal. The catalyst is characterized as chemisorbing at least 975 μmoles CO per gram of catalyst per gram noble metal during Cycle 2 of static carbon monoxide chemisorption analysis as described in Protocol A.

[0015] The present invention is also directed to an oxidation catalyst comprising a particulate carbon support, a first metal, and a noble metal, the support having at its surface metal particles comprising the first metal and the noble metal, wherein the metal particles comprise a core comprising the first metal and a shell at least partially surrounding the core and comprising the noble metal, wherein at least about 70% of the noble metal is present within the particle shell.

[0016] In a further embodiment, the present invention is directed to an oxidation catalyst comprising a particulate carbon support, platinum, and copper, the support having at its surface metal particles comprising platinum and copper, wherein the atom percent of platinum at the surface of the particles is at least about 10%.

[0017] In a still further embodiment, the present invention is directed to an oxidation catalyst comprising a particulate carbon support, a first metal, and a noble metal, the support having at its surface metal particles comprising the first metal and the noble metal, wherein the metal particles comprise a core comprising the first metal and a shell at least partially surrounding the core and comprising the noble metal; and the catalyst is characterized as chemisorbing at least 975 μmoles CO per gram of catalyst per gram noble metal during Cycle 2 of static carbon monoxide chemisorption analysis as described in Protocol A.

[0018] In another embodiment, the present invention is directed to an oxidation catalyst comprising a particulate carbon support, platinum, and copper, the support having at its surface metal particles comprising platinum and copper, wherein the atom percent of platinum at the surface of the particles is at least about 5%; and the catalyst is characterized as chemisorbing at least 500 μmoles CO per gram of catalyst per gram noble metal during Cycle 2 of static carbon monoxide chemisorption analysis as described in Protocol A.

[0019] In a still further embodiment, the present invention is directed to an oxidation catalyst comprising a particulate carbon support, a first metal, and a noble metal, the support having at its surface metal particles comprising the first metal and the noble metal, wherein the metal particles comprise a core comprising the first metal and a shell at least partially surrounding the core and comprising the noble metal; the noble metal constitutes less than 5% by weight of the catalyst; and the catalyst is characterized as chemisorbing at least about 800 μmoles CO per gram of catalyst per gram noble metal during Cycle 2 of static carbon monoxide chemisorption analysis as described in Protocol A.

[0020] The present invention is also directed to an oxidation catalyst comprising a particulate carbon support having metal particles at a surface thereof comprising a first metal and a second metal, wherein the electropositivity of the first metal is greater than the electropositivity of the second metal and the second metal is deposited by displacement of first metal ions of one or more regions of first metal of a catalyst precursor structure; and the weight ratio of the second metal to the first metal is at least about 0.25:1.

[0021] The present invention is also directed to processes for oxidizing a substrate selected from the group consisting of N-(phosphonomethyl)iminodiacetic acid or a salt thereof, formaldehyde, and formic acid. Generally, the process comprises contacting the substrate with an oxidizing agent in the presence of an oxidation catalyst prepared by the methods detailed herein and/or as described herein. For example, in one embodiment the catalyst comprises a first metal, a noble metal, and a porous carbon support, the catalyst comprising one or more first metal regions at the surface of the carbon support and one or more noble metal regions at the surface of the one or more first metal regions, wherein the first metal has an electropositivity greater than the electropositivity of the noble metal.

[0022] The present invention is further directed to various methods for preparing a catalyst comprising a first metal, a second metal, and a porous support having a surface comprising pores of a nominal diameter within a predefined range and pores of a nominal diameter outside the predefined range.

[0023] In one embodiment, the method comprises disposing a pore blocking agent within pores of the porous support having a nominal diameter within the predefined range, the pore blocking agent having at least one dimension relative to the openings of

the pores having a nominal diameter within the predefined range such that the pore blocking agent is preferentially retained within the pores; contacting the support with a first metal deposition bath comprising an aqueous medium and ions of the first metal, thereby depositing the first metal at the surface of the porous support within the pores having a nominal diameter outside the predefined range to form a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support among the pores of a nominal diameter outside the predefined range; and contacting the catalyst precursor structure with a second metal deposition bath comprising ions of the second metal, thereby depositing the second metal at the surface of the catalyst precursor structure.

[0024] In another embodiment, the method comprises contacting the support and a first metal deposition bath comprising an aqueous medium, ions of the first metal, and a coordinating agent that forms a coordination compound with the first metal having at least one dimension larger than the nominal diameter of the pores within the predefined range, thereby depositing the first metal at the surface of the support within the pores having a nominal diameter outside the predefined range to form a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support; and contacting the catalyst precursor structure with a second metal deposition bath comprising ions of the second metal, thereby depositing the second metal at the surface of the catalyst precursor structure.

[0025] The present invention is also directed to methods for preparing catalysts comprising a first metal, a second metal, and a porous carbon support.

[0026] In one embodiment, the method comprises contacting the porous carbon support with a first metal deposition bath

comprising ions of the first metal, thereby depositing the first metal at the surface of the porous carbon support to form a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support, wherein the first metal has an electropositivity greater than the electropositivity of the second metal; contacting the catalyst precursor structure with a second metal deposition bath comprising ions of the second metal, thereby depositing the second metal at the surface of the catalyst precursor structure by displacement of the first metal from one or more of the regions; and heating the catalyst precursor structure having the first and second metals deposited at the surface of the catalyst precursor structure to a temperature of at least about 500°C in a non-oxidizing environment.

[0027] In a further embodiment, the method comprises contacting the porous carbon support with a first metal deposition bath comprising ions of the first metal, thereby depositing the first metal at the surface of the porous carbon support to form a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support, wherein the carbon support has a Langmuir surface area of at least about 500 m^2/g and the first metal has an electropositivity greater than the electropositivity of the second metal; and contacting the catalyst precursor structure with a second metal deposition bath comprising ions of the second metal, thereby depositing the second metal at the surface of the catalyst precursor structure by displacement of the first metal from one or more of the regions.

[0028] The present invention is also directed to methods for preparing a catalyst comprising a first metal, a noble metal, and a porous support. In one embodiment, the method comprises contacting the support and a first metal deposition bath comprising an aqueous medium, ions of the first metal and a

coordinating agent that forms a coordination compound with the first metal, thereby depositing the first metal at the surface of the support to form a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support, wherein the first metal has an electropositivity greater than the electropositivity of the noble metal; and contacting the catalyst precursor structure with a noble metal deposition bath comprising ions of the noble metal, thereby depositing the noble metal at the surface of the catalyst precursor structure by displacement of the first metal from one or more of the regions.

[0029] In a further embodiment, the method comprises contacting the support with a first metal deposition bath comprising an aqueous medium and ions of the first metal, thereby depositing first metal at the surface of the support to form a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support, wherein the first metal has an electropositivity greater than the electropositivity of the noble metal; and contacting the catalyst precursor structure with a noble metal deposition bath comprising ions of the noble metal, thereby depositing the noble metal at the surface of the catalyst precursor structure by displacement of the first metal from one or more of the regions, wherein substantially all the noble metal is deposited by the displacement, or the noble metal ions consist essentially of noble metal ions having an oxidation number of 2.

[0030] In another embodiment, the method comprises contacting the support with a first metal deposition bath comprising an aqueous medium, ions of the first metal, and a pore blocking agent, thereby disposing the pore blocking agent within pores of the substrate having a nominal diameter within a predefined range, wherein the pore blocking agent has at least one dimension

relative to the opening of the pores of the predefined range sufficient such that the pore blocking agent is preferentially retained within the pores, and depositing first metal at the surface of the support within pores having a nominal diameter outside the predefined range, thereby forming a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support, wherein the first metal has an electropositivity greater than the electropositivity of the noble metal; and contacting the catalyst precursor structure with a noble metal deposition bath comprising ions of the noble metal, thereby depositing the noble metal at the surface of the catalyst precursor structure by displacement of the first metal from one or more of regions.

[0031] The present invention is also directed to methods for preparing a catalyst comprising a first metal, a noble metal, and a porous support having a surface comprising pores of a nominal diameter within a predefined range and pores of a nominal diameter outside the predefined range. In one embodiment, the method comprises contacting the support and a first metal deposition bath comprising an aqueous medium, ions of the first metal and a coordinating agent that forms a coordination compound with the first metal having at least one dimension larger than the nominal diameter of the pores within the predefined range, thereby depositing the first metal at the surface of the support within the pores having a nominal diameter outside the predefined range to form a catalyst precursor structure having one or more regions of the deposited first metal at the surface of the support; and contacting the catalyst precursor structure with a noble metal deposition bath comprising ions of the noble metal, thereby depositing the noble metal at the surface of the catalyst precursor structure.

[0032] The present invention is also directed to methods for preparing catalysts comprising copper, platinum, and a porous carbon support.

[0033] In one embodiment, the method comprises contacting the support with a copper deposition bath comprising copper ions and a coordinating agent in the absence of an externally applied voltage, thereby depositing copper at the surface of the porous carbon support to form a catalyst precursor structure having one or more regions of deposited copper at the surface of the support; and contacting the catalyst precursor structure and a platinum deposition bath comprising platinum ions, thereby depositing platinum at the surface of the catalyst precursor structure by displacement of copper from one or more of the regions.

[0034] In another embodiment, the method comprises contacting the support and a copper deposition bath comprising copper ions in the absence of an externally applied voltage, thereby depositing copper at the surface of the carbon support to form a catalyst precursor structure having one or more regions of deposited copper at the surface of the support, wherein the carbon support has a Langmuir surface area of at least about 500 m^2/g prior to deposition of copper thereon; and contacting the catalyst precursor structure and a platinum deposition bath comprising platinum ions, thereby depositing platinum at the surface of the catalyst precursor structure by displacement of copper from one or more of the regions.

[0035] In a further embodiment, the method comprises contacting the support and a copper deposition bath comprising copper ions in the absence of an externally applied voltage, thereby depositing copper at the surface of the carbon support to form a catalyst precursor structure having one or more regions of deposited copper at the surface of the support; contacting the

catalyst precursor structure and a platinum deposition bath comprising platinum ions, thereby depositing platinum at the surface of the catalyst precursor structure by displacement of copper from one or more of the regions; and heating the surface of the catalyst precursor having platinum at the surface of the one or more copper regions to a temperature of at least about 500°C in a non-oxidizing environment.

[0036] The present invention is also directed to methods for preparing catalysts comprising iron, platinum, and a porous carbon support.

[0037] In one embodiment, the method comprises contacting the support with an iron deposition bath comprising iron ions and a coordinating agent in the absence of an externally applied voltage, thereby depositing iron at the surface of the porous carbon support to form a catalyst precursor structure having one or more regions of deposited iron at the surface of the support; and contacting the catalyst precursor structure and a platinum deposition bath comprising platinum ions, thereby depositing platinum at the surface of the catalyst precursor structure by displacement of iron from one or more of the regions.

[0038] In another embodiment, the method comprises contacting the support and an iron deposition bath comprising iron ions in the absence of an externally applied voltage, thereby depositing iron at the surface of the carbon support to form a catalyst precursor structure having one or more regions of deposited iron at the surface of the support, wherein the carbon support has a Langmuir surface area of at least about 500 m^2/g prior to deposition of iron thereon; and contacting the catalyst precursor structure and a platinum deposition bath comprising platinum ions, thereby depositing platinum at the surface of the catalyst

precursor structure by displacement of iron from one or more of the regions.

[0039] In a further embodiment, the method comprises contacting the support and an iron deposition bath comprising iron ions in the absence of an externally applied voltage, thereby depositing iron at the surface of the carbon support to form a catalyst precursor structure having one or more regions of deposited iron at the surface of the support; contacting the catalyst precursor structure and a platinum deposition bath comprising platinum ions, thereby depositing platinum at the surface of the catalyst precursor structure by displacement of iron from one or more of the regions; and heating the surface of the catalyst precursor having platinum at the surface of the one or more iron regions in a non-oxidizing environment.

[0040] The present invention is also directed to methods for treating a porous substrate to prepare a modified porous substrate having a reduced surface area attributable to pores having a nominal diameter within a predefined range.

[0041] In one embodiment, the method comprises disposing a pore blocking agent within pores of the porous substrate having a nominal diameter within the predefined range, the pore blocking agent having at least one dimension relative to the opening of the pores having a nominal diameter within the predefined range sufficient such that the pore blocking agent is preferentially retained within the pores.

[0042] In another embodiment, the method comprises introducing a pore blocking compound into the pores of the porous substrate, the pore blocking compound being susceptible to a conformational change such that the pore blocking compound is retained within pores of the porous substrate having a diameter within the predefined range.

[0043] In a further embodiment, the method comprises introducing into the pores having a nominal diameter within a predefined range compounds capable of forming a pore blocking compound having at least one dimension such that the pore blocking compound is retained within the pores having a nominal diameter within a predefined range.

[0044] The present invention is also directed to methods for treating porous substrates having micropores and larger diameter pores to prepare a modified porous substrate having a reduced micropore surface area.

[0045] In one embodiment, the method comprises disposing a pore blocking agent within micropores of the porous substrate, the pore blocking agent having at least one dimension relative to the micropore openings such that the pore blocking agent is preferentially retained within the pores.

[0046] In another embodiment, the method comprises introducing a pore blocking compound into the micropores of the porous substrate, the pore blocking compound being susceptible to a conformational change such that the pore blocking compound is retained within micropores of the porous substrate.

[0047] In a further embodiment, the method comprises introducing into the micropores of the substrate compounds capable of forming a pore blocking compound having at least one dimension such that the pore blocking compound is retained within the micropores.

[0048] In a still further embodiment, the method comprises introducing a pore blocking composition into the micropores of the porous substrate, the pore blocking composition comprising a substituted cyclohexane derivative.

[0049] The present invention is also directed to methods for preparing a catalyst comprising a metal at the surface of a porous

substrate wherein the metal is preferentially excluded from pores of the porous substrate having a nominal diameter within a predefined range. In one embodiment, the method comprises (i) introducing one or more precursors of a pore blocking compound into pores of the porous substrate, wherein: at least one of the pore blocking compound precursors is susceptible to a conformational change to form a pore blocking compound that is retained within pores of the porous substrate having a nominal diameter within the predefined range, or at least two pore blocking compound precursors are capable of forming a pore blocking compound having at least one dimension such that the pore blocking compound is retained within pores of the porous substrate having a nominal diameter within a predefined range; (ii) preferentially removing the pore blocking compound from the pores of the porous substrate having a nominal diameter outside the predefined range to prepare a modified porous substrate having a reduced surface area attributable to pores having a nominal diameter within the predefined range; and (iii) contacting the surface of the modified porous substrate with a solution containing the metal.

[0050] In another embodiment, the present invention is directed to a porous substrate having a pore blocking compound within pores of the porous substrate having a nominal diameter within a predefined range. The pore blocking compound is retained within the pores having a nominal diameter within a predefined range due to the pore blocking compound having at least one dimension that is greater than openings of the pores having a nominal diameter within a predefined range, or the pore blocking compound exhibiting a conformation that prevents the pore blocking compound from exiting through openings of pores having a nominal diameter within the predefined range.

[0051] The present invention is directed to treated porous substrates having a pore blocking compound within micropores of the porous substrate. In one embodiment, the micropore surface area of the treated substrate is no more than about 70% of the micropore surface area of the porous substrate prior to treatment. In another embodiment, the pore blocking compound is selected from the group consisting of the condensation product of a substituted cyclohexane derivative and a glycol, the condensation product of a di-substituted cyclohexane derivative and a glycol, and combinations thereof.

[0052] Other objects and features will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0053] Figs. 1A-1C are graphical representations of pore blockers in accordance with the present invention.

[0054] Fig. 1D illustrates a conformational change of a pore blocker in accordance with the present invention.

[0055] Fig. 2 depicts heat treatment of a first and second metal-impregnated support in accordance with the present invention.

[0056] Figs. 3A/5A and 3B/5B transmission electron microscopy (TEM) results as described in Example 3.

[0057] Figs. 4A and 4B provide pore volume and surface area for treated and untreated substrates as described in Example 4.

[0058] Fig. 5C provides porosity data for catalysts analyzed as described in Example 19.

[0059] Fig. 5D provides pore volume results for catalysts analyzed as described in Example 20.

[0060] Figs. 6-13 are micrographs generated by scanning transmission electron microscopy (STEM) analysis for a carbon support and metal-impregnated supports as described in Example 21.

[0061] Fig. 14 provides results of line scan analysis for a metal-impregnated support as described in Example 21.

[0062] Figs. 15 and 16 are STEM micrographs for catalysts as described in Example 21.

[0063] Figs. 17 and 18 are results of energy dispersive spectroscopy (EDS) analysis of catalysts as described in Example 21.

[0064] Figs. 19-21 are STEM micrographs for reaction-tested catalysts as described in Example 21.

[0065] Fig. 22 provides results of line scan analysis for a reaction-tested catalyst as described in Example 21.

[0066] Figs. 23 and 24 are STEM micrographs for reaction-tested catalysts as described in Example 21.

[0067] Fig 25 provides results of line scan analysis for a reaction tested catalyst as described in Example 21.

[0068] Figs. 26 and 27 are EDS spectra for reaction-tested catalysts as described in Example 21.

[0069] Figs. 28 and 29 are TEM and STEM images for metal-impregnated supports as described in Example 22.

[0070] Figs. 30-31, 32-33, 34-35, and 36-37 are TEM images and corresponding line scan analysis results for metal-impregnated supports as described in Example 22.

[0071] Figs. 38 and 39 are TEM and STEM images for catalysts as described in Example 22.

[0072] Fig. 40 indicates the portion of catalyst analyzed by line scan analysis as described in Example 22.

[0073] Fig. 41 provides line scan analysis for the portion of the support identified in Fig. 40.

[0074] Fig. 42 indicates the portion of catalyst analyzed by line scan analysis as described in Example 22.

[0075] Fig. 43 provides line scan analysis for the portion of the support identified in Fig. 40.

[0076] Figs. 44 and 45 are TEM images utilized in particle size analysis as described in Example 23.

[0077] Fig. 46 provides particle size distribution data for catalyst analyzed as described in Example 23.

[0078] Figs. 47 and 48 are TEM images utilized in particle size analysis as described in Example 23.

[0079] Fig. 49 provides particle size distribution data for catalyst analyzed as described in Example 23.

[0080] Figs. 50 and 51 are X-ray diffraction results for a catalyst analyzed as described in Example 24.

[0081] Figs. 52-55 are nano-diffraction results for a metal particle analyzed as described in Example 24.

[0082] Fig. 56 and 57 provide reaction testing data as described in Example 25.

[0083] Fig. 58 provides reaction testing data of Example 26.

[0084] Figs. 59-62 provide reaction testing data of Example 27.

[0085] Figs. 63-65 provide reaction testing data of Example 28.

[0086] Figs. 66-68 provide reaction testing data of Example 29.

[0087] Figs. 69-71 provide reaction testing data of Example 30.

[0088] Figs. 72-78 provide reaction testing data of Example 31.

[0089] Figs. 79-84 provide reaction testing data of Example 32.

[0090] Fig. 85 provides reaction testing data of Example 33.

[0091] Figs. 86-90 provide reaction testing data of Example 34.

[0092] Figs. 91-95 provide reaction testing data of Example 35.

[0093] Figs. 96-98 provide reaction testing data of Example 36.

[0094] Fig. 99 provides reaction testing data of Example 37.

[0095] Fig. 100 provides reaction testing data of Example 38.

[0096] Figs. 101 and 102 provide reaction testing data of Example 39.

[0097] Fig. 103 provides platinum site density data as described in Example 20.

[0098] Fig. 104 provides reaction testing data of Example 41.

[0099] Figs. 105 and 106 provide reaction testing data of Example 42.

[00100] Fig. 107 provides reaction testing data of Example 43.

[00101] Fig. 108 provides reaction testing data of Example 44.

[00102] Fig. 109 provides X-Ray Diffraction (XRD) results for the catalyst described in Example 45.

[00103] Figs. 110 and 111 provide XRD results for the catalyst described in Example 46.

[00104] Fig. 111A provides platinum leaching data for catalysts described in Examples 46 and 48.

[00105] Figs. 112-115 provide XRD results for the catalysts described in Example 50.

[00106] Fig. 116 is a scanning transmission electron microscopy (STEM) micrograph described in Example 55.

[00107] Figs. 117 and 118 are energy dispersive x-ray (EDX) spectroscopy line scan results described in Example 55.

[00108] Figs. 119 and 120 are STEM photomicrographs described in Example 55.

[00109] Fig. 121 is an STEM micrograph described in Example 55.

[00110] Fig. 122 provides electron energy loss spectroscopy (EELS) line scan results described in Example 55.

[00111] Fig. 123 is an STEM micrograph described in Example 55.

[00112] Fig. 124 provides EELS line scan results described in Example 55.

[00113] Fig. 125 is an STEM micrograph described in Example 55.

[00114] Fig. 126 provides EELS line scan results described in Example 55.

[00115] Fig. 127 provides high resolution electron microscopy (HREM) photomicrographs described in Example 57.

[00116] Fig. 128 provides STEM micrographs described in Example 57.

[00117] Fig. 129 is an STEM micrograph described in Example 57.

[00118] Fig. 130 provides EDX line scan analysis results described in Example 57.

[00119] Fig. 131 is an STEM micrograph described in Example 57.

[00120] Fig. 132 provides EDX line scan analysis results described in Example 57.

[00121] Fig. 133 is an STEM photomicrograph described in Example 57.

[00122] Fig. 134 provides results of EELS line scan analysis described in Example 57.

[00123] Figs. 135-137 are HREM photomicrographs described in Example 57.

[00124] Fig. 138 provides XRD results described in Example 57.

[00125] Fig. 139 is an STEM micrograph described in Example 60.

[00126] Fig. 140 provides results of EELS line scan analysis described in Example 60.

[00127] Fig. 141 is an STEM micrograph described in Example 60.

[00128] Fig. 142 provides EDX line scan analysis results described in Example 60.

[00129] Fig. 143 is an STEM micrograph described in Example 60.

[00130] Fig. 144 provides results of EELS line scan analysis described in Example 60.

[00131] Fig. 145 provides EDX line scan analysis results described in Example 60.

[00132] Fig. 146 is an STEM micrograph described in Example 60.

[00133] Fig. 147 provides EDX line scan analysis results described in Example 60.

[00134] Fig. 148 provides XRD results described in Example 60.

[00135] Figs. 149 and 150 are STEM micrographs described in Example 60.

[00136] Fig. 151 provides EDX line scan analysis results described in Example 60.

[00137] Fig. 152 is an STEM micrograph described in Example 60.

[00138] Fig. 153 provides EDX line scan analysis described in Example 60.

[00139] Figs. 154 and 155 provide XRD results described in Example 61.

[00140] Figs. 155A and 155B provide microscopy results for a finished catalyst as described in Example 65.

[00141] Figs. 155C - 155F provide microscopy results for a finished catalyst described in Example 65.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[00142] Described herein are catalyst preparation methods providing improvements in metal utilization in supported, metal-containing catalysts. Generally, various embodiments of the present invention include controlling and/or directing metal deposition onto the surface of a porous substrate. Controlling or directing metal deposition can be used to address one or more problems associated with the preparation of conventional supported, metal-containing catalysts.

[00143] For example, one potential drawback associated with conventional platinum on carbon catalysts is the susceptibility of relatively small platinum-containing particles to leaching during liquid phase catalytic oxidation reactions as compared to larger metal-containing particles. Excessive leaching of metal particles results in metal loss and represents inefficient metal usage. Furthermore, in the case of PMIDA oxidation, these relatively small platinum-containing crystallites are believed to contribute to undesired by-product formation (e.g., IDA). Relatively small platinum-containing crystallites are also believed to be more susceptible to deactivation than larger particles (e.g., by deactivation of metal-containing active sites in the presence of the reaction medium and/or by coking of the catalyst). It is believed that a significant portion of the relatively small metal particles are at the surface of the carbon support within

relatively small pores and that the small pores may act to trap and prevent these relatively small platinum crystallites from agglomerating into larger particles that are generally more resistant to leaching and generally do not promote IDA formation. In addition, metal deposited at the surface of a porous substrate within the relatively small pores is believed to be less accessible to reactants than metal deposited within larger pores, and thereby contributes less to catalyst activity.

[00144] Various methods described herein for directing and/or controlling metal deposition generally involve treating porous substrates by disposing or introducing one or more pore blocking compounds within pores of a predefined size range. The methods described herein may be used to selectively block pores within a certain size domain without significantly affecting other pores of the substrate so as to provide advantageous catalytic surface area. As detailed herein, including the Examples, various embodiments of the present invention provide a porous substrate including a pore blocking compound disposed and preferentially retained within relatively small pores (e.g., micropores, or pores having a nominal diameter of less than about 20Å). The presence of the pore blocking compound within the pores of the substrate may be indicated by a reduced proportion of surface area attributable to the relatively small pores (e.g., a reduced proportion of micropore surface area) and/or by a reduced contribution to the porosity of the substrate by the relatively small pores. It is believed that the presence of the pore blocking compound within the micropores of the treated substrate reduces, and preferably substantially prevents, metal deposition at the substrate surfaces within these pores, thereby directing metal deposition to other surfaces of the substrate and within larger pores. The presence of the pore blocker is thus currently

believed to reduce formation of small metal crystallites within the micropores that are resistant to agglomeration, readily leached and/or deactivated, and represent inefficient metal usage.

[00145] In addition to or separate from the effect of controlling or directing the location of metal deposition (e.g., by disposing within or introducing a pore blocking compound into pores of a substrate), the manner of metal deposition may promote more efficient metal usage as well. For example, various catalysts described herein include and/or are prepared from a support having one or more regions of a first metal at the surface of the support, and a second metal at the surface of the one or more regions of the first metal.

[00146] The first metal is selected to have a greater electropositivity than the second metal and the second metal is deposited at the surface of the one or more regions of the first metal by displacement of the first metal from the one or more regions at the surface of the support. More particularly, the second metal may be deposited by near atom-for-atom replacement of the first metal by the second metal. It is currently believed that metal deposition in this manner promotes formation of a relatively thin layer comprising second metal atoms and may in fact form a near monolayer of second metal atoms deposited at the surface of the first metal regions (e.g., a layer of second metal atoms at the surface of the one or more regions of first metal no more than about 3 atoms thick). Heating the carbon support having the first and second metals thereon forms metal particles comprising the first and second metal. The metal particles formed contain the second metal in a form that represents more efficient second metal utilization. For example, the composition of a significant fraction of the metal particles is generally rich in first metal content, thereby providing a relatively low proportion

of unexposed second metal throughout the particles (e.g., a first metal-rich bimetallic alloy). Additionally or alternatively, metal particles formed upon subsequent heating may have a relatively thin shell comprising the second metal (e.g., a layer no more than about 3 atoms thick) at least partially surrounding a core predominantly comprising the first metal.

I. Porous Substrate Treatment

[00147] Disposing within and/or introducing a pore blocking agent or compound (also referred to herein as a pore blocker) into pores of a porous substrate generally comprises contacting the substrate with the agent or compound, or a precursor (or precursors) thereof. In one embodiment, the pore blocking compound is preferentially retained within pores of the substrate within a selected size domain (e.g., micropores) by virtue of having at least one dimension larger than the openings of the pores, thereby inhibiting the agent from exiting the selected pores. In various embodiments, the pore blocking agent may be formed from one or more pore blocking agent precursors introduced into the substrate pores. Additionally or alternatively, and regardless of whether the pore blocking agent is introduced into the pores or formed *in situ* (i.e., formed from one or more agent precursors introduced into the pores), the agent may be retained within pores of the substrate within a selected size domain by virtue of an induced conformational change in the pore blocking agent such that the pore blocking agent is dimensionally inhibited from exiting the selected pores. A conformational change in the pore blocking agent may be induced within selected pores by virtue of interactions between the pore blocking agent and the walls of the pores. In accordance with one embodiment, a pore blocking agent is disposed within and preferentially retained within

micropores of the porous substrate to produce a treated substrate for metal deposition exhibiting a reduced proportion of micropore surface area.

[00148] It is to be understood that reference to one or more precursors contemplates compositions that ultimately function as a pore blocking agent upon entry into pores (e.g., by virtue of at least one dimension of the compound and/or by virtue of a conformational change in the compound after entry into the pores). Additionally or alternatively, reference to one or more precursors may refer to one or more compounds that combine or react to form the pore blocking agent once disposed within and/or introduced into the pores of the substrate. Regardless of whether a compound that ultimately functions as the pore blocker is introduced into or disposed within the pores of the substrate, or whether components that combine to form the pore blocker are introduced into or disposed within the pores, the mechanism by which the pore blocker is believed to function (i.e., by virtue of having at least one dimension larger than pore openings, either initially or following a conformational change) is the same.

[00149] In various embodiments the pore blocker comprises a compound having at least one dimension such that, after entry into pores, the pore blocker is preferentially retained within those pores falling within a selected size domain. Of course, it is to be understood that the pore blocker likewise typically has at least one dimension that permits entry into the pores, but it is currently believed that the pore blocker typically assumes an orientation and/or conformation within the pores such that the dimension greater than the pore opening prevents the pore blocking compound from exiting the pore.

[00150] As noted above, in accordance with one embodiment, the pore blocker is preferentially retained within substrate

micropores. However, this does not exclude the pore blocker or precursor(s) thereof from also entering pores of a size that are not within this predefined range upon contact with the porous substrate. For example, pore blocker may enter pores having a nominal diameter greater than about 20Å (e.g., pores having a nominal diameter of from about 20Å to about 3000Å, commonly referred as meso- and macropores), but the pore blocker tends to subsequently exit and not be preferentially retained within these pores, although the pore blocking agent may remain in a minor portion of pores outside the micropore range.

A. Porous Substrate

[00151] Generally, the porous substrate or supporting structure for the catalytic metal-containing active phase may comprise any material suitable for deposition of one or more metals thereon. Preferably, the porous substrate is in the form of a carbon support. In general, the carbon supports used in the present invention are well known in the art including, for example, those detailed in U.S. Patent No. 6,417,133 to Ebner et al. and by Wan et al. in WO 2006/031938 (the entire contents of which are incorporated herein by reference for all relevant purposes). Activated, non-graphitized carbon supports are preferred for noble metal on carbon catalysts used for PMIDA oxidation and provide the catalyst with robust mechanical integrity and high surface area for the metal-containing active phase. However, activated, non-graphitized carbon supports are not necessarily preferred in all instances and it should be understood that suitable catalysts for various other applications may be prepared utilizing carbon supports that are not activated and/or non-graphitized. In various particularly preferred

embodiments, the supports are in the form of particulates (e.g., powders).

[00152] In various preferred embodiments (e.g., catalysts used for PMIDA oxidation), the carbon support contains a relatively low proportion of oxygen-containing functional groups (e.g., carboxylic acids, ethers, alcohols, aldehydes, lactones, ketones, esters, amine oxides, and amides). These functional groups may increase noble metal leaching and potentially increase noble metal agglomeration and particle growth during liquid phase oxidation reactions and thus reduce the ability of the catalyst to oxidize oxidizable substrates (e.g., PMIDA and/or formaldehyde). As used herein, an oxygen-containing functional group is "at the surface of the carbon support" if it is bound to an atom of the carbon support and is able to chemically or physically interact with compositions within the reaction mixture or with the metal atoms deposited on the carbon support. As described in U.S. Patent No. 6,417,133 and by Wan et al. in WO 2006/031938, many of the oxygen-containing functional groups that reduce noble metal resistance to leaching and sintering and reduce the activity of the catalyst desorb from the carbon support as carbon monoxide when the catalyst is heated at a high temperature (e.g., 900°C) in an inert atmosphere (e.g., helium or argon). Thus, measuring the amount of CO desorption from a fresh catalyst (i.e., a catalyst that has not previously been used in a liquid phase oxidation reaction) under high temperatures is one method that may be used to analyze the surface of the catalyst to predict noble metal retention and maintenance of catalyst activity. One way to measure CO desorption is by using thermogravimetric analysis with in-line mass spectroscopy ("TGA-MS"). Preferably, no more than about 1.2 mmole of carbon monoxide per gram of catalyst desorb from the catalyst of the present invention when a dry, fresh sample of the

catalyst, after being heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before being exposed to an oxidant following the heating in the hydrogen atmosphere, is heated in a helium atmosphere is subjected to a temperature which is increased from about 20°C to about 900°C at about 10°C per minute, and then held constant at about 900°C for about 30 minutes. More preferably, no more than about 0.7 mmole of carbon monoxide per gram of fresh catalyst desorb under those conditions, even more preferably no more than about 0.5 mmole of carbon monoxide per gram of fresh catalyst desorb, and most preferably no more than about 0.3 mmole of carbon monoxide per gram of fresh catalyst desorb. A catalyst is considered "dry" when the catalyst has a moisture content of less than about 1% by weight. Typically, a catalyst may be dried by placing it into a N_2 purged vacuum of about 25 inches of Hg and a temperature of about 120°C for about 16 hours.

[00153] As further described in U.S. Patent No. 6,417,133 and by Wan et al. in WO 2006/031938, measuring the number of oxygen atoms at the surface of a fresh catalyst support is another method to analyze the catalyst to predict noble metal retention and maintenance of catalytic activity. Using, for example, x-ray photoelectron spectroscopy, a surface layer of the support which is about 50 Å in thickness is analyzed. Preferably, this analysis for a support suitable for use in connection with the oxidation catalysts described herein indicates a ratio of carbon atoms to oxygen atoms at the surface of the support of at least about 20:1. More preferably, the ratio is at least about 30:1, even more preferably at least about 40:1, even more preferably at least about 50:1, and most preferably at least about 60:1. In addition, the ratio of oxygen atoms to metal atoms at the surface preferably is less than about 8:1. More preferably, the ratio is less than

about 7:1, even more preferably less than about 6:1, and most preferably less than about 5:1.

[00154] Typically, a support that is in particulate form may comprise a broad size distribution of particles. For powders, preferably at least about 95% of the particles are from about 2 to about 300 μm in their largest dimension, more preferably at least about 98% of the particles are from about 2 to about 200 μm in their largest dimension, and most preferably about 99% of the particles are from about 2 to about 150 μm in their largest dimension with about 95% of the particles being from about 3 to about 100 μm in their largest dimension. Particles greater than about 200 μm in their largest dimension tend to fracture into super-fine particles (i.e., less than 2 μm in their largest dimension), which may be more difficult to recover.

[00155] In the following discussion, specific surface areas of carbon supports and catalysts are typically provided in terms of the well-known Langmuir method using N_2. It is to be understood that these values generally correspond to those measured by the likewise well-known Brunauer-Emmett-Teller (B.E.T.) method using N_2.

[00156] The specific surface area of the carbon support prior to any treatment (e.g., disposing or introducing a pore blocking compound within pores of a substrate) in accordance with the present invention is generally at least about 500 m^2/g, at least about 750 m^2/g, at least about 1000 m^2/g, or at least about 1250 m^2/g. Typically, the specific surface area of the carbon support is from about 10 to about 3000 m^2/g, more typically from about 500 to about 2100 m^2/g, and still more typically from about 750 to about 1900 m^2/g or from about 1000 to about 1900 m^2/g. In certain embodiments, the preferred specific surface area is from about

1000 to about 1700 m^2/g, 1000 to about 1500 m^2/g, from about 1100 to about 1500 m^2/g, from about 1250 to about 1500 m^2/g, from about 1200 to about 1400 m^2/g, or about 1400 m^2/g. Further in accordance with the present invention, the porous carbon support generally has a pore volume of at least about 0.1 ml/g, at least about 0.2 ml/g, or at least about 0.4 ml/g. Typically, the porous carbon support has a pore volume of from about 0.1 to about 2.5 ml/g, more typically from about 0.2 to about 2.0 ml/g and, still more typically, of from about 0.4 to about 1.5 ml/g.

[00157] It is to be noted that the present discussion focuses on pore blocking treatment to reduce micropore surface area of porous carbon substrates or supports for use in noble metal-containing catalysts suitable for use in PMIDA oxidation. However, it is to be understood that methods for treating a porous substrate by introduction of a pore blocking compound as described herein are generally applicable to preferentially blocking other pore size domains, other types of porous catalyst supports and/or porous carbon substrates used as supports for metals other than noble metals. For example, the methods of the present invention are suitable for treatment of porous Raney metals or alloys often referred to as sponges, such as those described in U.S. Patent No. 7,329,778 to Morgenstern et al. and used as supports for copper-containing catalysts used in the dehydrogenation of primary amino alcohols. By way of further example, the methods of the present invention are also suitable for treatment of other non-carbon porous supports such as, for example, silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), zirconium oxide (ZrO_3), titanium oxide (TiO_2), and combinations thereof.

B. Pore Blocking

[00158] In accordance with the present invention, the pore blocker used to selectively block micropores may be selected from

a variety of compounds including, for example, various sugars (e.g., sucrose), 5- or 6-member ring-containing compounds (e.g., 1,3- and 1,4-disubstituted cyclohexanes), and combinations thereof. Compounds suitable for use in connection with selective blocking of micropores include 1,4-cyclohexanedimethanol (1,4-CHDM), 1,4-cyclohexanedione bis(ethylene ketal), 1,3- or 1,4-cyclohexanedicarboxylic acid, 1,4-cyclohexane dione monoethylene acetal, and combinations thereof.

[00159] In various embodiments, the pore blocker may comprise the product of a reaction (e.g., a condensation reaction) between one or more pore blocking compound precursors. Once formed, the resulting pore blocking compound may be preferentially retained within selected pores of the substrate by virtue of having at least one dimension that prevents the pore blocking compound from exiting the pores.

[00160] For example, it has been observed that the coupling product of a cyclohexane derivative and a glycol may be utilized as a micropore pore blocking agent for particulate carbon substrates used to support a noble metal or other metal catalyst. More particularly, the pore blocking agent may be the coupling product of a di-substititued, tri-substituted, or tetra-substituted cyclohexane derivative and a glycol. In particular, the cyclohexane derivative may be selected from the group consisting of 1,4-cyclohexanedione, 1,3-cyclohexanedione, 1,4-cyclohexanebis(methylamine), and combinations thereof. The glycol is generally selected from the group consisting of ethylene glycol, propylene glycol, and combinations thereof.

[00161] Generally, the substrate is contacted with a liquid comprising the pore blocking agent or one or more precursor(s) of the pore blocking agent. Typically, the substrate to be treated is contacted with a mixture or solution comprising one or more

pore blocking compounds or precursor(s) dispersed or dissolved in a liquid contacting medium (e.g., deionized water). For example, the substrate may be contacted with a mixture or solution including a cyclohexane derivative and a glycol, or a liquid contacting medium consisting essentially of the cyclohexane derivative and glycol. The substrate may also be sequentially contacted with liquids or liquid media comprising one or more of the precursors. The composition of the liquid including the pore blocking agent or a precursor(s) thereof contacted with the porous substrate is not narrowly critical and may be readily selected and/or optimized by one skilled in the art.

[00162] As noted, regardless of whether a compound that ultimately functions as a pore blocker is introduced into pores of the substrate or precursors that form the blocking compound are introduced into the substrate, pore blockers may be preferentially retained within selected substrate pores (e.g., micropores) by virtue of the conformational arrangement assumed by the pore blocking agent once disposed or formed within the pores. For example, it is currently believed that various pore blocker molecules transform from a more linear chair conformation to a bulkier boat conformation, which conduces trapping of the compound within the micropores. In particular, it is currently believed that various pore blocking agents including a hydrophilic end group will favor a boat conformation within the micropore(s) of a porous carbon support because of the nature of the carbon support (i.e., the boat conformation will be favored by a pore blocking compound having hydrophilic end groups because of the relatively hydrophobic nature of the carbon support surface). Examples of pore blocking compounds including a hydrophilic end group include 1,4-cyclohexanedicarboxylic acid and 1,4-cyclohexanedimethanol (CHDM).

[00163] A conformational change of a pore blocker also may be promoted or induced by manipulating the liquid medium comprising the pore blocking agent in contact with the substrate including, for example, adjusting the pH and/or adjusting the temperature of the liquid medium.

[00164] Figs. 1A-1C provide graphical representations of pre-formed pore blockers and pore blocker molecules formed from precursors within the pore (i.e., *in situ* coupling) that undergo a conformational change within the pore to selectively block or plug smaller pores. Conformational change of a cyclohexane pore blocker is shown generally in Fig. 1D. These depictions are for illustrative purposes and are not intended to limit the present invention.

[00165] As noted, it is believed that contacting the substrate with the pore blocking agent or precursors results in pore blocking agent being introduced into or disposed within substrate micropores, and within larger pores outside this predefined range. In order to provide a treated substrate in which the micropores within the predefined range are preferentially blocked, the substrate is subsequently contacted with a washing liquid to remove the blocking agent from pores outside the micropore domain (i.e., those pores in which the pore blocking agent will not be preferentially retained by virtue of the agent having at least one dimension larger than the pore opening). The precise composition of the washing liquid and manner of its contact with the substrate are not narrowly critical, but the substrate may suitably be contacted with deionized water for this purpose.

C. Treated Substrates

[00166] As noted, the substrate treatment method of the present invention is suitable for introducing a pore blocking

agent into the micropores of porous substrates (e.g., a particulate carbon support) and preferentially retaining the pore blocking agent in the micropores. Preferential retention of the pore blocking agent within micropores may be represented by the proportion of micropores in which the agent is retained. Typically, the pore blocking compound remains in at least about 2%, at least about 5%, at least about 10%, or at least about 20% of the micropores, basis the total number of substrate micropores.

[00167] Preferential retention of the pore blocking compound within micropores may also be indicated by the treated substrate surface area provided by micropores and provided by larger pores. It is believed that the presence of the pore blocking compound within micropores will cause at least a portion of these "blocked" pores to appear as a non-porous portion of the treated substrate during surface area measurement methods (e.g., the well-known Langmuir surface area measuring method), thereby reducing the proportion of surface area that would otherwise be attributable to the micropores if they were not blocked. This preferential blocking of the targeted pores results in a reduction in the surface area provided by the micropores (i.e., micropore surface area). For example, in various embodiments, the micropore surface area of the treated substrate is generally no more than about 70%, no more than about 60%, or no more than about 50% of the micropore surface area of the substrate prior to treatment by contact with the pore blocker. Preferably, the micropore surface area of the treated substrate is no more than about 40%, more preferably no more than about 30% and, still more preferably, no more than about 20% of the micropore surface area of the substrate prior to treatment.

D. Methods for Preparing Catalysts Using Treated Substrates

[00168] As detailed herein, catalysts may be prepared by a process generally comprising depositing one or more noble metals and optionally one or more promoter metals at the surface of a treated (i.e., pore blocked) substrate such as a porous carbon support and heating the carbon support having the noble metal and optional promoter(s) deposited thereon in a non-oxidizing environment.

[00169] The noble metal is generally selected from the group consisting of platinum, palladium, ruthenium, rhodium, iridium, silver, osmium, gold, and combinations thereof. In various preferred embodiments, the noble metal comprises platinum and/or palladium. In still further preferred embodiments, the noble metal is platinum. One or more promoter metals is generally selected from the group consisting of tin, cadmium, magnesium, manganese, nickel, aluminum, cobalt, bismuth, lead, titanium, antimony, selenium, iron, rhenium, zinc, cerium, zirconium, tellurium, germanium, and combinations thereof at a surface of the porous substrate and/or a surface of the noble metal.

[00170] The noble metal may be deposited in accordance with conventional methods known in the art including, for example, liquid phase deposition methods such as reactive deposition techniques (e.g., deposition via reduction of noble metal compounds and deposition via hydrolysis of noble metal compounds), ion exchange techniques, excess solution impregnation, and incipient wetness impregnation; vapor phase methods such as physical deposition and chemical deposition; precipitation; electrochemical deposition; and electroless deposition as described in U.S. Patent No. 6,417,133 and by Wan et al. in International Publication No. WO 2006/031938. In various

preferred embodiments, the noble metal is deposited via a reactive deposition technique comprising contacting the carbon support with a solution comprising a salt of the noble metal, and then hydrolyzing the salt. An example of a relatively inexpensive suitable platinum salt is hexachloroplatinic acid (H_2PtCl_6).

[00171] A promoter(s) may be deposited onto the surface of the treated carbon support before, simultaneously with, or after deposition of the noble metal onto the surface. Methods to deposit a promoter metal are generally known in the art, and include the methods noted above regarding noble metal deposition.

[00172] After the carbon support has been impregnated with the noble metal(s) and optional promoter(s), the surface of the catalyst is preferably heated to elevated temperatures, for example, in a heat treatment or calcining operation. For example, calcining may be carried out by placing the catalyst in a kiln (e.g., rotary kilns, tunnel kilns, and vertical calciners) through which a heat treatment atmosphere is passed.

[00173] Generally, the surface of the treated support impregnated with one or more metals is heated to a temperature of at least about 700°C, at least about 800°C, at least about 850°C, at least about 900°C, or at least about 950°C. Typically, the metal-impregnated support is heated to a temperature of from about 800°C to about 1200°C, preferably from about 850°C to about 1200°C, more preferably from about 900°C to about 1200°C, even more preferably from about 900°C to about 1000°C and especially from about 925°C to about 975°C.

[00174] The period of time that the impregnated support is subjected to elevated temperatures (including the time at which the support is heated at the maximum temperature) is not narrowly critical. Typically, in commercial scale apparatus, the metal-

impregnated support is heated at the maximum heat treatment temperature for at least about 10 minutes (e.g., at least about 30 minutes).

[00175] Preferably, the metal-impregnated support is heated in a non-oxidizing environment. The non-oxidizing environment may comprise or consist essentially of inert gases such as N_2, noble gases (e.g., argon, helium) or mixtures thereof. In certain embodiments, the non-oxidizing environment comprises a reducing environment and includes a gas-phase reducing agent such as, for example, hydrogen, carbon monoxide, or combinations thereof. The non-oxidizing environment in which the catalyst is heated may include other components such as ammonia, water vapor, and/or an oxygen-containing compound as described, for example, by Wan et al. in International Publication No. WO 2006/031938. In one embodiment, heat treatment following metal deposition preferably comprises high-temperature gas-phase reduction to remove oxygen-containing functional groups from the surface of the catalyst, thereby attaining a catalyst exhibiting the carbon monoxide desorption and/or carbon atom to oxygen atom surface ratio characteristics as described in Ebner et al. U.S. Patent No. 6,417,133.

[00176] In various preferred embodiments, the noble metal is alloyed with at least one promoter to form alloyed metal particles. For example, noble metal particles at a surface of the carbon support may comprise noble metal atoms alloyed with promoter metal atoms. In various other preferred embodiments, the noble metal is alloyed with two promoters (e.g., iron and cobalt). Catalysts comprising a noble metal alloyed with one or more promoters often exhibit greater resistance to metal leaching and further stability (e.g., from cycle to cycle) with respect to formaldehyde and formic acid oxidation. It is to be understood

that the term alloy as used herein generally encompasses any metal particle comprising a noble metal and at least one promoter (e.g., intermetallic compounds, substitutional alloys, multiphasic alloys, segregated alloys, and interstitial alloys as described by Wan et al. in International Publication No. WO 2006/031938).

[00177] Subjecting the metal-impregnated support to heat treatment generally provides agglomeration and/or sintering of metal particles at the surface of the support. Utilizing treated substrates having blocked micropores results in impregnated supports having a reduced proportion of relatively small metal-containing particles at the support surface within the micropore domain, which are generally more susceptible to leaching and/or deactivation, as compared to larger-sized noble metal-containing particles. Additionally or alternatively, metal-containing particles at the substrate surface outside the micropore domain are generally more accessible to reactants. By virtue of either or both of these effects, treated substrates of the present invention are believed to provide more efficient metal usage (e.g., an increase in effective catalytic metal surface area per unit weight) in the catalyst.

[00178] It is to be noted that persistence of the pore blocker in the treated substrate following post-metal deposition heat treatment is not critical to provide the above-noted advantages. In fact, it is currently believed that the pore blocker is most likely decomposed and/or otherwise removed from the substrate surface during calcining. But it is further currently believed that one or more of the above-noted advantages are achieved so long as the pore blocker is preferentially retained with the selected pores at the support surface during metal deposition in order to promote the desired metal dispersion.

E. Catalysts Prepared Using Treated Substrates

[00179] Substrates treated in accordance with the present method (i.e., pore blocked substrates) may be utilized as supports for metal-containing catalysts including, for example, catalysts including one or more noble metals (e.g., a noble metal such as platinum) deposited on a particulate carbon support. In addition, noble metal-containing catalysts prepared using substrates treated by the present invention may include one or more promoter(s) and may be prepared in a manner to exhibit one or more of the properties as described, for example, in U.S. Patent No. 6,417,133, International Publication No. WO 2006/031938, and U.S. Patent No. 6,956,005, the entire contents of which are incorporated herein by reference for all relevant purposes.

[00180] Generally, the noble metal constitutes less than about 8% by weight of the catalyst, typically less than about 7% by weight of the catalyst, more typically less than about 6% by weight of the catalyst. In various embodiments, the noble metal typically constitutes from about 1% to about 8% by weight of the catalyst, more typically from about 2% to about 7% by weight of the catalyst and, still more typically, from about 3% to about 6% by weight of the catalyst.

[00181] As noted, particulate carbon supports treated in accordance with the present invention to preferentially block micropores provide more efficient metal usage. Accordingly, effective catalysts may be prepared that contain noble metal in an amount below the above-noted limits and/or at or near the lower limits of one or more of the above-noted ranges. For example, in various embodiments, the noble metal constitutes less than about 5% by weight of the catalyst, less than about 4% by weight of the catalyst, or even less than about 3% by weight of the catalyst. By way of further example, in various embodiments the noble metal

typically constitutes from about 1% to about 5% by weight of the catalyst, more typically from about 1.5% to about 4% by weight of the catalyst and, still more typically, from about 2% to about 3% by weight of the catalyst. However, it should be understood that the present invention does not require that a treated substrate be used for preparation of a noble metal-containing catalyst including a reduced proportion of noble metal as compared to conventional catalysts. Namely, preparation of a catalyst including a treated porous substrate that provides more efficient metal usage at conventional noble metal loadings likewise represents an advance in the art (e.g., treated substrates of the present invention are currently believed to provide a reduced proportion of relatively small metal particles that are susceptible to leaching and represent inefficient metal usage, thereby contributing to improvements in catalytic activity and reduced undesired by-product (e.g., IDA) formation).

[00182] Generally, in accordance with some embodiments, at least one promoter (e.g., iron) constitutes less than about 2% by weight of the catalyst, less than about 1.5% by weight of the catalyst, less than about 1% by weight of the catalyst, less than about 0.5% by weight of the catalyst, or about 0.4% by weight of the catalyst. Typically, at least one promoter constitutes less than about 1% by weight of the catalyst, preferably from about 0.25% to about 0.75% by weight of the catalyst and, more preferably, from about 0.25% to about 0.6% by weight of the catalyst. In various preferred embodiments, the catalyst includes iron as a promoter. Additionally or alternatively, the catalyst includes cobalt as a promoter.

[00183] In various particularly preferred embodiments, the catalyst comprises both iron and cobalt promoters. Use of iron and cobalt generally provides benefits associated with use of iron

(e.g., activity and stability with respect to formaldehyde and formic acid oxidation). However, as compared to the presence of iron alone as a promoter, the presence of cobalt tends to reduce formation of certain by-products during oxidation of a PMIDA substrate (e.g., IDA). Moreover, IDA formation is believed to be directly related to total iron content of the catalyst. Thus, in various iron/cobalt co-promoter embodiments, iron content is essentially replaced by cobalt to reduce formation of IDA and other by-products while nevertheless providing sufficient activity towards oxidation of formaldehyde and formic acid. For example, as compared to a platinum on carbon catalyst containing 0.5% by weight iron in the absence of cobalt, a similar catalyst containing 0.25% by weight iron and 0.25% by weight cobalt typically provides comparable activity for PMIDA, formaldehyde and formic acid oxidation, while minimizing by-product formation.

[00184] In iron/cobalt co-promoter embodiments, the amount of each promoter at the surface of the carbon support (whether associated with the carbon surface itself, noble metal, or a combination thereof) is typically at least about 0.05% by weight, at least about 0.1% by weight or at least about 0.2% by weight. Furthermore, the amount of iron at the surface of the carbon support is typically from about 0.1 to about 4% by weight of the catalyst, preferably from about 0.1 to about 2% by weight of the catalyst, more preferably from about 0.1 to about 1% by weight of the catalyst and, even more preferably, from about 0.1 to about 0.5% by weight of the catalyst. Similarly, the amount of cobalt at the surface of the carbon support is typically from about 0.1 to about 4% by weight of the catalyst, preferably from about 0.1 to about 2% by weight of the catalyst, more preferably from about 0.2 to about 1% by weight of the catalyst and, even more preferably, from about 0.2 to about 0.5% by weight of the

catalyst. In such an embodiment, the weight ratio of iron to cobalt in the catalyst is generally from about 0.1:1 to about 1.5:1 and preferably from about 0.2:1 to about 1:1. For example, the catalyst may comprise about 0.1% by weight iron and about 0.4% by weight cobalt or about 0.2% by weight and about 0.2% by weight cobalt.

[00185] As understood by those skilled in the art, the metal content of the catalysts can be freely controlled within the ranges described herein (e.g., by adjusting the concentration and relative proportions of the metal source(s) used in a liquid phase reactive deposition bath).

II. First and Second Metal-Containing Catalysts

[00186] Various preferred embodiments of the present invention are directed to catalysts that comprise and/or are prepared from a porous substrate or support having one or more regions of a first metal at its surface, and a second metal at the surface of the one or more regions of the first metal. In such embodiments, the first metal is selected to have an electropositivity greater than the electropositivity of the second metal (i.e., the first metal is higher than the second metal in the electromotive series). Oxidation of the first metal provides electrons for reduction of second metal ions present in the deposition bath to thereby deposit second metal atoms at the surface of the one or more regions of the first metal. The first metal oxidation and second metal reduction and deposition occur substantially simultaneously and second metal atoms are deposited at the surface of the one or more regions of the first metal by displacement of first metal ions from the one or more regions into the deposition bath. Metal deposition in this manner may be referred to as spontaneous, or redox displacement deposition. (See, for example, U.S. Patent No.

6,670,301 to Adzic et al. and U.S. Patent Nos. 6,376,708, 6,706,662 and 7,329,778 to Morgenstern et al.) Preferably, the sacrificial first metal is less expensive than the second metal.

[00187] As detailed herein, deposition of the second metal by displacement deposition is preferably conducted and controlled in a manner that provides preferential deposition of the second metal at the surface of the one or more regions of the first metal. That is, the second metal is preferentially deposited at the surface of the first metal region(s) by displacement deposition over deposition of the second metal at the support surface and/or deposition of the second metal at the surface of already-deposited second metal.

[00188] Without being bound to a particular theory, it is currently believed that the source of second metal ions may promote preferential deposition of the second metal onto the one or more regions of first metal. More particularly, it is currently believed that second metal sources that provide second metal ions at lower oxidation numbers (e.g., +2) provide slower, more controlled metal deposition as compared to sources that provide noble metal ions at higher oxidation numbers (e.g., +4). Second metal ions at such higher oxidation numbers are believed to be more readily reduced in the presence of electrons generated by oxidation of the first metal which provides a greater driving force for deposition of the second metal. This greater driving force is believed to increase the rate of second metal deposition which, in turn, is believed to promote less discriminate deposition of the second metal. More particularly, the greater driving force for deposition of second metal ions is believed to promote deposition of second metal atoms onto the support and/or onto the surface of already-deposited second metal atoms. Accordingly, it is currently believed that as the oxidation state

of second metal ions decreases, preferential (e.g., selective) deposition of the noble metal directed onto one or more regions of first metal by displacement of first metal atoms over deposition onto the carbon support and/or already-deposited second metal atoms generally increases.

[00189] In addition, it is currently believed that deposition of second metal atoms utilizing sources that provide ions at relatively low oxidation numbers proceeds in a manner that generally reduces the complexity of the displacement deposition process to promote the desired preferential deposition of the second metal directed onto the first metal regions. For example, displacement deposition utilizing sources that provide second metal ions at relatively low oxidation numbers proceeds readily in the absence of precise control of concentration of the second metal source and/or deposition time.

[00190] In accordance with the present invention, it is currently believed that a significant fraction, if not substantially all, of the second metal deposited by controlled displacement of a first metal provides domains or regions at the surface of one or more regions of the first metal characterized as comprising a relatively thin layer of second metal atoms (e.g., no more than about 5 atoms thick, or no more than about 3 atoms thick), rather than agglomerating to form metal-containing particles. In certain preferred embodiments, preparation of the catalyst by the present method may provide a near monolayer of second metal (e.g., a layer of second metal atoms no more than about 3 atoms in thickness, no more than about 2 atoms in thickness, and preferably from about one to about two atoms in thickness).

[00191] Further in accordance with the present invention, it is currently believed that deposition of the second metal by

displacement of first metal atoms from one or more regions of first metal provides a structure (e.g., a catalyst precursor structure) that, upon heat treatment at elevated temperatures, provides metal particles that include the second metal in a form that represents more efficient second metal utilization. In various embodiments, the metal particles are typically first metal-rich (i.e., contain an excess of first metal atoms over second metal atoms) and it is currently believed that the particles include one or more bimetallic alloys. In contrast, conventional noble metal-containing catalysts typically include particles comprising an atomic excess of noble metal atoms. In this manner, the first metal-rich particles are believed to include the noble (i.e., second) metal in a form that represents a reduced proportion of noble metal distributed throughout the particle and, accordingly, represents reduced unexposed, and potentially unutilized noble metal atoms throughout the particle structure. But an excess of first metal is not required to provide an improvement in metal utilization. However, to the extent that the proportion of first metal to second metal is increased, improvements in second metal utilization may be realized. Accordingly, various embodiments of the present invention contemplate selecting first and second metal combinations that are amenable to forming alloys that include at least an equivalent atomic proportion of first metal (M_1) to second metal (M_2). More particularly, in various embodiments there is a preference for selecting first and second metal combinations that provide bimetallic alloys of first and second metal, $M_{1x}M_{2y}$, where the atomic ratio of x:y is greater than or equal to 1. Further in accordance with these and various other preferred embodiments, the metal particles include bimetallic alloys in which the atomic ratio of x:y is greater than about 2, or greater than about 3.

For example, in the case of copper and platinum first and second metals, respectively, the metal particles at the surface of the support may include CuPt and/or Cu_3Pt bimetallic alloys. By way of further example, in the case of tin and platinum first and second metals, respectively, at least some of the metal particles may include Pt_2Sn_3, $PtSn_2$, and/or $PtSn_4$ bimetallic alloys. In the case of iron and platinum first and second metals, respectively, the metal particles at the surface of the support may include, for example, Fe_3Pt, FePt, $Fe_{0.75}Pt_{0.25}$.

[00192] Additionally or alternatively, it is also currently believed that at least some of the supported metal particles produced upon calcination of a catalyst precursor structure prepared by displacement deposition of a noble (i.e., second) metal as detailed herein include a relatively thin layer or shell comprising second metal atoms (e.g., a layer of second metal atoms no more than about 3 atoms thick) at least partially surrounding a core comprising the first metal. The core generally comprises a relatively high concentration of first metal (e.g., greater than about 50 atom percent). The combination of a first metal-rich core and second metal-containing shell provides a relatively low proportion of unexposed second metal and, thus, provides improvements in exposed metal surface area per unit metal weight. It is currently believed that particles exhibiting such a core-shell arrangement may generally provide a greater improvement in second metal utilization over conventional supported noble metal catalysts as compared to particles generally characterized as first metal-rich (i.e., a greater increase in exposed second metal surface area per unit second metal weight). Thus, as the fraction of core-shell particles at the surface of the support increases, metal utilization in the catalyst likewise increases. Accordingly, in various preferred embodiments, the catalyst

includes a predominant fraction of metal particles exhibiting a core-shell arrangement. However, it is to be noted that improvements in metal utilization are nonetheless provided by virtue of the presence of metal particles generally rich in first metal content, regardless of the presence of any particles characterized as exhibiting a core-shell arrangement.

[00193] It is to be noted that reference to a porous substrate such as a carbon support having first and second metals deposited thereon (i.e., a first and second metal-containing support) as a catalyst precursor structure does not exclude catalytic activity of these impregnated supports in the absence of subsequent heat treatment. In fact, experimental evidence indicates that metal-impregnated supports prepared in this manner may function as effective catalysts. Accordingly, elsewhere herein (including the claims) porous substrates having a first metal deposited thereon (e.g., a first metal-impregnated support) are likewise referred to as catalyst precursor structures. But in various preferred embodiments, the first and second metal-impregnated support is heated at elevated temperatures to provide the catalyst (sometimes referred to herein as a finished catalyst).

[00194] Experimental evidence indicates that catalysts (i.e., both catalyst precursor structures and finished catalysts) prepared as detailed herein utilizing a noble metal and a first, sacrificial metal layer are at least as active as conventional noble metal on carbon catalysts on a per unit metal weight basis. Without being bound to a particular theory, it is currently believed that active sites or domains of second metal provided by the method of the present invention provide an increase in catalytic surface area per unit metal weight as compared to conventional metal-containing catalysts prepared by methods that

do not include displacement deposition of the second metal onto one or more regions of a first, sacrificial metal.

[00195] Conventional noble metal on carbon catalysts generally include noble metal-containing particles at the surface of the support formed by agglomeration and/or sintering of noble metal atoms and/or noble metal-containing particles. This agglomeration typically occurs during post-deposition heat treatment of a noble metal-impregnated support at relatively high temperatures. Metal particles of conventional noble metal catalysts formed by agglomeration of deposited metal at the surface of a support, typically include the noble metal distributed throughout the entire particle (e.g., the particles exhibit a composition profile of relatively constant noble metal concentration throughout). Particle stability (e.g., resistance to leaching and/or deactivation under reaction conditions) generally increases with increased particle size, but exposed metal catalytic surface area per unit metal weight typically decreases in larger particles. Thus, despite the increased stability, an abundance of relatively large noble metal-containing particles and the attendant lower catalytic metal surface area per unit metal weight represents less efficient metal usage. Advantageously, first metal-rich particles and/or metal particles comprising a noble (i.e., second) metal-containing shell and first metal-containing core prepared in accordance with various embodiments of the present invention generally represent more efficient metal usage. For example, as noted, the first metal-rich particles are believed to include the second metal in a form (e.g., a bimetallic alloy including an atomic excess of first metal) that provides a reduced proportion of unexposed second metal.

[00196] Additionally or alternatively, and as detailed elsewhere herein, larger, more stable metal particles in

accordance with the present invention are not associated with an unacceptable decrease in effective catalytic second metal surface area since an increase in particle size is generally associated with an increase in the size of the first metal-rich core. For example, experimental evidence indicates relatively constant thickness of the second metal-containing shell over a range of particle sizes. Accordingly, as particle size increases, the fraction (atom and/or weight) of the particle provided by the first metal-rich core generally increases while the fraction of the particle provided by the second metal-containing shell generally decreases. However, the exposed second metal surface area increases with increased particle size. For example, as compared to a particle including a core 1 nm in diameter, at constant second metal shell thickness, a particle including a core 10 nm in diameter may provide up to a 100-fold increase in exposed surface area of the second metal-containing shell.

[00197] One mechanism for deactivation of conventional noble metal on carbon catalysts prepared by deposition of noble metal in the absence of a sacrificial metal involves over-oxidation of platinum as a result of charge build-up among the active sites comprising particles of agglomerated noble metal atoms. It is currently believed that metal-containing particles in which a second metal-containing shell at least partially surrounds a first metal-containing core result in reduced over-oxidation of the catalyst. In this manner, the form of the catalyst provides an improvement in activity. With regard to a catalyst precursor structure, it is currently believed that preferential deposition of second metal by displacement of first metal to form domains or active sites less prone to agglomeration to form metal-containing particles than metal deposited in the absence of a sacrificial metal provides greater dispersion of charge among the active sites

and, thus, reduced catalyst deactivation by over-oxidation of the metal.

[00198] It is to be noted that a certain degree of agglomeration of second metal to form primarily second metal-containing particles may occur in first and second metal-containing catalysts prepared in accordance with the present invention. However, it is currently believed that any such agglomeration occurs to a lesser extent than observed in catalysts prepared without a first, sacrificial metal and, in any event, second metal agglomeration is not believed to occur to any significant degree that prevents achieving the above-noted benefits of improved metal utilization.

[00199] It is also currently believed that the above-described methods utilizing a first, sacrificial metal layer may be utilized in conjunction with the methods for treating porous substrates detailed elsewhere herein. For example, a first metal may be deposited onto a porous support first treated in accordance with the methods detailed herein (e.g., a substrate having a pore blocking compound disposed and/or preferentially retained within its micropores), followed by deposition of a second metal onto one or more regions of the deposited first metal. In this manner, it is currently believed that deposition of both the one or more regions of the first metal, and subsequent deposition of the second metal thereon are preferentially directed outside the relatively small pore (e.g., micropore) domain of the substrate, thereby providing advantageous dispersion of the first and second metals and contributing to one or more of the above-noted benefits with respect to metal utilization.

A. First Metal

[00200] In those embodiments of the present invention in which the catalyst or precursor includes one or more regions of a first metal at the surface of the support, the first metal is generally selected from the group consisting of vanadium, tungsten, molybdenum, gold, osmium, iridium, tantalum, palladium, ruthenium, antimony, bismuth, arsenic, mercury, silver, copper, titanium, tin, lead, germanium, zirconium, cerium, nickel, cobalt, iron, chromium, zinc, manganese, aluminum, beryllium, magnesium, lithium, barium, cesium, and combinations thereof. In various preferred embodiments, the first metal is selected from the group consisting of copper, iron, tin, nickel, cobalt, and combinations thereof. In various other preferred embodiments, the first metal comprises copper, tin, nickel, or a combination thereof. In various other preferred embodiments, the first metal is tin or the first metal is copper. In still further embodiments, the first metal comprises cobalt, copper, iron and combinations thereof. In various preferred embodiments, the first metal is copper. In various other preferred embodiments, the first metal is iron. In still further preferred embodiments, the first metal is cobalt.

[00201] Generally, the support is contacted with a deposition bath comprising ions of the first metal and one or more other components to deposit the first metal at the surface of the support. At least two events occur during deposition of the first metal at the surface of the support: (1) nucleation (i.e., deposition of first metal atoms at the surface of the support) and (2) particle growth (i.e., agglomeration of deposited first metal atoms). As used herein, the term region(s) of first metal refers to a group of agglomerated first metal atoms at the surface of the support. It is currently believed that the sizes, or dimensions of these regions (i.e., the proportion of support surface area over

which a region of first metal is deposited) may directly impact the effectiveness/suitability of the catalyst.

[00202] For example, the proportion of deposition, or exchange sites for second metal deposition decreases along with decreasing dimensions of first metal regions. In addition, resistance to leaching and/or deactivation under reaction conditions generally decreases as one or more dimensions of the first metal region size decrease. Thus, it is preferred that the dimensions of the first metal regions are sufficiently resistant to metal leaching and provide a sufficient proportion of sites for second metal deposition. Accordingly, one or more conditions of first metal deposition are preferably controlled to provide a suitable balance between nucleation and agglomeration (i.e., particle growth) and, thus, provide first metal regions of suitable dimensions that provide sufficient exchange sites for deposition of second metal, are stable themselves and, thus, promote deposition of stable domains, or regions of second metal. For example, as detailed elsewhere herein, first and second metal-containing supports preferably include an excess of first metal, which contributes to providing the second metal in a form that promotes more efficient metal utilization.

[00203] In addition to achieving a desirable balance between nucleation and agglomeration, the location, or dispersion of the one or more regions of first metal at the support surface may impact metal utilization. That is, the considerations noted above generally concerning deposition of metal among relatively small pores generally likewise apply to deposition of one or more first metal regions and the dispersion of these regions among the pores of porous substrates is currently believed to affect catalyst performance. Accordingly, one or more conditions of first metal deposition are generally controlled and/or selected to provide a

desired dispersion of first metal regions. Thus, generally, conditions of first metal deposition preferably promote deposition of the first metal at the support surface to provide regions of first metal at the support having one or more dimensions that provide a suitable proportion of exchange sites for deposition of second metal at the surface of the first metal regions. More particularly, it is currently believed that the dimensions of the first metal regions preferably provide a suitable excess of deposited first metal with respect to the desired proportion of second metal to be deposited. For example, as detailed elsewhere herein, supports having first and second metals deposited thereon in accordance with the present invention may be characterized by a minimum atom ratio of first metal to second metal.

1. Coordinating Agents / Pore Blocking

[00204] In various preferred embodiments, preferential deposition of the first metal outside relatively small pores (e.g., the micropore domain) of the substrate may be promoted by the presence of one or more components of the first metal deposition bath. More particularly, dispersion of first metal in this manner may be promoted by the presence of one or more components of the deposition bath referred to herein as coordinating agent(s).

[00205] It is currently believed that a component of the first metal deposition bath may function as a coordinating agent by forming one or more coordination bonds with the first metal and that the thus formed coordination compound may be unable to enter certain relatively small pores of the substrate, thereby preventing coordinated first metal from depositing among those portions of the substrate surface. It is to be understood that the precise form of any coordination bond(s) between the compound

and metal, or the precise form of any coordination compound thus formed are not narrowly critical. However, it is currently believed that a coordination compound generally includes an association or bond between the first metal ion and one or more binding sites of one or more ligands. The coordination number of a metal ion of a coordination compound generally corresponds to the number of other ligand atoms linked thereto. Ligands may be attached to the central metal ion by one or more coordinate covalent bonds in which the electrons involved in the covalent bonds are provided by the ligands (i.e., the central metal ion can be regarded as an electron acceptor and the ligand can be regarded as an electron donor). The typical donor atoms of the ligand include, for example, oxygen, nitrogen, and sulfur. The ligands can provide one or more potential binding sites; ligands offering two, three, four, etc., potential binding sites are termed bidendate, tridendate, tetradentate, etc., respectively. Just as one central atom can coordinate with more than one ligand, a ligand with multiple donor atoms can bind with more than one central atom. Coordinating compounds including a metal ion bonded to two or more binding sites of a particular ligand are typically referred to as chelates.

[00206] Additionally or alternatively, a coordinating agent as described herein may promote dispersion of the first metal at the support surface by virtue of the coordination bonds between the coordinating agent and metal to be deposited retarding or delaying reduction of the metal ions and metal deposition at the support surface while promoting dispersion of the first metal over the support surface. The strength of coordination between the coordinating agent and metal generally influences the effectiveness of the agent for promoting dispersion of the first metal over the support surface. Unless the strength of

coordination reaches a minimum threshold, the effect of the agent on dispersion will not be noticeable to any significant degree and the degree of coordination that prevails in the deposition bath will essentially mimic water solvation. As the strength of coordination between the agent and metal increases, a greater concentration of reducing agent may be utilized and/or a relatively strong reducing agent (e.g., metal hydride) may be included in the deposition bath to promote reduction of the coordination complex and/or first metal reduction and deposition. Coordinating agent and/or ligand(s) derived therefrom present in the deposition bath may effectively function as a pore blocking compound during and/or after first metal deposition. For example, once the coordination bond(s) between the first metal and the coordinating agent have been broken, the agent or ligand(s) may be disposed within micropores of the support.

[00207] In accordance with the foregoing regarding deposition bath components that may function as coordinating agents, in these and various other preferred embodiments, such components of the first metal deposition bath may promote desirable dispersion of the one or more regions of first metal by virtue of a pore blocking function. That is, in addition to preventing entry of coordinated first metal into certain pores of the substrate, components of the first metal deposition bath described as coordinating agents may themselves be deposited among certain, relatively small pores of the porous substrate, thereby inhibiting, and preferably substantially preventing, deposition of first metal within the relatively small pores. Generally, these compounds are believed to function as pore blocking compounds during first metal deposition and that preferential deposition of first metal and pore blocking may occur substantially simultaneously to provide a first metal-impregnated substrate.

[00208] But it is to be understood that treating a porous substrate in accordance with the methods detailed above to dispose within and/or introduce a pore blocking compound into pores of the substrate, followed by metal deposition, likewise provides suitable substrates.

[00209] A variety of compounds that function as coordinating agents and/or pore blocking compounds may be included in the first metal deposition bath to provide one or more of the above-noted effects. Generally, these compounds are selected from the group consisting of various sugars, 5- or 6-member ring-containing compounds (e.g., 1,3- and 1,4-disubstituted cyclohexanes), polyols, Rochelle salts, acids, amines, citrates, and combinations thereof. For example, the compound may be selected from the group consisting of sucrose, sorbitol, mannitol, xylitol, Rochelle salts (potassium sodium tartrates), ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetetraacetic acid (HEDTA), nitrilotriacetic acid (NTA), N,N,N',N'- tetrakis(2-hydroxypropyl)ethylenediamine, and combinations thereof.

[00210] It is to be noted that the advantageous effects provided by the presence of these compounds referred to herein as coordinating agents or pore blockers are based in part on experimental evidence. While it is currently believed that one or more of these compounds provide either or both of the coordinating and pore blocking functions, it should be understood that the present invention is not dependent on either or both of these theories and does not require one or more compounds providing either or both of these functions.

[00211] In various preferred embodiments (e.g., those in which the first metal is copper or iron), the deposition bath comprises sucrose that is believed to function as a coordinating agent and/or pore blocking compound. In addition to these effect(s) in

accordance with the preceding discussion, its presence may offer other advantages. For example, as detailed elsewhere herein, first metal deposition may proceed more readily at higher pH. The coordinating effect of sucrose allows for deposition of the first metal at higher pH since the coordinating effect reduces the risk of excessive first metal precipitation at higher pH.

[00212] Generally, the coordinating agent/pore blocker, or a combination of agents/blockers, is present in the first metal deposition bath at a concentration of at least about 10 g/L, at least about 20 g/L, or at least about 30 g/L. Preferably, this component of the first metal deposition bath is present at a concentration of from about 10 g/L to about 115 g/L, from about 25 g/L to about 100 g/L, or from about 40 g/L to about 85 g/L. Further in accordance with these and various other preferred embodiments, the weight ratio of coordinating agent to first metal in the deposition bath is generally at least about 3:1, typically at least about 5:1 and, more typically, at least about 8:1. For example, generally the weight ratio of coordinating agent to first metal in the deposition bath is generally from about 3:1 to about 20:1, typically from about 5:1 to about 15:1 and, more typically, from about 8:1 to about 12:1.

2. Electroless Plating of First Metal

[00213] Generally and in accordance with the foregoing, deposition of first metal at the surface of the support may be conducted in accordance with conventional methods known in the art. Thus, typically first metal deposition is conducted by electroless plating in which the support is contacted with a deposition bath generally comprising a source of the first metal in the absence of an externally applied voltage. The deposition bath generally comprises a reducing agent that reduces ions of the

first metal to form metal atoms that are deposited at the surface of the support.

[00214] Generally, the source of the first metal is a first metal salt including, for example, first metal sulfates, first metal nitrates, first metal chlorides, first metal tartrates, first metal phosphates, and combinations thereof. The concentration of first metal in the deposition bath is generally selected in view of the desired first metal content. Typically, the source of first metal is present in the deposition bath at a concentration of at least about 0.25 g/L, at least about 1 g/L, at least about 2.5 g/L, or at least about 4 g/L. For example, the first metal source may be present in the deposition bath at a concentration of from about 1 to about 20 g/L, from about 2.5 to about 12.5 g/L, or from about 4 to about 10 g/L.

3. Copper Deposition

[00215] The following discussion focuses on deposition of copper as the first metal onto a porous carbon support. However, as detailed elsewhere herein, it should be understood that the present invention likewise contemplates deposition of first metals other than copper onto carbon supports, and deposition of copper and other first metals onto non-carbon supports.

(a) Sources of Copper

[00216] Sources of copper ions suitable for use in the methods of the present invention include copper salts such as the nitrate, sulfate, chloride, acetate, oxalate, and formate salts of copper, and combinations thereof. Salts containing copper in the divalent state (i.e., Cu(II)) are generally preferred including, for example, copper sulfate.

(b) Copper Loading in Deposition Bath

[00217] First metal loading in the deposition bath may affect the quality (e.g., resistance to leaching) and/or suitability (e.g., dispersion of first metal over a sufficient portion of support surface) of first metal deposition. More particularly, the relative proportions of first metal and support are currently believed to impact first metal deposition. Agglomeration, or particle growth, and the dimensions of the resulting regions of first metal may increase with increased copper loading. As noted above, the dimensions of the first metal regions are preferably controlled to promote a suitable balance between dispersion and stability of the first and second metals. Accordingly, the concentration of copper in the deposition bath satisfies the above-noted limits and/or is within the above-noted ranges.

[00218] For example, typically copper is present in the first metal deposition bath at a concentration of at least about 0.25 g/L, more typically at least about 1 g/L, still more typically at least about 2 g/L, and even more typically at least about 3 g/L (e.g., at least about 5 g/L). Preferably, copper is present in the first metal deposition bath at a concentration of from about 0.25 to about 15 g/L, more preferably from about 1 to about 12 g/L and, still more preferably, from about 2 to about 10 g/L.

(c) Reducing Agents

[00219] Suitable reducing agents include those generally known in the art including, for example, sodium hypophosphite (NaH_2PO_2), formaldehyde (CH_2O) and other aldehydes, formic acid (HCOOH), salts of formic acid, salts of borohydride (e.g., sodium borohydride ($NaBH_4$)), salts of substituted borohydrides (e.g., sodium triacetoxyborohydride ($Na(CH_3CO_2)_3BH$)), sodium alkoxides, hydrazine (H_2NNH_2), and ethylene glycol. In various preferred embodiments,

formaldehyde is the preferred reducing agent. For copper deposition in non-aqueous deposition baths, gaseous hydrogen is often the preferred reducing agent since it is generally readily soluble in organic solvents.

[00220] The manner of addition of reducing agent to the deposition bath is not narrowly critical, but in various embodiments the reducing agent is added at a relatively slow rate (e.g., over a period of from about 5 minutes to 3 hours, or over a period of from about 15 minutes to about 1 hour) to a slurry of the support and first metal in water or an alcohol and under an inert atmosphere (e.g., N_2). If the reducing agent is instead first added to the copper salt, it preferably may be added to a solution which contains the copper salt and also a coordinating agent (e.g., chelator). The presence of the chelator inhibits the reduction of the copper ions before the copper-salt solution is combined with the support and which, as detailed herein, may likewise promote advantageous deposition of first metal throughout the surface of the support.

[00221] Typically, in the case of formaldehyde as the reducing agent, the reducing agent is present in the first metal deposition bath at a concentration of at least about 1 g/L, more typically at least about 2 g/L and, still more typically, at least about 5 g/L. For example, in the case of formaldehyde as the reducing agent, preferably formaldehyde is present in the deposition bath at a concentration of from about 1 to about 20 g/L, more preferably from about 2 to about 15 g/L and, still more preferably, from about 5 to about 10 g/L.

[00222] Additionally or alternatively, in the case of a formaldehyde reducing agent, generally formaldehyde and the first metal (e.g., copper) are present in the deposition bath at a weight ratio of formaldehyde to first metal of at least about

0.5:1, and typically at least about 1:1. For example, in various embodiments, the weight ratio of formaldehyde to first metal in the deposition bath is from about 0.5:1 to about 5:1, from about 1:1 to about 3:1, or from about 1:1 to about 2:1.

(d) Temperature

[00223] The temperature of the deposition bath may affect nucleation and agglomeration (e.g., particle growth) that occur during first metal deposition. For example, generally nucleation (i.e., metal deposition) and agglomeration increase with increasing deposition bath temperature.

[00224] Thus, preferably the temperature of the deposition bath does not reach a level that promotes metal agglomeration and/or metal leaching under reaction conditions to an undesired degree. Reducing the temperature of the plating bath generally suppresses nucleation to a greater degree than agglomeration. Accordingly, the temperature of the plating bath is preferably high enough so that nucleation is not retarded to an unacceptable degree. In accordance with the present invention, it is currently believed that first metal deposition baths having a temperature of from about 5°C to about 60°C generally address these concerns and provide suitable deposition of the first metal. Preferably, the temperature of the first metal deposition bath is from about 10°C to about 50°C; more preferably, the temperature of the first metal deposition bath is from about 20°C to about 45°C. It is to be noted that reference to the temperature of the first metal deposition bath may refer to the temperature of the bath prior to and/or during contact of the deposition bath and the support.

(e) Agitation

[00225] Preferably the first metal deposition bath is agitated to promote dispersion of the first metal over the surface of the support. Agitation may also promote diffusion of the reducing agent throughout the support. Experimental evidence indicates that sufficient agitation may contribute to improvements in catalytic activity. However, excessive agitation of the deposition bath may cause dispersion of copper to a degree that provides first metal regions that may be less resistant to leaching than less dispersed regions. For example, undesirably high dispersion may result in deposition of a portion of first metal within the relatively small pores of the support that is less prone to agglomeration to form first metal regions generally resistant to leaching.

[00226] In addition, it is currently believed that the type of agitator may impact deposition of the first metal. Experimental evidence indicates that the first metal (e.g., copper) may deposit onto the agitator surface resulting in reduced first metal deposition onto the carbon support and, therefore, reduced sites for deposition of second metal. For example, first metal may deposit onto the surface of agitators that include or are constructed of metal (e.g., coated metal agitators). Thus, in various preferred embodiments, the agitator is constructed of material that generally prevents, and preferably substantially completely prevents first metal deposition at the surface of the agitator. For example, the agitator may preferably be constructed of glass, or various other materials that preferably avoid first metal deposition at the agitator surface.

(f) Deposition pH

[00227] Copper deposition is generally more effective at higher pH (e.g., greater than about 8, greater than about 9, or greater than about 10). In fact, as deposition bath pH increases, copper deposition through reduction and precipitation onto the support may proceed at a rate that may hinder sufficient dispersion of the first metal over the support surface. In addition to the above-noted benefits, the presence of a coordinating agent such as sucrose is currently believed to retard copper precipitation at high pH and thereby promote sufficient dispersion of the metal over the surface of the support. Formation of a coordination complex between the first metal and a coordinating agent is generally enhanced at the above-noted pH levels. However, at certain levels the pH of the deposition bath may negatively impact solvation of first metal ions and first metal reduction and deposition. Accordingly, in various preferred embodiments in which a coordinating agent is present in the deposition bath, the pH of the deposition bath is from about 8 to about 13, or from about 9 to about 12.

4. Iron Deposition

[00228] In various preferred embodiments, the first metal is iron. Generally, deposition of iron at the surface of the support may be conducted in accordance with conventional methods known in the art (e.g., electroless plating). Thus, typically iron deposition is conducted by a process comprising contacting the support with a deposition bath comprising a source of the first metal in the absence of an externally applied voltage. For example, iron may be deposited via electroless deposition using methods generally known in the art including, for example, those described in U.S. Patent No. 6,417,133 and by Wan et al. in

International Publication No. WO 2006/031938. In various embodiments, as detailed below, the deposition bath comprises a reducing agent that reduces ions of the first metal that are deposited at the surface of the support.

(a) Sources of Iron

[00229] Suitable sources of iron include iron salts such as the nitrate, sulfate, chloride, acetate, oxalate, and formate salts, and combinations thereof. In various preferred embodiments, the source of iron comprises iron chloride (i.e., $FeCl_3$), iron sulfate (i.e., $Fe_2(SO_4)_3$), or a combination thereof.

[00230] The concentration of iron source in the deposition bath is not narrowly critical and is generally selected in view of the desired metal content and/or the composition of the source. Often, the source of iron is present in the deposition bath at a concentration of at least about 5 g/L and more typically from about 5 to about 20 g/L. In various embodiments, the entire proportion of the source of iron is introduced into the deposition bath prior to, during, or after addition of the carbon support to the deposition bath and/or the vessel containing deposition bath. Additionally or alternatively (including as described in the working Examples), the source of iron may be metered, or pumped into the deposition bath and/or a vessel containing the carbon support. In this regard it is to be understood that metered addition of the source of iron is controlled to provide deposition of a suitable proportion of iron at the support surface, regardless of the concentration of iron source in the deposition bath at any point(s) during iron deposition.

(b) Iron Loading in Deposition Bath

[00231] As with other first metals (e.g., copper as described above), iron loading in the deposition bath may affect the quality and/or dispersion of iron deposition over a sufficient portion of the support surface. The concentration of iron in the deposition bath is generally controlled to address these concerns and others (e.g., agglomeration of first metal). For example, typically iron is present in the first metal deposition bath at a concentration of at least about 2 g/L, more typically at least about 3 g/L and, still more typically, at least about 4 g/L. Preferably, iron is present in the deposition bath at a concentration of from about 2 to about 8 g/L, more preferably from about 3 to about 6 g/L and, still more preferably, from about 4 to about 5 g/L.

(c) Reducing Agents

[00232] To provide a driving force for deposition of a second metal thereon, preferably iron is deposited in an at least partially reduced state, e.g., as Fe^{+2} and/or its fully reduced state as Fe^{0}. Thus, in various embodiments, the iron first metal deposition bath comprises a reducing agent. Any reducing agent is generally utilized under the conditions set forth above regarding copper deposition (e.g., concentration of reducing agent, etc.). Suitable reducing agents include sodium hypophosphite (NaH_2PO_2), formaldehyde (CH_2O), formic acid (HCOOH), salts of formic acid, sodium borohydride ($NaBH_4$), sodium triacetoxyborohydride ($Na(CH_3CO_2)_3BH$)), sodium alkoxides, hydrazine (H_2NNH_2), and ethylene glycol. In view of the greater electropositivity of iron as compared to copper, stronger reducing agents for iron first metal deposition may be preferred as compared to those preferred for copper first metal deposition. Thus, in various preferred

embodiments the reducing agent is sodium borohydride or ethylene glycol.

[00233] In those embodiments in which the reducing agent is sodium borohydride and/or ethylene glycol, the molar ratio of reducing agent to iron deposited is generally at least 1, typically at least about 2, and more typically at least about 3. Typically in accordance with these embodiments, the molar ratio of sodium borohydride to iron deposited is form about 1 to about 5 and, more typically, from about 2 to about 4.

(d) Temperature

[00234] As with copper deposition, the temperature of the deposition bath affects iron nucleation and agglomeration. Generally, the temperature of the deposition bath is sufficient to provide suitable nucleation and agglomeration, but preferably not at a level that promotes first metal agglomeration to an undesired degree. Generally, iron deposition bath temperatures ranging from about 5°C to about 60°C may be utilized to provide suitable catalysts. Often, the temperature of the iron deposition bath is above ambient conditions in order to provide sufficient nucleation and, more particularly, suitable dispersion of first metal over the support surface. Thus, typically the temperature of the iron deposition bath is from about 25°C to about 60°C and, more typically, from about 25°C to about 45°C.

(e) Agitation

[00235] The iron first metal deposition bath is typically agitated to promote dispersion of iron over the surface of the support. As in copper deposition, agitation may also promote diffusion of the reducing agent throughout the support. Any

agitation during first metal deposition is generally conducted in accordance with the above description regarding copper deposition.

(f) Deposition pH

[00236] As with copper deposition, iron deposition generally proceeds more readily as deposition pH increases. Thus, typically the iron deposition pH is at least about 8, at least about 9, or at least about 10. Also as with iron deposition, the presence of a coordinating agent (e.g., sucrose) is currently believed to retard iron precipitation at high pH and thereby promote sufficient dispersion of the metal over the surface of the support. As noted, formation of a coordination complex between the first metal and a coordinating agent is generally enhanced at the above-noted pH levels. But at certain pH levels, deposition bath pH may negatively impact solvation or iron ions and first metal reduction and deposition. Thus, in various preferred embodiments the pH of the iron deposition bath is from about 8 to about 13, or from about 9 to about 12.

5. First Metal Deposition Atmosphere

[00237] Regardless of the precise conditions of first metal deposition and the dispersion of first metal deposited at the support surface, oxidation of deposited first metal may reduce the proportion of first metal exchange sites available for second metal deposition. Accordingly, in various preferred embodiments, the first metal is deposited onto the support in the presence of a non-oxidizing environment (e.g., a nitrogen atmosphere). Additionally or alternatively, water and/or other deposition bath components are degassed to remove dissolved oxygen using methods known to those skilled in the art.

B. Second Metal

[00238] Conventional noble metal-containing catalysts are generally prepared by depositing a noble metal at the surface of a support, typically a porous carbon support. Agglomeration of noble metal into particles, thereby reducing exposed metal catalytic surface area, has been observed with these methods. In particular, an abundance of relatively large metal-containing particles may represent inefficient usage of the metal by virtue of these particles providing a relatively low exposed catalytic surface area per unit metal.

[00239] In accordance with various embodiments of the present invention, noble metal-containing catalysts are prepared by a method in which the noble metal is deposited in a manner that increases the exposed metal catalytic surface area per unit weight of metal. More particularly, the noble metal is deposited at the surface of one or more regions of first metal by displacement of first metal from the regions. It is currently believed that deposition of the noble metal utilizing a first, sacrificial metal results in reduced noble metal agglomeration. For example, as noted elsewhere herein, deposition of the noble metal in this manner provides a catalyst precursor structure in which the noble metal deposited at the surface of one or more regions of a first metal is less prone to agglomeration than noble metal deposited directly onto the surface of a porous support. It is further currently believed that, upon heat treatment of supports having thereon noble metal deposited in this manner, metal particles are formed that provide improved noble (second) metal utilization (e.g., greater exposed metal catalytic surface area per unit metal weight).

[00240] Generally, the second metal is deposited onto a first metal-impregnated support by contact of the metal-impregnated

support and a second metal deposition bath. More particularly, the second metal is generally deposited via electroless deposition in which the first metal-impregnated support and second metal deposition bath are contacted in the absence of an externally applied voltage.

[00241] As noted, in various embodiments, the second metal is a noble metal. Typically, the noble metal is selected from the group consisting of platinum, palladium, ruthenium, rhodium, iridium, silver, osmium, gold, and combinations thereof. In various preferred embodiments, the noble metal comprises platinum. In still other preferred embodiments, the noble metal comprises more than one metal (e.g., platinum and palladium or platinum and gold).

[00242] The following discussion focuses on deposition of platinum as the second metal, but it is to be understood that the present invention likewise contemplates utilizing any or all of the above-noted noble metals as the second metal. In addition, suitability of a combination of metals for use in displacement deposition of a second metal onto one or more regions of a first metal generally depends on their relative electropositivities. Thus, the present invention is not limited to deposition of noble metals as the second metal. For example, two metals designated as candidate first metals elsewhere herein may provide the first and second metals so long as their relative electropositivities allow displacement deposition of the second metal onto one or more regions of the first metal.

[00243] Suitable sources of platinum include those generally known in the art for use in liquid phase deposition of platinum and include, for example, H_2PtCl_4, H_2PtCl_6, K_2PtCl_4, Na_2PtCl_6, and combinations thereof. Thus, in various embodiments, the second metal deposition bath comprises a source of platinum including a

platinum salt comprising platinum at an oxidation state of +2 and/or +4. As noted, in various preferred embodiments, the source of platinum provides platinum ions exhibiting an oxidation state of +2. However, it is to be understood that effective catalysts may be prepared utilizing sources of platinum that provide platinum ions having other oxidation states (e.g., +4), and sources of platinum that provide platinum ions that comprise platinum ions exhibiting oxidation states other than +2. Similarly, sources of noble metals other than platinum and second metal sources generally that provide metal ions at lower oxidation states are likewise preferred. For example, it is currently believed that palladium provided by Na_2PdCl_4 and $PdCl_2$ may be utilized to prepare active catalyst comprising palladium as the second metal.

[00244] Generally, the source of platinum is present in the second metal deposition bath in a proportion that provides a molar concentration of second metal ions less than the concentration of first metal ions in the first metal deposition bath. Typically, the molar ratio of copper ions in the first metal deposition bath to noble metal ions in the second metal deposition bath is greater than 1, more typically at least about 2 and, even more typically at least about 3 (e.g., at least about 5). In various preferred embodiments, the molar ratio of copper ions in the first metal deposition bath to noble metal ions in the second noble metal deposition bath is typically greater than 1 to about 20, more typically from about 2 to about 15, still more typically from about 3 to about 10 and, even more typically, from about 5 to about 7.5.

[00245] Generally, the first metal-impregnated support is not subjected to elevated temperatures prior to contact with the second metal deposition bath. That is, the catalyst precursor

structure is preferably not subjected to temperatures that would promote formation of metal-containing particles (e.g., through agglomeration of first metal particles). For example, the first and second metal-impregnated support is generally subjected to temperatures of no more than about 200°C, no more than about 150°C, and preferably no more than about 120°C prior to contact with the second metal deposition bath.

[00246] Typically, the metal-impregnated support and second metal deposition bath are contacted at a temperature of at least about 5°C, typically at least about 10°C and, more typically, at least about 15°C. Preferably, the first metal-impregnated support and the second metal deposition bath are contacted at a temperature of from about 10°C to about 60°C, from about 20°C to about 50°C, or from about 25°C to about 45°C.

[00247] Often, the second metal deposition bath has a pH less than the pH of the first metal deposition bath and is from about 1 to about 12 or from about 1.5 to about 10. In accordance with various embodiments, the pH of the deposition bath is from about 2 to about 7 or from about 3 to about 5. Such pH conditions have been observed to be suitable for deposition of a noble (second) metal onto one or more regions of copper first metal. In various preferred embodiments, the first metal is iron. As compared to copper, iron may be more readily leached from the surface of the support as the pH of the deposition bath decreases. Thus, in accordance with those embodiments in which the first metal is iron, the pH of the noble (second) metal deposition bath is typically from about 4 to about 9, and preferably from about 5 to about 8 (e.g., about 7).

[00248] As noted above, preferably the first metal is deposited in an environment that avoids oxidation of deposited

first metal that may reduce the proportion of first metal exchange sites available for second metal deposition. Likewise, in various preferred embodiments, the second metal is also deposited onto the first metal-impregnated support in a non-oxidizing environment (e.g., a nitrogen atmosphere) to avoid oxidation of deposited first and second metal.

C. First and Second Metal-Impregnated Support

[00249] As noted, preferably the first metal deposited at the support surface provides suitable exchange sites for deposition of second metal at the surface of one or more regions of first metal and, more particularly, an excess of exchange sites for second metal deposition. Accordingly, typically the atom ratio of first metal to second metal of the first and second metal-impregnated support (i.e., catalyst precursor structure) is at least about 1.5, more typically at least about 2 and, still more typically, at least about 3 (e.g., at least about 4 or at least about 5). Preferably, the atom ratio of first metal to second metal of the first and second metal-impregnated support is from about 1.5 to about 15 more preferably from about 2 to about 15, still more preferably from about 3 to about 10 and, even more preferably, from about 4 to about 8.

[00250] As noted, heat treatment of the impregnated support provides first and noble (second) metal-containing particles at the support surface including the noble (second) metal in a form that provides advantageous metal utilization. An excess of first metal atoms to second metal atoms on the impregnated support is believed to result in formation of such particles. For example, the excess of first metal to second metal atoms on the impregnated support provides first metal-rich particles that include a relatively low proportion of unexposed noble (second) metal

throughout the particles (e.g., a bimetallic alloy having an excess of first metal atoms).

[00251] Additionally or alternatively, and as generally depicted in Fig. 2, heat treatment of the first and second metal-impregnated support may form metal particles comprising a core and a shell at least partially surrounding the core. It is currently believed that the composition of the core and shell indicate improvements in metal utilization and, more particularly, improvements in second metal (e.g., noble metal) utilization. For example, the core of these particles is generally first metal-rich, thereby providing a relatively low proportion of unexposed second metal throughout the particles.

[00252] As the atom ratio of first metal to second metal in the catalyst precursor increases, the extent to which the first metal-rich core is surrounded by a second metal-containing shell may decrease. For example, a relatively high excess of first metal exchange sites for second metal deposition may result in a portion of exchange sites that do not participate in displacement deposition of noble (second) metal. Such particles may be prepared from catalyst precursors in which the atom ratio is near or above the above-noted upper limit of first metal to second metal atom ratios (e.g., about 10 or higher). Although less preferred, it should be understood that a decrease in the degree to which the core is surrounded by a second metal-containing shell does not necessarily indicate a lack of improved second metal utilization. These particles may nonetheless provide improved metal utilization based on, for example, a first metal-rich core that provides a relatively low proportion of unexposed, and potentially unutilized noble (second) metal. However, it is currently believed that the structure of the particles may shift toward increased coverage of the first metal-rich core by the

second metal-containing shell. More particularly, this shift in form of the particles may comprise leaching of first metal from the metal particle at the support surface during use of the catalyst in liquid phase reactions. Second metal may likewise be removed or leached from the particles, but it is currently believed that first metal is removed from the particles to a greater degree than second metal. Accordingly, the atom ratio of first metal to second metal approaches more preferred ranges and it is currently believed that as a result of this removal the structure of particles shifts to more preferred (i.e., more extensive) coverage of the first metal-rich core by the second metal-containing shell. After a period of use, the leaching of first metal from the metal particles on the support surface generally decreases. Following such a period of use, it is currently believed that catalysts comprising particles having a more preferred ratio of first metal to second metal atoms with the attendant shift in structure, thereafter exhibit performance characteristics comparable to catalysts prepared using the more preferred ratios of first metal to second metal atoms. This "self-correcting" behavior has been observed, for example, in connection with catalysts in which the first metal is copper and the second metal is platinum.

D. Heat Treatment of First and Second Metal-Impregnated Supports

[00253] As noted, it is to be understood that the metal-impregnated support of the present invention is a suitable catalyst as described in the working examples detailed herein. However, typically in accordance with various preferred embodiments, the metal-impregnated support is treated at elevated temperatures generally as detailed elsewhere herein (e.g., in the

presence of a non-oxidizing environment at temperatures in excess of about 800°C) to form a finished catalyst. Typically, the metal-impregnated support is heated to temperatures from about 400°C to about 1000°C, more typically from about 500°C to about 950°C, still more typically from about 600°C to about 950°C and, even more typically, from about 700°C to about 900°C. Subjecting metal-impregnated supports to such temperatures provides finished catalysts exhibiting reduced metal leaching and improved metal utilization as detailed elsewhere herein (e.g., catalysts comprising first metal-rich particles and/or particles including a first metal-rich core at least partially surrounded by a second metal-rich shell).

[00254] Stable metal particles (i.e., resistant to leaching) are currently believed to be readily formed in the case of first and second metal-impregnated supports in which the first metal is iron and the second metal is platinum. Iron and platinum-impregnated supports (i.e., iron-platinum catalyst precursors) have been observed to exhibit suitable stability during reaction testing. Preferably, however, the iron-platinum catalyst precursor is subjected to elevated temperatures to prepare a finished catalyst. It is currently believed that heating the iron-platinum impregnated support improves activity. But, in view of the advantageous stability of the iron and platinum-impregnated supports, suitable catalysts may be prepared therefrom by heating the catalyst precursor to temperatures within, but at or near the lower limits of the above-noted ranges. Thus, in accordance with certain embodiments, platinum-iron impregnated supports are subjected to a maximum temperature of from about 400°C to about 750°C, or from about 500°C to about 650°C to prepare a finished catalyst.

[00255] As noted, the degree of first and second metal alloying generally increases with increasing temperature to which the metal-impregnated support is subjected. Accordingly, subjecting the iron/platinum-impregnated support to a relatively low maximum temperature is currently believed to provide a relatively low degree of iron and platinum alloying. Although catalysts of the present invention include the first and second metals in a form that represents efficient metal utilization (e.g., a first metal-rich alloy), alloy formation unavoidably results in unexposed noble (second) metal. Thus, preparing iron and platinum-containing catalysts by subjecting the metal-impregnated support to relatively low temperature may contribute to improved metal utilization. However, in this regard it is to be noted that preparing iron and platinum-containing catalysts by subjecting the supports to higher temperatures, e.g., in the ranges noted above such as 700°C or higher, is likewise currently believed to provide catalysts that represent more efficient metal utilization.

E. Iron and Platinum Deposition Protocols

[00256] Suitable iron and platinum-containing catalysts generally may be prepared in accordance with the above discussion regarding iron (first metal) and platinum (second metal) deposition, both in accordance with the above discussions concerning first and second metals generally, and specifically iron and platinum. However, in accordance with the present invention it has been discovered that advantageous catalysts are provided by combinations of particular features of iron (first metal) and platinum (second metal) deposition.

[00257] For example, in various preferred embodiments, the iron (first metal) deposition bath comprises ethylene glycol as a

reducing agent, but does not comprise a separate coordinating agent (e.g., sucrose). However, it is to be understood that the ethylene glycol reducing agent may, in fact, function as a coordinating agent to a certain degree.

[00258] In still other preferred embodiments, the iron deposition bath comprises both a reducing agent and a coordinating agent. In various such embodiments, ethylene glycol is the reducing agent and sucrose is the coordinating agent. In further such embodiments, ethylene glycol and sodium borohydride are utilized as reducing agents for iron deposition, and the iron deposition bath also comprises sucrose as a coordinating agent.

[00259] In various other preferred embodiments, the iron (first metal) deposition bath comprises sodium borohydride as a reducing agent generally in accordance with the above discussion. The iron deposition bath does not comprise a separate coordinating agent (e.g., sucrose).

F. First and Second Metal-Containing Catalysts

[00260] As noted, first and noble (second) metal-impregnated supports typically contain an excess of first metal atoms over second metal atoms. In accordance with these and various other embodiments, generally the first metal constitutes at least about 1% by weight, at least about 1.5% by weight, or at least about 2% by weight of the catalyst. Typically the first metal constitutes at least about 3% by weight, at least about 4% by weight, or at least about 5% by weight of the catalyst. For example, preferably the first metal constitutes from about 3% to about 25% by weight of the catalyst, more preferably from about 4% to about 20% by weight of the catalyst and, still more preferably, from about 5% to about 15% by weight of the catalyst. In various other

embodiments (e.g., those in which iron is the first metal), the first metal constitutes from about 1% to about 10% by weight, more preferably from about 1.5% to about 8% by weight and, still more preferably, from about 2% to about 5% (e.g., about 4%) by weight of the catalyst.

[00261] In accordance with the foregoing, catalysts of various embodiments of the present invention generally contain at least about 1% by weight noble (second) metal, at least about 2% by weight noble metal, or at least about 3% by weight noble metal. Typically, the catalysts contain less than about 8% by weight noble metal, more typically less than about 7% by weight noble metal and, still more typically, less than about 6% by weight noble metal. In accordance with various preferred embodiments, the catalysts contain less than about 5% or less than about 4% by weight noble metal (e.g., from about 1% to about 3% by weight noble metal). Catalysts prepared as detailed herein more efficiently utilize the noble (second) metal as compared to conventional catalysts, thereby providing catalysts at least as active or even more active than conventional noble metal-containing catalysts. For example, catalysts can be prepared that include metal loadings similar to conventional noble metal-containing catalysts, but are generally more active and, in various preferred embodiments, much more active than conventional noble metal-containing catalysts. In this manner, catalytic activity can be increased without an increase in noble metal loading, which may be undesired due to processing limitations. In various embodiments, active catalysts can be prepared that contain from about 3% to about 6% by weight noble metal, or from about 4% to about 5% by weight noble metal.

[00262] By way of further example, more efficient metal usage by catalysts of the present invention allows preparation of

catalysts that include a reduced proportion of second metal as compared to conventional noble metal-containing catalysts, but that are at least as active and, in various preferred embodiments, more active than conventional noble metal-containing catalysts. In this manner, catalysts of the present invention can provide activities equivalent to those provided by conventional noble metal-containing catalysts at lower noble metal loadings, or greater catalytic activities at equivalent noble metal loadings. For example, in various embodiments, active catalysts may be prepared that contain from about 1% to about 5% by weight, from about 1.5% to about 4% by weight, or from about 2% to about 3% by weight noble metal.

[00263] In various embodiments, first metal to second metal atom ratio in metal particles at the surface of the catalyst support generally increases with increasing particle size. It is currently believed that as particle size increases the portion of the particle constituting the first metal-rich core increases, while the portion (i.e., weight fraction) of the particles constituting the second metal-containing shell decreases. As previously noted, larger metal-containing particles are generally more resistant to leaching from the surface of the catalyst support. However, a significant fraction of larger particles is generally undesired in conventional noble metal-containing catalysts because as particle size increases the proportion of noble metal distributed within the particle that does not contribute to effective catalytic surface area increases. . Thus, a relatively high proportion of large particles comprising a second metal-rich shell in accordance with the present invention provides improved stability, without the sacrifice in exposed noble (second) metal catalytic surface area associated with

relatively large particles in conventional noble metal-containing catalysts.

[00264] For example, in various embodiments, the catalyst includes metal-containing particles characterized by a particle size, as determined using electron microscopy, such that a significant fraction (e.g., at least about 80%, at least about 90%, or at least about 95%, number basis) of the particles are from about 5 to about 60 nm, or from about 5 to about 40 nm in their largest dimension. In addition, the thickness of the second metal-containing shells of the particles within these size distributions nm is typically less than about 3 nm, more typically less than about 2 nm, and preferably less than about 1 nm (e.g., less than about 0.8 nm or less than about 0.6 nm).

[00265] Improvements in metal utilization may be characterized by an increase in the proportion of exposed noble (second) metal of the catalyst. More particularly, improvements in metal utilization may be indicated by an increase in the surface area of exposed noble metal per unit weight catalyst per unit weight noble metal. The total exposed noble metal surface area of catalysts of the present invention may be determined using static carbon monoxide chemisorption analysis, including Protocol A described in Example 67. The carbon monoxide chemisorption analysis described in Example 67 includes first and second cycles. Catalysts of the present invention subjected to such analysis are generally characterized as chemisorbing at least about 500 μmoles of carbon monoxide per gram catalyst per gram noble metal and, more generally, at least about 600 μmoles of carbon monoxide per gram catalyst per gram noble metal. Typically, catalysts of the present invention are characterized as chemisorbing at least about 700, at least about 800, at least about 900, at least about 975,

at least about 1000, or at least about 1100 μmoles of carbon monoxide per gram catalyst per gram noble metal.

[00266] An alternative or additional indicator of efficient metal utilization is the proportion of the noble (second) metal of the catalyst that may be found within a shell at least partially surrounding a first metal-rich core. Generally, at least about 10%, at least about 20%, at least about 30%, at least about 40%, or at least about 50% of the noble metal is present within the shell of the metal particles. Typically, at least about 60% and, more typically, at least about 70% (e.g., at least about 80% or at least about 90%) of the noble metal is present within the shell of the metal particles.

[00267] Additionally or alternatively, efficient metal utilization may be indicated by the proportion of noble (second) metal at the surface of metal particles. That is, efficient metal utilization may be indicated by the proportion of noble metal at the surface of first metal-rich particles, e.g., second metal present in an alloy and/or within a second metal-rich shell at least partially surrounding a first metal-rich core. Generally, the atom percent of noble metal at the surface of first and noble (second) metal-containing particles is at least about 2%, or at least about 5%. Typically, the atom percent of noble metal at the surface of first and noble metal-containing particles is at least about 10%, more typically at least about 20%, even more typically at least about 30%, and preferably at least about 40% (e.g., at least about 50%).

[00268] Energy dispersive x-ray spectroscopy (EDX) line scan analysis results for catalysts of the present invention (e.g., as described in Protocol B in Example 68) also indicate efficient metal utilization. More particularly, line scan analysis results for metal particles of catalysts of the present invention indicate

a distribution of noble (second) metal in which a significant fraction of the noble (second) metal is present within a shell at least partially surrounding a first metal-rich core. Additionally or alternatively, line scan analysis results for metal particles of catalysts of the present invention indicate a noble metal distribution in which a significant fraction of the noble metal is disposed at or near the surface of a metal particle(s).

[00269] Efficient metal utilization in particles of catalysts of the present invention is indicated by a second metal distribution that produces an EDX line scan signal that does not vary significantly over a scanning region. As used herein, the term scanning region refers to the portion of the largest dimension of the particle analyzed over which a relatively low degree of variation in second metal signal indicates improved metal utilization. A relatively constant second metal line scan signal over a scanning region corresponding to a significant portion of the largest dimension of the particle indicates that a significant fraction of the second metal is distributed near the surface of the particle rather than throughout the metal particle. By contrast, the latter type of distribution would cause the second metal signal to increase (decrease) significantly in that portion of the scanning region where the probe is directed to a thicker (thinner) dimension of the particle. For example, in various embodiments, the second metal signal generated during EDX line scan analysis of a particle at the surface of a catalyst in accordance with the present invention varies by no more than about 25%, no more than about 20%, no more than about 15%, no more than about 10%, or no more than about 5% across a scanning region that is a least about 70% of the largest dimension of at least one particle. In further embodiments, the second metal signal varies by no more than about 20%, no more than about 15%, no more than

about 10%, or no more than about 5% across a scanning region that is at least about 60% of the largest dimension of at least one particle. In still further embodiments, the second metal signal varies by no more than about 15%, no more than about 10%, or no more than about 5% across a scanning region that is at least about 50% of the largest dimension of at least one particle.

[00270] The particles having metal distributions characterized by EDX line scan analysis as detailed above are typically first metal-rich and, more particularly, typically include the second metal and first metal at an atomic ratio of second metal to first metal in a particle(s) analyzed of less than 1:1. Typically, the second metal to first metal atomic ratio of the particle(s) is less than about 0.8:1 and, more typically, less than about 0.6:1 (e.g., less than about 0.5:1).

[00271] Generally, the first and second metal particle(s) of catalysts of the present invention having a second metal distribution characterized by EDX line scan analysis indicating efficient metal utilization have a largest dimension of at least about 6 nm, typically at least about 8 nm, more typically at least about 10 nm and, still more typically, at least about 12 nm.

[00272] The relative magnitudes of first and second metal signals across the scanning region may also indicate first and second metal distributions in a form that indicates efficient metal utilization. More particularly, generally in accordance with various embodiments, the ratio of the maximum first metal signal to the maximum second metal signal across the scanning region is at least about 1.5:1, at least about 2:1, or at least about 2.5:1. Typically, the ratio of the maximum first metal signal to the maximum second metal signal across the scanning region is at least about 3:1, at least about 4:1, or at least about 5:1.

[00273] It is to be understood that efficient metal utilization may be indicated by identification of at least one particle at the surface of the catalyst support having a noble (second) metal distribution characterized as described above. That is, the population of metal particles at the surface of the catalyst support may include both particles satisfying one or more of the noble metal distribution characteristics and those that do not. However, metal utilization is enhanced as the proportion of metal particles exhibiting these preferred noble metal distribution characteristics increases and typically a plurality of metal particles will possess these characteristics. More typically, the second metal distribution of each of a portion (number basis) of the particles at the surface of the support indicates efficient metal utilization. Generally, at least about 1%, at least about 5%, at least about 10%, at least about 15%, at least about 20%, or at least about 25% of the metal particles satisfy the second metal distribution characteristics. Typically, at least about 30%, at least about 35%, at least about 40%, at least about 45%, at least about 50%, at least about 55%, at least about 60%, or at least about 65% of the metal particles satisfy the second metal distribution characteristics. The proportion of metal particles satisfying one or more of the noble metal distribution characteristics is somewhat dependent upon the particular first metal and second metal combination. For example, catalysts prepared with copper and platinum as the first and second metals, respectively, have been observed to produce catalysts in which a large portion of metal particles at the surface thereof possess these preferred noble metal distribution characteristics. Accordingly, in these and other preferred embodiments, at least about 70%, at least about 75%, at least about 85%, or at least about 90% of the metal particles at the

surface of the support satisfy one or more of the second metal distribution characteristics determined by EDX line scan analysis.

[00274] As previously noted, in various embodiments of the present invention (e.g., in which copper is the first metal and platinum is the second metal) the second metal-rich shell may provide relatively low coverage of the first metal-rich core and, during subsequent use of the catalyst, the structure of the particles may shift toward increased coverage of the first metal-rich core by the second metal-containing shell. This shift generally comprises leaching of the first metal from the metal particles at the support surface. Second metal may be removed or leached from the particles, but to a lesser degree than first metal is removed from the particles. This behavior has been observed to provide a shift toward preferred first metal to second metal atomic ratios.

[00275] Platinum-iron catalysts of the present invention have been observed to behave as described. That is, during use, iron and platinum may be leached from the metal particles at the surface of the catalyst and, more particularly, iron is leached from the particles to a greater degree than platinum. Leaching in this manner may proceed in accordance with the "self-correcting" mechanism described above in connection with platinum-copper catalysts. However, leaching may also proceed to form platinum-iron particles of advantageous structures. Rather than compensating for a relatively low excess of first metal to second metal to provide a structure in which the atomic ratio of first metal to second metal is at a suitable excess, leaching of first metal predominates over any leaching of second metal to such a degree that one or more particles are provided that exhibit minimal, if any, excess of first metal to second metal. In fact, in various embodiments, a catalyst structure exhibiting an excess

of second metal to first metal is achieved. Although these particles may not include a first metal-rich alloy or a first metal-rich core at least partially surrounded by a second metal-rich shell, they do nonetheless provide improved metal utilization.

[00276] In various such embodiments, the metal particles at the surface of the catalyst are in the form of a structure comprising a discontinuous shell comprising a layer of first metal atoms and a layer (e.g., monolayer) of second metal atoms at the surface of the first metal atoms. Reference to a shell in connection with these embodiments does not indicate the presence of a continuous or discontinuous shell surrounding a relatively continuous core. Rather, shell refers to the overall structure of the resulting particle. The shell structure may surround an inner region including first metal, but the inner regions of the shell structure are not in the form of a relatively continuous first metal-rich core surrounded by the outer regions of the shell structure. The discontinuous porous shell generally comprises pores and, more particularly, nanopores (i.e., pores having a size in their largest dimension of from about 1 to about 6 nanometers (nm), or from about 2 to about 5 nm). In this manner, the shell structure may be referred to as a discontinuous nanoporous shell. In accordance with such embodiments, the atomic ratio of iron (first metal) to platinum (second metal) is generally less than 1:1, typically from about 0.25:1 to about 0.9:1, more typically from about 0.4:1 to about 0.75:1 and, more typically, from about 0.4:1 to about 0.6:1 (e.g., about 0.5:1). Further in accordance with these embodiments, the layer or regions of first metal generally have a thickness of no more than about 5 first metal atoms, typically no more than about 3 first metal atoms and, still more typically, no more than about 2 first metal atoms.

Additionally or alternatively, the layer or regions of second metal atoms generally have a thickness of no more than about 5 second metal atoms, typically no more than about 4 second metal atoms, more typically no more than about 3 second metal atoms and, more typically, no more than about 2 second metal atoms.

[00277] Extensive leaching of metal from catalyst particles to form platinum-iron "shell" particles has been observed to occur during use under certain conditions (e.g., acidic conditions prevailing during oxidation of PMIDA). Experimental evidence indicates that catalysts including platinum-iron shell particles are effective for use in, for example, the liquid phase oxidation of PMIDA. Thus, rather than simply relying on formation of the shell structure during use, catalysts including platinum-iron shell particles may be prepared by a process generally as described above for preparation of platinum-iron catalysts further including treatment for leaching of metals from one or more particles of the catalyst prior to or during use of the catalyst. Generally, treatment for metal leaching to form platinum-iron shell particles comprises contacting a platinum-iron catalyst with a suitable liquid medium. Typically, the liquid medium is acidic and the catalyst is contacted with the liquid medium at a temperature of at least about 5°C, or at least about 15°C.

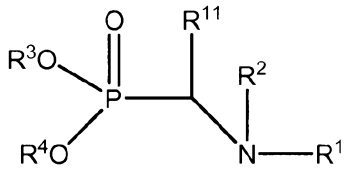
III. Use of Oxidation Catalysts

[00278] Oxidation catalysts of the present invention may be used for liquid phase oxidation reactions. Examples of such reactions include the oxidation of alcohols and polyols to form aldehydes, ketones, and acids (e.g., the oxidation of 2-propanol to form acetone, and the oxidation of glycerol to form glyceraldehyde, dihydroxyacetone, or glyceric acid); the oxidation of aldehydes to form acids (e.g., the oxidation of formaldehyde to form formic acid, and the oxidation of furfural to form 2-furan carboxylic

acid); the oxidation of tertiary amines to form secondary amines (e.g., the oxidation of nitrilotriacetic acid (NTA) to form iminodiacetic acid (IDA)); the oxidation of secondary amines to form primary amines (e.g., the oxidation of IDA to form glycine); and the oxidation of various acids (e.g., formic acid or acetic acid) to form carbon dioxide and water.

[00279] The above-described catalysts are especially useful in liquid phase oxidation reactions at pH levels less than 7, and in particular, at pH levels less than 3. One such reaction is the oxidation of PMIDA or a salt thereof to form an N-(phosphonomethyl)glycine product in an environment having pH levels in the range of from about 1 to about 2. This reaction is often carried out in the presence of solvents which solubilize noble metals and, in addition, the reactants, intermediates, or products often solubilize noble metals.

[00280] The oxidation catalyst disclosed herein is particularly suited for catalyzing the liquid phase oxidation of a tertiary amine to a secondary amine, for example in the preparation of glyphosate and related compounds and derivatives. For example, the tertiary amine substrate may correspond to a compound of Formula I having the structure



(Formula I)

wherein R^1 is selected from the group consisting of $R^5OC(O)CH_2$- and $R^5OCH_2CH_2$-, R^2 is selected from the group consisting of $R^5OC(O)CH_2$-, $R^5OCH_2CH_2$-, hydrocarbyl, substituted hydrocarbyl, acyl, $-CHR^6PO_3R^7R^8$, and $-CHR^9SO_3R^{10}$, R^6, R^9 and R^{11} are selected from the group consisting of hydrogen, alkyl, halogen and $-NO_2$, and R^3, R^4, R^5, R^7, R^8 and are independently selected from the group consisting of hydrogen, hydrocarbyl, substituted hydrocarbyl and a metal ion. Preferably,

R^1 comprises $R^5OC(O)CH_2$-, R^{11} is hydrogen, R^5 is selected from hydrogen and an agronomically acceptable cation and R^2 is selected from the group consisting of $R^5OC(O)CH_2$-, acyl, hydrocarbyl and substituted hydrocarbyl.

[00281] As noted above, the oxidation catalyst of the present invention is particularly suited for catalyzing the oxidative cleavage of a PMIDA substrate to form N-(phosphonomethyl)glycine product. In such an embodiment, the catalyst is effective for oxidation of by-product formaldehyde to formic acid, carbon dioxide and/or water. More particularly, it is currently believed that catalysts of the present invention may provide improvements in activity for PMIDA, formaldehyde, and/or formic acid oxidation as compared to conventional noble metal-containing catalysts, either generally or on a per unit metal weight basis.

[00282] As is recognized in the art, the liquid phase oxidation of N-(phosphonomethyl)iminodiacetic acid substrates may be carried out in a batch, semi-batch or continuous reactor system containing one or more oxidation reaction zones. The oxidation reaction zone(s) may be suitably provided by various reactor configurations, including those that have back-mixed characteristics, in the liquid phase and optionally in the gas phase as well, and those that have plug flow characteristics. Suitable reactor configurations having back-mixed characteristics include, for example, stirred tank reactors, ejector nozzle loop reactors (also known as venturi-loop reactors) and fluidized bed reactors. Suitable reactor configurations having plug flow characteristics include those having a packed or fixed catalyst bed (e.g., trickle bed reactors and packed bubble column reactors) and bubble slurry column reactors. Fluidized bed reactors may also be operated in a manner exhibiting plug flow characteristics. The configuration of the oxidation reactor system, including the number of oxidation reaction zones and the oxidation reaction conditions are not critical to the practice of the present invention. Suitable oxidation reactor systems and oxidation reaction conditions for liquid phase catalytic oxidation of an N-

(phosphonomethyl)iminodiacetic acid substrate are well-known in the art and described, for example, by Ebner et al., U.S. Patent No. 6,417,133, by Leiber et al., U.S. Patent No. 6,586,621, and by Haupfear et al., U.S. Patent No. 7,015,351, the entire disclosures of which are incorporated herein by reference.

[00283] The description below discloses with particularity the use of catalysts described above acting as the catalyst to effect the oxidative cleavage of a PMIDA substrate to form an N-(phosphonomethyl)glycine product. It should be recognized, however, that the principles disclosed below are generally applicable to other liquid phase oxidative reactions, especially those at pH levels less than 7 and those involving solvents, reactants, intermediates, or products which solubilize noble metals.

[00284] To begin the PMIDA oxidation reaction, it is preferable to charge the reactor with the PMIDA substrate, catalyst, and a solvent in the presence of oxygen. The solvent is most preferably water, although other solvents (e.g., glacial acetic acid) are suitable as well.

[00285] The reaction may be carried out in a wide variety of batch, semi-batch, and continuous reactor systems. The configuration of the reactor is not critical. Suitable conventional reactor configurations include, for example, stirred tank reactors, fixed bed reactors, trickle bed reactors, fluidized bed reactors, bubble flow reactors, plug flow reactors, and parallel flow reactors.

[00286] When conducted in a continuous reactor system, the residence time in the reaction zone can vary widely depending on the specific catalyst and conditions employed. Typically, the residence time can vary over the range of from about 3 to about 120 minutes. Preferably, the residence time is from about 5 to about 90 minutes, and more preferably from about 5 to about 60 minutes. When conducted in a batch reactor, the reaction time typically varies over the range of from about 15 to about 120 minutes.

Preferably, the reaction time is from about 20 to about 90 minutes, and more preferably from about 30 to about 60 minutes.

[00287] In a broad sense, the oxidation reaction may be practiced in accordance with the present invention at a wide range of temperatures, and at pressures ranging from sub-atmospheric to super-atmospheric. Use of mild conditions (e.g., room temperature and atmospheric pressure) have obvious commercial advantages in that less expensive equipment may be used. However, operating at higher temperatures and super-atmospheric pressures, while increasing capital requirements, tends to improve phase transfer between the liquid and gas phase and increase the PMIDA oxidation reaction rate.

[00288] Preferably, the PMIDA oxidation reaction is conducted at a temperature of from about 20 to about 180°C, more preferably from about 50 to about 140°C, and most preferably from about 80 to about 110°C. At temperatures greater than about 180°C, the raw materials tend to begin to slowly decompose.

[00289] The pressure used during the PMIDA oxidation generally depends on the temperature used. Preferably, the pressure is sufficient to prevent the reaction mixture from boiling. If an oxygen-containing gas is used as the oxygen source, the pressure also preferably is adequate to cause the oxygen to dissolve into the reaction mixture at a rate sufficient such that the PMIDA oxidation is not limited due to an inadequate oxygen supply. The pressure preferably is at least equal to atmospheric pressure. More preferably, the pressure is from about 30 to about 500 psig, and most preferably from about 30 to about 130 psig.

[00290] The concentration of the catalyst prepared in accordance with the present invention in the reaction mixture is preferably is from about 0.1 to about 10% by weight ([mass of catalyst ÷ total reaction mass] x 100%). More preferably, the catalyst concentration preferably is from about 0.1 to about 5% by weight, still more preferably from about 0.2 to about 5% by weight and, most preferably, from about 0.3 to about 1.5% by weight. Concentrations greater than about 10% by weight are difficult to

filter. On the other hand, concentrations less than about 0.1% by weight tend to produce unacceptably low reaction rates.

[00291] As noted, catalysts prepared in accordance with the methods of the present invention provide for efficient metal utilization. Thus, catalysts of the present invention may provide sufficient activity at lower catalyst loadings as compared to loadings associated with conventional noble metal-containing catalysts. Accordingly, catalysts loadings in accordance with the present invention may suitably be at or near the lower limits of the above-noted ranges. However, it is to be understood that utilizing a lower catalyst loading is not a critical aspect of the present invention. In fact, a further aspect of the present invention involves utilizing the catalysts of the present invention at loadings similar to those associated with conventional noble metal-containing catalysts while providing improved catalytic activity based on the improvements in metal utilization.

[00292] The concentration of PMIDA substrate in the feed stream is not critical. Use of a saturated solution of PMIDA substrate in water is preferred, although for ease of operation, the process is also operable at lesser or greater PMIDA substrate concentrations in the feed stream. If the catalyst is present in the reaction mixture in a finely divided form, it is preferred to use a concentration of reactants such that all reactants and the N-(phosphonomethyl)glycine product remain in solution so that the catalyst can be recovered for re-use, for example, by filtration. On the other hand, greater concentrations tend to increase reactor through-put. Alternatively, if the catalyst is present as a stationary phase through which the reaction medium and oxygen source are passed, it may be possible to use greater concentrations of reactants such that a portion of the N-(phosphonomethyl)glycine product precipitates.

[00293] Normally, a PMIDA substrate concentration of up to about 50% by weight ([mass of PMIDA substrate ÷ total reaction mass] x 100%) may be used (especially at a reaction temperature of from about 20 to about 180°C). Preferably, a PMIDA substrate

concentration of up to about 25% by weight is used (particularly at a reaction temperature of from about 60 to about 150°C). More preferably, a PMIDA substrate concentration of from about 12 to about 18% by weight is used (particularly at a reaction temperature of from about 100 to about 130°C). PMIDA substrate concentrations below 12% by weight may be used, but are less economical because a relatively low payload of N-(phosphonomethyl)glycine product is produced in each reactor cycle and more water must be removed and energy used per unit of N-(phosphonomethyl)glycine product produced. Relatively low reaction temperatures (i.e., temperatures less than 100°C) often tend to be less advantageous because the solubility of the PMIDA substrate and N-(phosphonomethyl)glycine product are both relatively low at such temperatures.

[00294] The oxygen source for the PMIDA oxidation reaction may be any oxygen-containing gas or a liquid comprising dissolved oxygen. Preferably, the oxygen source is an oxygen-containing gas. As used herein, an oxygen-containing gas is any gaseous mixture comprising molecular oxygen which optionally may comprise one or more diluents which are non-reactive with the oxygen or with the reactant or product under the reaction conditions.

[00295] Examples of such gases are air, pure molecular oxygen, or molecular oxygen diluted with helium, argon, nitrogen, or other non-oxidizing gases. For economic reasons, the oxygen source most preferably is air, oxygen-enriched air, or pure molecular oxygen.

[00296] Oxygen may be introduced by any conventional means into the reaction medium in a manner which maintains the dissolved oxygen concentration in the reaction mixture at a desired level. If an oxygen-containing gas is used, it preferably is introduced into the reaction medium in a manner which maximizes the contact of the gas with the reaction solution. Such contact may be obtained, for example, by dispersing the gas through a diffuser such as a porous frit or by stirring, shaking, or other methods known to those skilled in the art.

[00297] The oxygen feed rate preferably is such that the PMIDA oxidation reaction rate is not limited by oxygen supply. If the

dissolved oxygen concentration is too high, however, the catalyst surface tends to become detrimentally oxidized, which, in turn, tends to lead to more leaching of noble metal present in the catalyst and decreased formaldehyde activity (which, in turn, leads to more NMG being produced). Generally, it is preferred to use an oxygen feed rate such that at least about 40% of the oxygen is utilized. More preferably, the oxygen feed rate is such that at least about 60% of the oxygen is utilized. Even more preferably, the oxygen feed rate is such that at least about 80% of the oxygen is utilized. Most preferably, the rate is such that at least about 90% of the oxygen is utilized. As used herein, the percentage of oxygen utilized equals: (the total oxygen consumption rate ÷ oxygen feed rate) x 100%. The term "total oxygen consumption rate" means the sum of: (i) the oxygen consumption rate ("R_i") of the oxidation reaction of the PMIDA substrate to form the N-(phosphonomethyl)glycine product and formaldehyde, (ii) the oxygen consumption rate ("R_{ii}") of the oxidation reaction of formaldehyde to form formic acid, and (iii) the oxygen consumption rate ("R_{iii}") of the oxidation reaction of formic acid to form carbon dioxide and water.

[00298] In various embodiments of this invention, oxygen is fed into the reactor as described above until the bulk of PMIDA substrate has been oxidized, and then a reduced oxygen feed rate is used. This reduced feed rate preferably is used after about 75% of the PMIDA substrate has been consumed. More preferably, the reduced feed rate is used after about 80% of the PMIDA substrate has been consumed. Where oxygen is supplied as pure oxygen or oxygen-enriched air, a reduced feed rate may be achieved by purging the reactor with (non-enriched) air, preferably at a volumetric feed rate which is no greater than the volumetric rate at which the pure molecular oxygen or oxygen-enriched air was fed before the air purge. The reduced oxygen feed rate preferably is maintained for from about 2 to about 40 minutes, more preferably from about 5 to about 20 minutes, and most preferably from about 5 to about 15 minutes. While the oxygen is being fed at the reduced rate, the

temperature preferably is maintained at the same temperature or at a temperature less than the temperature at which the reaction was conducted before the air purge. Likewise, the pressure is maintained at the same or at a pressure less than the pressure at which the reaction was conducted before the air purge. Use of a reduced oxygen feed rate near the end of the PMIDA reaction allows the amount of residual formaldehyde present in the reaction solution to be reduced without producing detrimental amounts of AMPA by oxidizing the N-(phosphonomethyl)glycine product.

[00299] Reduced losses of noble metal may be observed with this invention if a sacrificial reducing agent is maintained or introduced into the reaction solution. Suitable reducing agents include formaldehyde, formic acid, and acetaldehyde. Most preferably, formic acid, formaldehyde, or mixtures thereof are used. Experiments conducted in accordance with this invention indicate that if small amounts of formic acid, formaldehyde, or a combination thereof are added to the reaction solution, the catalyst will preferentially effect the oxidation of the formic acid or formaldehyde before it effects the oxidation of the PMIDA substrate, and subsequently will be more active in effecting the oxidation of formic acid and formaldehyde during the PMIDA oxidation. Preferably from about 0.01 to about 5% by weight ([mass of formic acid, formaldehyde, or a combination thereof total reaction mass] x 100%) of sacrificial reducing agent is added, more preferably from about 0.01 to about 3% by weight of sacrificial reducing agent is added, and most preferably from about 0.01 to about 1% by weight of sacrificial reducing agent is added.

[00300] In certain embodiments, unreacted formaldehyde and formic acid are recycled back into the reaction mixture for use in subsequent cycles. In this instance, an aqueous recycle stream comprising formaldehyde and/or formic acid also may be used to solubilize the PMIDA substrate in the subsequent cycles. Such a recycle stream may be generated by evaporation of water, formaldehyde, and formic acid from the oxidation reaction mixture in order to concentrate and/or crystallize product

N-(phosphonomethyl)glycine. Overheads condensate containing formaldehyde and formic acid may be suitable for recycle.

[00301] Typically, the concentration of N-(phosphonomethyl)glycine in the product mixture may be as great as 40% by weight, or greater. Preferably, the N-(phosphonomethyl)glycine concentration is from about 5 to about 40%, more preferably from about 8 to about 30%, and still more preferably from about 9 to about 15%. Concentrations of formaldehyde in the product mixture are typically less than about 0.5% by weight, more preferably less than about 0.3%, and still more preferably less than about 0.15%.

[00302] Following the oxidation, the catalyst preferably is subsequently separated by filtration. The N-(phosphonomethyl)glycine product may then be isolated by precipitation, for example, by evaporation of a portion of the water and cooling.

[00303] In certain embodiments, it should be recognized that the catalyst of this invention has the ability to be reused over several cycles, depending on how oxidized its surface becomes with use. Even after the catalyst becomes heavily oxidized, it may be reused by being reactivated. To reactivate a catalyst having a heavily oxidized surface, the surface preferably is first washed to remove the organics from the surface. It then preferably is reduced in the same manner that a catalyst is reduced after the noble metal is deposited onto the surface of the support, as described above.

[00304] Noble metal-containing catalysts including a treated porous substrate prepared by the present method may also be used in combination with a supplemental promoter as described, for example, in U.S. Patent No. 6,586,621, U.S. Patent No. 6,963,009, the entire contents of which are incorporated herein by reference for all relevant purposes.

[00305] N-(phosphonomethyl)glycine product prepared in accordance with the present invention may be further processed in

accordance with many well-known methods in the art to produce agronomically acceptable salts of N-(phosphonomethyl)glycine commonly used in herbicidal glyphosate compositions. As used herein, an "agronomically acceptable salt" is defined as a salt which contains a cation(s) that allows agriculturally and economically useful herbicidal activity of an N-(phosphonomethyl)glycine anion. Such a cation may be, for example, an alkali metal cation (e.g., a sodium or potassium ion), an ammonium ion, an isopropyl ammonium ion, a tetra-alkylammonium ion, a trialkyl sulfonium ion, a protonated primary amine, a protonated secondary amine, or a protonated tertiary amine.

IV. Additional Embodiments

A. Pore Blocking

[00306] With regard to disposing or depositing a pore blocking compound within substrate pores as detailed elsewhere herein, it is to be noted that the present invention is not limited to disposing or depositing a pore blocking compound within the smallest substrate pores (e.g., micropores). That is, various embodiments of the present invention are directed to disposing or depositing a pore blocker within pores of an intermediate or larger size range. In this manner, various embodiments of the present invention provide further opportunities for controlling the sizes of pores that are blocked (i.e., further opportunities for controlling, or tuning blocking of pores). For example, in addition to micropores, porous carbon supports that may be treated by the present method have pores of larger dimensions (e.g., pores having a largest dimension of from about 20Å to about 3000Å).

[00307] Disposing or depositing a pore blocking agent within pores of a size above the micropore size range proceeds generally in accordance with the above-described method. For example, the

substrate may be contacted with the pore blocking compound and/or one or more precursors. Further in accordance with the above-described method, the pore blocker may be retained within the targeted pores by virtue of exhibiting at least one dimension larger than the openings of the targeted pores. And regardless of whether the pore blocking agent is introduced into the targeted pores or formed *in situ*, the pore blocker may be retained within the targeted pores by virtue of a conformational arrangement of the pore blocker.

[00308] As noted above, when relatively small pores are targeted by the pore blocker, the pore blocker may enter the non-targeted pores and subsequently exit therefrom (e.g., by virtue of contacting with a liquid washing medium). It is to be noted that a pore blocker targeting intermediate and/or larger size may not enter the pores smaller than the targeted pores. However, this does not impact the goal of blocking of intermediate and/or larger sized pores.

[00309] It is currently believed that a variety of compounds are suitable as pore blocking compounds for the purpose of blocking pores above the micropore size range. For example, the pore blocker may be selected from the group consisting of various hydrophilic polymers (e.g., various polyethylene glycols), and combinations thereof.

[00310] In various embodiments, the intermediate and/or larger size pore blocker may comprise the product of a reaction between one or more pore blocking compound precursors. For example, it has been observed that the coupling product of a ketone and a dihydric alcohol may be utilized as a pore blocker.

[00311] As with micropores as noted above, it is believed that the presence of the pore blocking compound within targeted pores outside the micropore domain will cause at least a portion of the

"blocked" pores to appear as a non-porous portion of the substrate during surface area measurements, thereby reducing the proportion of surface area that would otherwise be provided by the targeted pores if they were not blocked. This blocking of the targeted pores is currently believed to provide a reduction in the surface area of the treated substrate provided by the targeted pores. For example, in various embodiments, the surface area of the treated substrate provided by the pores outside (i.e., above) the micropore size range is generally no more than about 80% or no more than about 70% of the surface area of the substrate provided by these pores prior to treatment. Typically, the surface area of the treated substrate provided by the targeted pores is no more than about 60% and more typically no more than about 50% of the surface area of the substrate provided by these pores prior to treatment.

B. Pore Blocking of Catalyst Pores

[00312] As noted, persistence of the pore blocker in treated substrates of the present invention is not critical to provide the advantages described above (e.g., a reduced proportion of metal crystallites at the surface of a porous carbon support among relatively small pores of the substrate surface). And it is currently believed that the pore blocker is most likely decomposed and/or otherwise removed from the substrate surface before calcining. In various alternative embodiments, the methods for treating porous substrates may be applied to treatment of finished catalysts. For example, catalysts comprising a noble metal deposited onto a carbon support may be treated by depositing a pore blocker at the surface of the catalyst within its relatively small pores. It is currently believed that the presence of the pore blocker within the relatively small pores may promote

preferential contact of reactants with the deposited metal among the intermediate and larger-sized porous regions within which the deposited metal is more accessible to the reactants. In this manner, conversion of reactants to products may be promoted by reducing the proportion of reactants that contact deposited metal among the relatively small porous regions in which the deposited metal may be relatively inaccessible to the reactants. By way of further example, treating carbon-supported catalysts suitable for in preparation of DSIDA from DEA in accordance with the methods detailed are currently believed to provide catalysts including a reduced proportion of exposed noble metal and, accordingly, reduced by-product (e.g., glycine and/or oxalate). However, it is to be understood that treatment of finished catalyst (i.e., carbon or metal-containing having one or more metals deposited thereon) is not a critical aspect of the invention and that catalysts prepared using substrates treated by the present methods have proven to be effective catalysts.

C. Non-carbon supports

[00313] In addition to treatment of porous carbon supports as detailed herein, the method of the present invention for blocking certain pores of a substrate may be used to treat non-carbonaceous supports. More particularly, the methods detailed herein may be used for treatment of porous metal alloys often referred to as metal sponges. Metal sponge alloys that may be treated by the present method are described, for example, in U.S. Patent No. 5,627,125, U.S. Patent No. 5,916,840, U.S. Patent No. 6,376,708, and U.S. Patent No. 6,706,662, the entire contents of which are incorporated herein by reference for all relevant purposes. It is currently believed that treated metal-containing substrates may

exhibit one or more of the above-noted properties concerning treated porous carbon substrates.

D. Preparation of Carboxylic Acids

[00314] In addition to PMIDA oxidation as detailed elsewhere herein, catalysts including treated substrates prepared by the present method are currently believed to be suitable for use in other reactions. For example, catalysts including treated substrates prepared by the present method may be used in the preparation of carboxylic acids including, for example, the preparation of disodiumiminodiacetic acid (DSIDA) by dehydrogenation of diethanolamine (DEA). More particularly, catalysts including treated substrates of the present invention may address one or more issues that may be observed with conventional catalysts utilized in preparation of carboxylic acids such as DSIDA. For example, suitable catalysts often include copper deposited over the surface of a carbon support having a noble metal (e.g., platinum or palladium) at its surface. It is currently believed that at least a portion, and possibly a significant fraction of the noble metal may remain exposed after deposition of the copper. Excessive exposed noble metal is undesired since it is believed to promote formation of various undesired by-products (e.g., glycine and oxalate). A substantial portion, if not nearly all the exposed noble metal is believed to be at the surface of the support within relatively small pores that are inaccessible to copper during its deposition. Other catalysts suitable for preparation of carboxylic acids include copper deposited at the surface of metal-containing (e.g., nickel-containing) sponges. As with exposed noble metal at the surface of carbon-supported catalysts, metal support surface that is not coated by the copper within relatively small pores of the metal

sponge support are believed to contribute to formation of undesired by-products. It is currently believed that selective blocking of relatively small pores of substrates in accordance with the methods detailed herein may be used to prepare effective carbon- and metal-supported catalysts that may address one or more of the above-noted issues.

[00315] Preparation of DSIDA from DEA using a catalyst comprising a substrate treated as detailed herein generally proceeds in accordance with methods known in the art including, for example, U.S. Patent Nos. 5,627,125, U.S. Patent No. 5,916,840, U.S. Patent No. 6,376,708, and U.S. Patent No. 6,706,662, the entire contents of which are incorporated herein by reference for all relevant purposes.

[00316] The present invention is illustrated by the following examples which are merely for the purpose of illustration and not to be regarded as limiting the scope of the invention or the manner in which it may be practiced.

EXAMPLES

[00317] The following non-limiting examples are provided to further illustrate the present invention.

I. Pore Plugging

Example 1

[00318] Three carbon supports were treated to determine the effectiveness of candidate pore blocking compounds. Support A had a total Langmuir surface area of approximately 1500 m^2/g (including total micropore surface area of approximately 1279 m^2/g and total macropore surface area of approximately 231 m^2/g). Support B had a total Langmuir surface area of approximately 2700 m^2/g (including total micropore surface area of approximately 1987 m^2/g and total macropore surface area of approximately 723 m^2/g). Support C had a total Langmuir surface area of approximately 1100 m^2/g (including total micropore surface area of approximately 876 m^2/g and total macropore surface area of approximately 332 m^2/g).

[00319] The candidate pore blocking compounds were 1,4-cyclohexanedione, ethylene glycol, and the diketal product of a coupling reaction between 1,4-cyclohexanedione and ethylene glycol (i.e., 1,4-cyclohexanedione bis(ethylene ketal)).

[00320] Support samples (30 g) were contacted with a solution of 1,4-cyclohexanedione in ethylene glycol (6g/40g) at approximately 25°C for approximately 60 minutes. The pH of the slurry was adjusted to approximately 1 by addition of concentrated hydrochloric acid and agitated by stirring for approximately 60 minutes. The pH of the slurry was then adjusted to approximately 8.5 by addition of 50 wt.% sodium hydroxide solution. The slurry was then filtered to isolate the treated support, which was washed

using deionized water at a temperature of approximately 90°C. (mechanism one)

[00321] Support samples (2 g) were also contacted with a solution of 1,4-cyclohexanedione bis(ethylene ketal) in water (0.6g/40g) at approximately 25°C for approximately 60 minutes. (mechanism two)

[00322] As controls, samples of carbon A were also separately treated by contact with (1) ethylene glycol and (2) 1,4-cyclohexanedione.

[00323] The treated supports were analyzed by the well-known Langmuir method to determine their surface area (SA) profiles (e.g., total surface area, surface area attributed to micropores, and surface area attributed to macropores). The results are shown in Table 1.

Table 1

Support	Mechanism	% of original micropore SA	% of original macropore SA
Carbon A	One	24.2	74.9
Carbon A	Two	34.4	70.9
Carbon A	Control One	93.7	98.7
Carbon A	Control Two	68.9	94.4
Carbon B	One	55.6	78.7
Carbon B	Two	65.4	81.5
Carbon C	One	17.9	76.8
Carbon C	Two	22	72.3

[00324] As shown, both mechanism one and mechanism two provided a reduction in micropore and macropore surface areas for each of supports A-C, and more particularly a greater reduction in micropore surface area as compared to the reduction in macropore surface area (e.g., a three times greater reduction in micropore surface area). The percentage reduction in surface area for carbon B is believed to be lower than that observed for the other two carbons because of its higher surface area. However, it should be noted that the percentage of micropore surface area reduction for carbon B nonetheless corresponds to an absolute reduction of approximately 900 m^2/g.

[00325] The control testing of carbon A with ethylene glycol provided minimal reduction in micropore and macropore surface areas, while the control testing with 1,4-cyclohexanedione provided a greater reduction in micropore and macropore surface areas, but to a much lesser degree than associated with both

mechanism one and mechanism two. Thus, it is believed that the components combine to form the pore blocking compound that provides greater reduction in surface area than either component alone or the cumulative reduction provided by each.

Example 2

[00326] Carbons A, B, and C (30 g) described in Example 1 were each treated by contacting with solutions of 1,4-cyclohexanedione in ethylene glycol (6 g/40 g) at approximately 25°C for approximately 60 minutes. Each carbon was also treated by contacting with solutions of 1,3-cyclohexanedione in ethylene glycol (1 g/50 g) at approximately 25°C for approximately 120 minutes. Carbon C was also treated by contacting with a solution of 1,4-cyclohexanedione in 1,2-propanediol (1 g/50 g) at approximately 25°C for approximately 60 minutes. Surface area analysis results are shown in Table 2. As shown, each combination of dione and diol provided reduction of micropore and macropore surface areas, and more particularly preferential reduction in micropore surface area.

Table 2

Sample	Dione	Diol	% of original micropore SA	% of original macropore SA
Carbon A	1,4-disubstituted	Ethylene Glycol	22.6	75.8
Carbon A	1,3-disubstituted	Ethylene Glycol	58.4	84
Carbon B	1,4-disubstituted	Ethylene Glycol	55.6	78.7
Carbon B	1,3-disubstituted	Ethylene Glycol	32.2	39.8
Carbon C	1,4-disubstituted	Ethylene Glycol	17.9	76.8
Carbon C	1,3-disubstituted	Ethylene Glycol	45	75.6
Carbon C	1,4-disubstituted	1,2-Propanediol	14.4	67.5
Carbon C	1,3-disubstituted	1,2-Propanediol	56.1	80.7

Example 3

[00327] This example provides transmission electron microscopy results (TEM) for a platinum on carbon catalyst prepared using Carbon B treated as described in Example 1 (mechanism one). The catalyst contained approximately 5 wt.% platinum and was prepared generally as detailed herein (e.g., by liquid phase deposition of

platinum onto the treated carbon support), followed by treatment at elevated temperatures in a non-oxidizing environment. For comparison purposes, a catalyst including 5 wt.% platinum on Carbon B that was not treated was also analyzed. The TEM analysis was conducted generally as described by Wan et al. in International Publication No. WO 2006/031198.

[00328] The results for the catalyst including the untreated and treated carbons are shown in Figs. 3A/5A and 3B/5B, respectively. These results suggest a reduction in relatively small platinum-containing particles (e.g., having a particle size less than 4 nm) for the catalyst prepared using the treated support.

[00329] The TEM results generally correspond to high density regions of the substrates including primarily micropores and these results indicate higher platinum density among these regions for the catalyst including the untreated support.

Example 4

[00330] This example provides surface area analysis results for a carbon support of the type described in U.S. Patent Nos. 4,624,937 and 4,696,771 to Chou et al. (designated MC-10) treated in accordance with the present invention. Support samples were treated in accordance with both mechanism one and mechanism two described above in Example 1. The support had an initial micropore Langmuir surface area of approximately 1987 m^2/g and an initial macropore Langmuir surface area of approximately 723 m^2/g. Micropore and macropore surface area retention results for the treated supports are shown in Table 3.

Table 3

Support	Plugging Mechanism	% of original micropore SA	% of original macropore SA
MC-10	One	55.6	78.7
MC-10	Two	65.4	81.5

[00331] Figs. 4A and 4B provide pore volume data for untreated and treated MC-10 supports.

Example 5

[00332] This example provides results of carbon monoxide (CO) chemisorption analysis for the platinum-containing catalysts of Example 4. CO chemisorption is an analysis method suitable for estimating the proportion of exposed metal, and the analysis was conducted generally in accordance with "Protocol A" described in Example 67 herein and Example 23 of WO 2006/031938, incorporated herein by reference.

[00333] The results are shown in Table 4. The lower CO chemisorption for the catalyst including a treated carbon support (38.6 and 43.3 μmol CO/gram versus 54.7 μmol CO/gram catalyst) indicate a reduced proportion of exposed noble metal for the platinum-containing catalyst prepared using the treated carbon support.

Table 4

Catalyst	Cycle 2 CO μmol/ g catalyst
Pt on regular MC-10	54.7
Pt on modified MC-10	38.6/43.3

Example 6

[00334] Catalysts containing approximately 5 wt.% Pt and approximately 0.5 wt.% Fe were prepared generally as detailed herein using untreated MC-10 carbon supports, and MC-10 carbon supports treated in accordance with both mechanism one and mechanism two described in Example 1. These catalysts were tested in PMIDA oxidation generally under the conditions set forth in Example 7; the results are shown in Table 5. The Catalyst (1) included an untreated support. Catalysts (2) and (3) each included supports treated in accordance with mechanism two detailed above in Example 1. Catalyst (2) was prepared by a method that included filtration of the copper-impregnated support prior to platinum deposition. Catalyst (3) was prepared by a method that did not include filtration of the copper-impregnated support prior to platinum deposition (i.e., a one-pot method as described in Example 16).

Table 5

Catalyst (1)						
Run Number	1	2	3	4	5	6
Run Time, min	43.0	46.2	47.8	50.6	50.8	52.0
GLY wt.%	5.413	5.600	5.620	5.678	5.556	5.748
PMIDA wt.%	0.034	0.034	0.094	0.134	0.075	0.149
CH_2O wt.%	0.150	0.182	0.199	0.211	0.190	0.209
FORMIC wt.%	0.384	0.455	0.521	0.516	0.505	0.512
IDA wt.%	0.074	0.046	0.031	0.030	0.030	0.027
Pt in soln. (ppm)	0.03	0.07	0.07	0.09	0.08	0.12
Fe in soln.(ppm)	5.4	1.9	2.3	2.3	2.0	1.6
Catalyst (2)						
Run Number	1	2	3	4	5	6
Run Time, min	43.0	45.1	48.8	47.2	47.6	48.3
GLY wt.%	5.363	5.543	5.541	5.592	5.557	5.604
PMIDA wt.%	0.036	0.097	0.022	0.129	0.154	0.177
CH_2O wt.%	0.125	0.143	0.105	0.139	0.144	0.169
FORMIC wt.%	0.389	0.456	0.435	0.479	0.484	0.508
IDA wt.%	0.086	0.052	0.041	0.033	0.031	0.028
Pt in soln.(ppm)	0.05	0.14				
Fe in	6.3	1.9				

soln.(ppm)						
Catalyst (3)						
Run Number	1	2	3	4	5	6
Run Time, min	43.0	46.3	46.7	48.5	48.5	49.8
GLY wt.%	5.475	5.596	5.543	5.649	5.790	5.980
PMIDA wt.%	0.058	0.141	0.167	0.136		
CH_2O wt.%	0.175	0.171	0.192	0.191	0.208	0.222
FORMIC wt.%	0.466	0.505	0.547	0.565		
IDA wt.%	0.073	0.044	0.030	0.026	0.025	0.022
Pt in soln.(ppm)						
Fe in soln.(ppm)						

GLY = Glyphosate IDA = Iminodiacetic Acid

FORMIC = Formic Acid ppm = Parts Per Million

II. Catalyst Precursors; First and Second Metal-Containing Catalysts; Catalyst Precursor Structures

[00335] The following Examples describe preparation of catalysts as detailed herein, their testing by various characterization methods, and their testing in PMIDA oxidation. The following Examples also provide comparisons of catalysts prepared as detailed herein, and various other metal-containing carbon-supported catalysts. For example, the following Examples provide comparisons to carbon-supported catalysts including 5 wt.% Pt, 0.1 wt.% Fe, and 0.4 wt.% Co, and carbon-supported catalysts including 5 wt.% Pt and 0.5 wt.% Fe. These catalysts were

prepared generally as described by Wan et al. in International Publication No. WO 2006/031938.

Example 7

[00336] Catalysts prepared as described herein and comparison samples were tested in PMIDA oxidation conditions also generally described by Wan et al. in International Publication No. WO 2006/031938. For example, PMIDA oxidation cycles were conducted in a glass reactor (200 ml commercially available from Ace Glass Inc.) containing a reaction mass (approx. 140 g) which included water (approx. 128 g), approximately 8.2 wt.% PMIDA (approx. 11.48 g), and a catalyst loading of approximately 0.18 wt.% (0.25 g). The oxidations were generally conducted at a temperature of approximately 100°C, under a pressure of approximately 60 psig, and an oxygen flow rate of approximately 100 cc/min. Unless noted otherwise, reaction cycles were conducted to an endpoint determined by generation of approximately 1600 cm^3 of carbon dioxide.

[00337] As described in the following Examples and accompanying figures, various data were collected, including cycle time, metal leaching, residual formaldehyde (HCHO) content, residual formic acid (HCOOH) content, iminodiacetic acid (IDA) formation, N-methyl-N-(phosphonomethyl)glycine (NMG) formation, total carbon dioxide (CO_2) generation, etc.

Example 8

[00338] This example details preparation of a catalyst containing a nominal Pt content of approximately 2.5 wt.% and a nominal Cu content of approximately 5 wt.% Cu on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g.

[00339] Activated carbon (approx. 10g), $CuSO_4 \cdot 5H_2O$ solution (approx. 2.07 g), sucrose (approx. 5.67 g), degassed deionized water (approx. 30g), and degassed 1M NaOH (70 g) were mixed in a baffled beaker. The mixture was agitated at ambient conditions (approx. 25°C) for approx. 20 minutes. Formaldehyde (approx. 2.25 g of 37 wt.% solution) was added to the mixture and the resulting slurry was heated to approx. 30°C and agitated for approx. 60 minutes.

[00340] The resulting slurry was filtered, washed with degassed deionized water, re-slurried in deionized water, and 1M HCl was added to provide a pH of approx. 1.5.

[00341] A solution of K_2PtCl_4 (approx. 0.557 g) in degassed water (15 g) was added to the slurry, followed by continued stirring for 60 minutes at ambient conditions. The slurry was filtered, and the recovered metal-impregnated support was washed with water, and dried under vacuum at approx. 110°C. A total of 12.12 g of dried metal-impregnated support was recovered. Elemental analysis indicated a composition of approx. 2.04wt.%. Pt and approx. 1.93 wt.% Cu on carbon.

[00342] The catalyst precursor was then heated at elevated temperatures up to approximately 815°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 60 minutes. Elemental analysis indicated final metal contents of approx. 2.34% wt. Pt and approx. 2.22 wt.% Cu.

[00343] As detailed below, catalysts prepared by heating the metal-impregnated support at varying temperatures were also tested. In addition, various metal-impregnated supports were also tested for their catalytic activity.

Example 9 (copper plating at ambient temperature)

[00344] Preparation of nominal 2%Pt3.45%Cu on activated carbon catalyst: The following were added to a baffled beaker including approx. 10g of activated carbon: $CuSO_4 \bullet 5H_2O$ solution (1.410 g), 3.866 g of sucrose, 90 g of degassed deionized water, and 5.974 g of 50 wt.% NaOH. The mixture was stirred at approx. 22°C for approx. 10 minutes using a mechanical agitator. Following stirring, approx. 1.468g of 37 wt.% formaldehyde solution was added and the resulting slurry was stirred at approx. 22°C for 60 minutes. The slurry was then filtered and washed twice in the filter, and then re-slurried in water to pH of approx. 2.0 by addition of 1.5M degassed HCl. To this slurry was added a solution of K_2PtCl_4 (0.444 g) in 15 g of degassed water, followed by stirring for approximately 60 minutes under ambient conditions. The slurry was then heated to approx. 65°C, followed by stirring for an additional 30 minutes. The resulting slurry was then filtered and washed with water and dried under vacuum at approx. 110°C. A total of 11.389g of dried material was recovered.

Example 10

[00345] Preparation of nominal 2.5%Pt5%Cu on activated carbon: The following was added to approx. 10g of activated carbon in a baffled beaker: 2.072g of a $CuSO_4 \bullet 5H_2O$ solution, 5.694 g of sucrose, 30g of degassed deionized water, and 70g of degassed 1M NaOH was added. The mixture was heated to approx. 35°C using a mechanical agitator. To this mixture was added 2.249g of 37 wt.% formaldehyde solution and the resulting slurry was heated to approx. 33-35°C, followed by continued stirring for 60 minutes. The slurry was filtered and washed with degassed deionized water in the filter, and then re-slurried in water at pH of approx. 1.5

by adding 0.5M HCl. A solution of 0.557g of K_2PtCl_4 in 15g of degassed water was then added to the slurry, followed by continued stirring for 60 minutes under ambient conditions. Then the slurry was heated to approx. 60°C and stirred for an additional 30 minutes. The resulting slurry was filtered and washed with water, and dried under vacuum at approx. 110°C. A total of 11.701g of dried material was recovered. Upon heat treatment to a maximum temperature of approx. 950°C in the presence of an argon/hydrogen atmosphere (2%/98%) (v/v) for 120 minutes, a final catalyst composition indicating a weight loss of approximately 12.1 wt.% during heating was recovered.

Example 11 (no washing after copper deposition)

[00346] Preparation of nominal 2%Pt4%Cu on activated carbon: The following was added to a baffled beaker including approx. 10g of activated carbon: 1.643g of $CuSO_4 \bullet 5H_2O$ solution, 4.509 g of sucrose, 90g of degassed deionized water, and 4.625g of 50wt.% NaOH. The mixture was heated to approx. 30°C for approx. 10 minutes with a mechanical agitator. To this slurry was added 1.706g of 37 wt.% formaldehyde solution and the resulting slurry was heated to approx. 30-35°C, followed by continued stirring for approx. 90 minutes. Then the slurry was filtered, and then without washing re-slurried in water to pH 2.02 by adding 1M degassed HCl. A solution of 0.454g of K_2PtCl_4 in 10g of degassed water was then added to the slurry, followed by continued stirring for 60 minutes at ambient conditions. The resulting slurry was then heated to approx. 60°C and stirred for an additional 30 minutes. This slurry was then filtered and washed with water, and dried under vacuum at approx. 110°C. A total of 11.720 g of dried material was recovered. During heat treatment to a maximum temperature of

approximately 950°C in the presence of an argon/hydrogen atmosphere (2%/98%) (v/v) for approximately 120 minutes, the sample lost approximately 13.5% weight.

Example 12

[00347] Preparation of nominal 2%Pt3.75%Cu on activated carbon: The following was added to a baffled beaker including approx. 10 g of activated carbon 1.533g of $CuSO_4 \bullet 5H_2O$ solution, 4.210 g of sucrose, 90g of degassed deionized water, and 4.300g of 50 wt.% NaOH was added. This mixture was heated to approx. 30°C and stirred for approx. 10 minutes using a mechanical agitator. To this mixture was added 1.507g of 37 wt.% formaldehyde and the slurry was heated to approx. 30-35°C, followed by continued stirring for 60 minutes. The slurry was filtered and the recovered solids washed once in the filter, and then re-slurried in water to a pH of 1.97 by adding 1M degassed HCl. A solution of 0.452g of K_2PtCl_4 in 10g of degassed water was then added to the slurry, followed by continued stirring for 60 minutes under ambient conditions. Then the slurry was heated to approx. 60°C and stirred for 30 more minutes. The slurry was filtered and washed with water, dried under vacuum at approx. 110°C. A total of 11.413g of dried material was recovered. Upon heat treatment to a maximum temperature of approximately 950°C in the presence of a 2%/98% (v/v) H_2/Ar atmosphere for 120 minutes, the sample lost approximately 12.5% weight.

Example 13 (platinum deposition at higher temperature)

[00348] Preparation of nominal 2%Pt4%Cu on activated carbon: The following were added to a baffled beaker including 10g of

activated carbon: 1.645g of $CuSO_4 \bullet 5H_2O$ solution, 4.502 g of sucrose, 90g of degassed deionized water, and 4.636g of 50wt.% NaOH. The mixture was stirred under ambient conditions for approx. 20 minutes with a mechanical agitator. Then 1.721g of 37% formaldehyde was added and the slurry was heated to approx. 30-35°C, followed by continued stirring for 70 minutes. Then the slurry was filtered and washed once in the filter, and then re-slurried in water to pH 2.95 by adding 1M degassed HCl. A solution of 0.455g of K_2PtCl_4 in 10g of degassed water was then added to the slurry, followed by continued stirring for 45 minutes at 40-45°C. Then the slurry was heated to 60°C and stirred for 30 more minutes. The slurry was filtered and the recovered solids washed with water, and dried under vacuum at approx. 110°C. A total of 12.008g of dried material was recovered. Upon heat treatment at a maximum temperature of approx. 950°C in the presence of a (2%/98%)(v/v) H_2/Ar atmosphere for approx. 120 minutes, the sample lost approximately 12.6% weight.

Example 14

[00349] Preparation of nominal 3%Pt6%Cu on activated carbon: The following were added to a baffled beaker including 10g of activated carbon: 2.507g of $CuSO_4 \bullet 5H_2O$ solution, 6.878 g of sucrose, 90g of degassed deionized water, and 6.974g of 50wt.% NaOH. The mixture was heated to 30°C and stirred for approx. 10 minutes with a mechanical agitator. Then 2.444g of 37% formaldehyde was added and the slurry was heated to approx. 35-37°C, followed by continued stirring for 45 minutes. Then the slurry was filtered and washed twice in the filter, and then re-slurried in water to pH 1.97 by adding 1M degassed HCl. A solution of 0.700g of K_2PtCl_4 in 20g of degassed water was then added to the

slurry, followed by continued stirring for 60 minutes under ambient conditions. Then the slurry was heated to 60°C and stirred for an additional 30 minutes. The slurry was then filtered and washed with water, and dried under vacuum at approx. 110°C. A total of 11.868g of dried material was recovered. Upon heat treatment at a maximum temperature of approx. 950°C in the presence of (2%/98%) (v/v) H_2/Ar atmosphere for 120 minutes, the sample lost approximately 12.5% weight.

Example 15 (higher platinum content and platinum deposition temperature)

[00350] Preparation of nominal 4%Pt8%Cu on activated carbon: The following were added to a baffled beaker including approx. 10g of activated carbon: 3.420g of $CuSO_4 \bullet 5H_2O$ solution, 9.375 g of sucrose, 100g of degassed deionized water, and 9.675g of 50wt.% NaOH. The mixture was heated to 30°C and stirred for 10 minutes with a mechanical agitator. Then 3.331g of 37% formaldehyde was added and the resulting slurry was heated to approx. 30-35°C, followed by continued stirring for 90 minutes. Then the slurry was filtered and washed once in the filter, and then re-slurried in water to pH 1.97 by adding 1M degassed HCl. A solution of 0.964g of K_2PtCl_4 in 20g of degassed water was then added to the slurry, followed by continued stirring for 45 minutes at 45°C. Then the slurry was heated to 60°C and stirred for an additional 45 minutes. The slurry was then filtered and washed with water, and dried under a vacuum at approx. 110°C. A total of 12.283g of dried material was recovered. Upon heat treatment to a maximum temperature of approx. 950°C in the presence of a 2%/98% (v/v) H_2/Ar atmosphere for 120 minutes, the sample lost approximately 12.6% weight.

Example 16 (one-pot recipe)

[00351] Preparation of nominal 2%Pt4%Cu on activated carbon: The following were added to baffled beaker including 10g of activated carbon: 1.644g of $CuSO_4 \bullet 5H_2O$ solution, 4.509 g of sucrose, 90g of degassed deionized water, and 4.715g of 50 wt.% NaOH. The mixture was heated to 30°C and stirred for 10 minutes with a mechanical agitator. Then 1.736g of 37% formaldehyde was added and the slurry was heated to approx. 30-35°C, followed by continued stirring for 90 minutes. Then the slurry was acidified to pH 2.98 by adding 1M degassed HCl. A solution of 0.454g of K_2PtCl_4 in 10g of degassed water was then added to the slurry, followed by continued stirring for 60 minutes at ambient conditions. Then the slurry was heated to 60°C and stirred for 30 more minutes. The slurry was then filtered and washed with water, and dried under vacuum at approx. 110°C. A total of 11.864g of dried material was recovered. Upon heat treatment at approx. 950°C in the presence of a (2%/98%) (v/v) H_2/Ar for 120 minutes, the sample lost approximately 12.2% weight.

Example 17

[00352] Preparation of nominal 2%Pt4%Cu on activated carbon: The following were added to a baffled beaker including 10g of activated carbon: 1.645g of $CuSO_4 \bullet 5H_2O$ solution, 4.509 g of sucrose, 90g of degassed deionized water, and 4.630g of 50wt.% NaOH. The mixture was heated to 30°C and stirred for 10 minutes with a mechanical agitator. Then 1.710g of 37% formaldehyde was added and the slurry was heated to approx. 30-35°C, followed by continued stirring for 90 minutes. Then the slurry was filtered and washed once in the filter, and then re-slurried in water to pH 2.01 by adding 1M degassed HCl. A solution of 0.570g of H_2PtCl_6 in

15g of degassed water was then added to the slurry, followed by continued stirring for 60 minutes at ambient conditions. Then the slurry was heated to 60°C and stirred for an additional 30 minutes. The slurry was then filtered and washed with water, and dried under vacuum at approx. 110°C.

Example 18

[00353] Preparation of nominal 2%Pt/4%Cu on activated carbon: The following were added to a baffled beaker including approx. 10g of activated carbon: 1.644g of $CuSO_4 \bullet 5H_2O$ solution, 4.517 g of sucrose, 70g of degassed deionized water, and 4.701g of 50wt.% NaOH. The mixture was heated to 30°C and stirred for approx. 10 minutes with a mechanical agitator. Then 1.705g of 37% formaldehyde diluted to 17.10g with degassed water was added, and the slurry was heated at approx. 30-35°C, followed by continued stirring for 60 minutes. Then the slurry was filtered and washed once in the filter, and then re-slurried in water to pH 1.99 by adding 1M degassed HCl. A solution of 0.460g of K_2PtCl_4 in 10g of degassed water was then added to the slurry, followed by continued stirring for 60 minutes at ambient conditions. Then the slurry was heated to 60°C and stirred for 30 more minutes. It was then filtered and washed with water, and dried under vacuum at approx. 110°C. A total of 11.203g of dried material was recovered.

Example 19

[00354] This Example details surface area (SA) and CO chemisorption analysis for catalysts of varying platinum and copper contents prepared generally in accordance with the conditions detailed herein in Example 7, and tested in PMIDA

oxidation for 10 cycles generally under the conditions set forth in Example 7.

Table 6

Description	Average C	10 cycle 955°C-120 (temp/time) 2%Pt/ 3.45% Cu/C	10 cycle 955°C-120 3%Pt/ 6% Cu/C	10 cycle 955°C-120 2%Pt/ 3.45% Cu/C	10 cycle 815°C-60 2.5%Pt/ 7.5% Cu/C	10 cycle 955°C-120 2%Pt/ 4% Cu/C	10 cycle spent 955°C-120 treated 2%Pt/ 4% Cu/C	10 cycle spent 955°C-120 treated 2%Pt/ 3.75% Cu/C
Langmuir SA (m^2/g)	1499	1307	1208	1230	970	1236	1240	1254
t-plot micro SA (m^2/g)	1193	1065	984	1002	776	1019	1017	1034
Pore diameter (Å)	15.6	19.9	20.0	19.9	20.1	19.7	19.8	19.7
Meso-macro pore SA (m^2/g)	293.184	235.358	220.629	223.477	189.809	214.329	219.437	216.215
20-40	175.666	147.013	137.710	139.592	119.950	133.968	136.617	134.627
40-80	77.937	60.166	56.648	57.408	48.620	54.628	56.582	55.397
80-150	25.781	18.164	16.873	16.961	13.806	16.522	16.811	16.678
150-400	11.205	7.963	7.469	7.518	5.954	7.177	7.463	7.468
400-1000	2.159	1.736	1.630	1.685	1.251	1.672	1.666	1.680
1000-2000	0.396	0.315	0.297	0.313	0.228	0.331	0.298	0.315
2000-3000	0.04	0.001	0.002	0.000	0.000	0.031	0.000	0.050
Total meso-macro pore SA (m^2/g)	293.184	235.358	220.629	223.477	189.809	214.329	219.437	216.215
Pt(0)[µmol CO/g]	NA	17.2	27.5	14.6	19.3	13.9	14.2	17.8
Total Pt [µmol CO/g]	NA	21.9	34.9	20	30.1	19.5	19.2	20.6

Table 7

Pore diameter (Å)	Average C (3lots)	10 cycle 955°C-120 (temp/time) 2%Pt/ 3.45% Cu/C	10 cycle 955°C-120 3%Pt/ 6% Cu/C	10 cycle 955°C-120 2%Pt/ 3.45% Cu/C	10 cycle 815°C-60 2.5%Pt/ 7.5% Cu/C	10 cycle 955°C-120 2%Pt/ 4% Cu/C	10 cycle spent 955°C-120 treated 2%Pt/ 4% Cu/C	10 cycle spent 955°C-120 treated 2%Pt/ 3.75% Cu/C
<4.0	0.0541	0.0475	0.0475	0.0474	0	0.0478	0.0379	0.0476
4.0-4.6	0.1072	0.0853	0.0758	0.0759	0.0952	0.0765	0.0851	0.0856
4.7-5.2	0.063	0.0568	0.0473	0.0567	0.0471	0.0572	0.0565	0.0569
5.3-6.0	0.063	0.0568	0.0566	0.0473	0.0356	0.0476	0.0472	0.0474
6.1-7.1	0.0465	0.0369	0.0454	0.0459	0.0329	0.0462	0.0459	0.0458
7.2-8.0	0.0346	0.0254	0.0241	0.0254	0.0239	0.0254	0.0331	0.025
8.1-9.0	0.0235	0.0224	0.0142	0.0221	0.0133	0.0226	0.0207	0.022
9.1-13.4	0.0589	0.0567	0.0538	0.0513	0.0424	0.0533	0.0498	0.0517
13.5-16.5	0.0216	0.017	0.016	0.0164	0.0129	0.0159	0.0196	0.0191
16.6-21.4	0.0274	0.0241	0.0248	0.023	0.0211	0.024	0.0214	0.0212
21.5-27.0	0.0254	0.021	0.018	0.02	0.0156	0.0174	0.0179	0.0176
total micropore volume (cc/g)	0.5252	0.4499	0.4235	0.4314	0.34	0.4339	0.4351	0.4399

[00355] Fig. 5C provides porosity data for each of the catalysts tested.

Example 20

[00356] This example provides surface area (SA) and pore volume (PV) analysis data for a carbon support treated by contact with sucrose generally in accordance with the method described below. Also provided are results for a nominal 2%Pt/3.45%Cu/C catalyst prepared using a carbon support treated by contact with sucrose generally as described below, along with copper and platinum deposition generally as described in Example 12. The metal impregnated support was not subjected to elevated temperatures.

[00357] Carbon support (10 g) was added to a mixture including degassed H_2O (approx. 100 g), sucrose (approx. 3.8 g), 1M NaOH (approx. 6.15 g). To prepare the sucrose mixture, the sucrose was first added to the water followed by addition of NaOH, which was followed by addition of approx. 1.9 g of 37 wt.% formaldehyde solution. After approximately 60 minutes at approximately 25°C, the mixture was acidified to pH of approximately 4.8 by addition of 2M HCl. The mixture was then stirred for approximately 45 minutes at approximately 25°C, then filtered to isolate the support and the support was dried for approx. 10 hours in a vacuum oven at a temperature of approx. 110°C in the presence of nitrogen. Approx. 11.5 g of treated support was recovered.

[00358] Both the catalyst and treated support were analyzed by surface area and pore volume analyses generally as described by Wan et al. in International Publication No. WO 2006/031938. The surface area and pore volume analysis results are shown in

Tables 8 and 9, respectively. Fig. 5D also provides the pore volume results.

Table 8

Description	Average Carbon	Precursor, 2%Pt/3.45%Cu/C	Sucrose adsorbed onto Carbon
Langmuir SA (m^2/g)	1499	957	954
t-plot micro pore SA (m^2/g)	1193	727	726
meso-macro pore SA (m^2/g)	293.184	222.314	219.061
20-40	175.666	136.964	133.600
40-80	77.937	58.165	58.144
80-150	25.781	17.608	17.651
150-400	11.205	7.676	7.743
400-1000	2.159	1.625	1.672
1000-2000	0.396	0.276	0.251
2000-3000	0.04	0.000	0.000
total meso-macro pore SA (m^2/g)	293.184	222.314	219.061

Table 9

Pore diameter (Å)	Average carbon (3 lots)	Precursor, 2%Pt/3.45%Cu/C	Sucrose adsorbed onto carbon
<4.0	0.0541	0.0191	0.0193
4.0-4.6	0.1072	0.0478	0.0483
4.7-5.2	0.063	0.0381	0.0385
5.3-6.0	0.063	0.0475	0.0385
6.1-7.1	0.0465	0.0366	0.0464
7.2-8.0	0.0346	0.0243	0.0171
8.1-9.0	0.0235	0.0197	0.0222
9.1-13.4	0.0589	0.0443	0.0465
13.5-16.5	0.0216	0.0182	0.0149
16.6-21.4	0.0274	0.0207	0.0238
21.5-27.0	0.0254	0.018	0.0177
total micro PV (cc/g)	0.5252	0.3343	0.3332

[00359] As shown in these results, reductions in total surface area, micropore surface area, and meso-/macropopre surface were approx. equivalent for the catalyst in which sucrose was present in the copper deposition bath, and for the carbon support treated by contact with sucrose alone. Based on these results, it is believed that a significant portion, if not substantially all, of the surface area reduction for the finished catalyst as compared to the starting support is based on the presence of sucrose in the copper deposition bath.

Example 21

[00360] This example details microscopy results for the following samples:

(1) a carbon support having a total Langmuir surface of approx. 1500 m^2/g (including micropore surface area of approx. 1200 m^2/g and meso-/macropore surface area of approx. 300 m^2/g);

(2) the carbon support of (1) containing a nominal copper content of approx. 3.45 wt.% deposited generally in accordance with Example 12;

(3) a nominal 2%Pt/3.45%Cu/C catalyst including support (1) and prepared generally as described in Example 12, but prior to heating at elevated temperatures;

(4) the nominal 2%Pt/3.45%Cu/C catalyst of (3) after heating at temperatures of approximately 950°C.

[00361] Microscopy analysis was generally conducted as described in Example 46.

Carbon support

[00362] Fig. 6 is a STEM micrograph of the surface of the carbon support.

Cu-impregnated support

[00363] Figs. 7 and 8 are STEM micrographs of the surface of the Cu-impregnated support. These results indicate Cu regions of irregular morphology and size deposited at the surface of the carbon support.

Pt/Cu-impregnated support (prior to heat treatment)

[00364] Figs. 9-12 are micrographs of the surface of the Pt/Cu impregnated support prior to treatment at elevated temperatures. These results indicate regions of Cu deposited

at the surface of the carbon support having Pt deposited thereon that have generally retained the irregular morphology and size of the deposited Cu regions.

[00365] Fig. 13 provides a STEM micrograph for a portion of the impregnated support. The portion marked "Spectrum Image" was subjected to line scan analysis, the results of which are shown in Fig. 14. As shown, the line scan analysis indicates the presence of copper and platinum throughout the Spectrum Image portion.

Pt/Cu/C catalyst (after heating)

[00366] Fig. 15 is an STEM photomicrograph and Fig. 16 is a high resolution TEM (HRTEM) photomicrograph of a portion of the Pt/Cu/C catalyst after heating at elevated temperatures. These Figs. indicate a change in the morphology of the Pt/Cu regions. These results indicate formation of spherical particles of sizes ranging from approx. 1 nm to approx. 15nm.

[00367] Figs. 17 and 18 are EDS spectra for particles of varying sizes. As particle size increases, the atom ratio of copper to platinum increases, indicating relatively constant amount of platinum among of the particles. It is currently believed that thickness of the platinum layer is relatively constant over a range of particle size.

Pt/Cu/C catalyst used in 3 PMIDA reaction cycles

[00368] Figs. 19-21 are STEM photomicrographs for a portion of a catalyst used in 3 PMIDA reaction cycles under the above-noted conditions. These results indicate the presence of stable particles of varying sizes, including those in the range of from approx. 1-1.5 nm.

[00369] Fig. 22 provides line scan data for the portion of the catalyst surface marked "Spectrum Image" in Fig. 21. Based on detection of Cu over the entire Spectrum Image, with the highest copper content at the center of the particle while the platinum signal remained relatively flat, these results suggest the presence of a relatively thin outer platinum-containing shell (i.e., no more than 3 atoms thick). That is, since the line scan analysis utilized an X-ray beam of approx. 1 nm (10 Å) in size this suggests the presence of a platinum-containing shell having a thickness of no more than 3 platinum atoms (atomic size of platinum is 3Å).

Pt/Cu/C catalyst used in 30 PMIDA reaction cycles

[00370] These results are for catalysts tested for 30 reaction cycles. The STEM photomicrographs of Figs. 23 and 24 indicate the presence of stable particles of varying sizes, including approx. 1-1.5 nm. Fig. 25 provides line scan data for the portion marked "Spectrum Image" in Fig. 24. These results also indicate a relatively thin layer of platinum as both the platinum and copper signals began to be detected at the same point by the X-ray beam having a size of approx. 1 nm, again indicating the presence of a platinum-containing shell less than 1 nm (i.e., less than 3 platinum atoms) thick.

[00371] Figs. 26 and 27 provide EDS spectra for particles of approx. 2 nm and 9 nm in size. As shown, the atom percent of copper increased significantly with particle size, including the presence of a copper-rich core.

Example 22

[00372] This example details results of microscopy analysis conducted generally as described in Example 46 for: (1) a

nominal 2%Pt/3.45%Cu/C catalyst precursor prepared as described in Example 9, and (2) a nominal 2%Pt/3.45%Cu/C catalyst prepared from the precursor (1) (e.g., heating of the precursor to a maximum temperature of approximately 950°C).

[00373] Figs. 28 and 29 are TEM and STEM images for precursor (1). Figs. 30-37 provide TEM images and corresponding line scan data for portions of the precursor surface. As shown by the line scans, platinum and copper were detected throughout the particle.

[00374] Figs. 38 and 39 are TEM and STEM images for catalyst (2). Figs. 40 and 42 indicate the portion of the catalyst surface analyzed by line scans, the results of which are shown in Figs. 41 and 43, respectively. The line scan results indicate the presence of platinum throughout the particles.

Example 23

[00375] This example provides particle size distribution analysis for a nominal 2%Pt/3.45%Cu/C catalyst prepared as described in Example 9. Fifteen images of the type shown in Figs. 44 and 45 were used for determining the size of a total of 1177 particles. The size distribution of the measured particles is shown in Fig. 46. This example also provides particle size distribution analysis for the catalyst after use in PMIDA oxidation for 4 reaction cycles under the conditions described in Example 7. Fourteen images of the type shown in Figs. 47 and 48 were used to determine the size of 1319 particles. The size distribution of the measured particles is shown in Fig. 49.

Example 24

[00376] This example provides X-ray diffraction results for a nominal 2%Pt/3.45%Cu/C catalyst prepared as described in Example 12.

[00377] Figs. 50 and 51 provide diffraction results for an area of the catalyst surface having a diameter of approximately 1 μm, measured using selected area electron diffraction (SAED). Based on the generation of FCC (face centered cubic) indices (i.e., the results denoted 113, 022, 002, and 111) and primitive cubic indices (i.e., the results denoted 300, 221, 310, and 210), the SAED results indicate the presence of a CuPt alloy phase (likely a Cu_3Pt) alloy phase. The results may also indicate the presence of a metallic copper phase.

[00378] Figs. 52 and 53 provide nanodiffraction results from a single particle at the surface of the support. The nanodiffraction results are obtained by focusing an X-ray beam having a diameter of approximately 50 nm in diameter on a portion of the catalyst surface. Based on the generation of primitive cubic indices (i.e., 010, 100, and 01-1), these results also indicate the presence of a CuPt alloy phase (likely Cu_3Pt). The indices denoted 200 and 11-1 are believed to be evidence of the presence of a Cu phase, Pt phase, or further evidence of a CuPt alloy phase. Figs. 54 and 55 highlight nanodiffraction results (the circled portions) indicating the presence of a metallic copper phase.

[00379] The following Examples 25-42 provide reaction testing data for various catalysts prepared generally as described in Examples 8-18. Various parameters (e.g., metal loading, metal deposition temperature, and heat treatment temperature) were modified to determine the effect, if any, on catalyst performance. Unless specifically noted otherwise, the

metal-impregnated support was heated to a maximum temperature of approximately 955°C in the presence of a hydrogen (2%)/argon atmosphere. The catalysts were generally tested in PMIDA oxidation under the conditions set forth in Example 7.

Example 25

[00380] Catalysts: (1) 2.5%Pt/10%Cu; (2) 2.5%Pt/20%Cu; (3) 2.5%Pt/7.5%Cu; and (4) 5%Pt/0.1%Fe/0.4%Co. (nominal compositions)

[00381] Fig. 56 provides cycle time data for each of (1)-(4) for nine reaction cycles.

[00382] Fig. 57 provides platinum leaching data for (1) and (2) for each of nine reaction cycles.

Example 26

[00383] Catalysts: (1) 2.5%Pt/7.5%Cu; (2) 2.5%Pt/5%Cu; (3) 5%Pt/0.1%Fe/0.4%Co; and (4) 720°C/2.5%Pt/10%Cu. (nominal compositions)

[00384] Fig. 58 provides cycle time data for each of (1)-(4) for nine reaction cycles.

Example 27

[00385] Catalysts: (1) 2.5%Pt/10%Cu and (2) 720°C/2.5%Pt/10%Cu. (nominal compositions)

[00386] Each catalyst was tested for 10 reaction cycles.

[00387] Fig. 59 provides cycle time data.

[00388] Fig. 60 provides IDA generation data.

[00389] Figs. 61 and 62 provide residual formaldehyde and formic acid concentration, respectively.

[00390] Table 10 provides a comparison of platinum leaching for the two catalysts. As shown, less platinum was leached from the catalyst prepared including heat treatment at 720°C.

Table 10

Pt/Parts per Million (ppm)		
Cycle	2.5%Pt10%Cu	720°C-2.5%Pt10%Cu
1	0.103	<0.02
2		
3	0.0715	<0.02
4		
5	0.0539	<0.02
6		
7	0.0514	<0.02
8		
9	0.0507	0.0202
10		

Example 28

[00391] Catalysts: (1) 2.5%Pt/7.5%Cu; (2) 815°C/2.5%Pt/7.5%Cu; and (3) 5%Pt/0.1%Fe/0.4%Co. (nominal compositions) Each catalyst was tested for nine reaction cycles.

[00392] Fig. 63 provides cycle time data for each of (1)-(3).

[00393] Figs. 64 and 65 provide residual formaldehyde and formic acid concentration, respectively for each of (1)-(3).

Example 29

[00394] Catalysts: (1) 815°C/2.5%Pt/7.5%Cu; (2) 815°C/2.5%Pt/7.5%Cu; and (3) 5%Pt/0.1%Fe/0.4%Co. (nominal compositions) Each catalyst was tested for nine reaction cycles.

[00395] Fig. 66 provides cycle time data for each of (1)-(3).

[00396] Figs. 67 and 68 provide residual formaldehyde and formic acid concentration, respectively, for each of (1)-(3).

Example 30

[00397] Catalysts: (1) 815°C/2.5%Pt/7.5%Cu; (2) 815°C/2.5%Pt/5%Cu; (3) 5%Pt/0.1%Fe/0.4%Co; (4) 815°C/2.5%Pt/3%Cu. (nominal compositions) Each catalyst was tested for ten reaction cycles.

[00398] Fig. 69 provides IDA generation results for each of (1)-(4).

[00399] Figs. 70 and 71 provide residual formaldehyde and formic acid concentration, respectively, for each of (1)-(4).

Example 31

[00400] Catalysts: (1) 815°C/2.5%Pt/5%Cu; (2) 715°C/2.5%Pt/5%Cu; (3) 615°C/2.5%Pt/5%Cu; and (4) 5%Pt/0.1%Fe/0.4%Co. (nominal compositions) Each catalyst was tested for ten reaction cycles and various parameters were compiled for nine or each of the ten reaction cycles.

[00401] Fig. 72 provides cycle time results.

[00402] Figs. 73 and 74 provide residual formaldehyde and formic acid concentrations, respectively.

[00403] Fig. 75 provides platinum leaching results.

[00404] Fig. 76 provides IDA generation results.

[00405] Fig. 77 provides NMG generation results.

[00406] Fig. 78 provides total CO_2 generation results.

Example 32

[00407] Catalysts: (1) 915°C/2%Pt/4%Cu (heated in a hydrogen containing atmosphere, i.e., reduced); (2) 910°C/2%Pt/4%Cu (heated in an inert atmosphere, i.e., calcined); and (3) 5%Pt/0.1%Fe/0.4%Co. (nominal compositions) Each catalyst was tested for nine reaction cycles.

[00408] As shown in Fig. 79, cycle time was similar for each of (1)-(3), but cycle time for catalyst (3) was slightly higher for cycles 3 through 8.

[00409] Fig. 80 provides formaldehyde generation results.

[00410] Fig. 81 provides formic acid generation results.

[00411] As shown in Fig. 82, IDA generation was substantially equivalent for each catalyst during cycles 3 through 9.

[00412] The results shown in Fig. 83 indicate reduced NMG generation for each of the 2%Pt catalysts as compared to the 5%Pt catalyst.

[00413] Fig. 84 provides total CO_2 generation results.

Example 33

[00414] This example provides platinum leaching results for the following catalysts: (1) 815°C/2.5%Pt/5%Cu; (2) 815°C/2.5%Pt/3%Cu; (3) 910°C/2%Pt/4%Cu; (4) 908°C/2%Pt/3.6%Cu; and (5) 975°C/2%Pt/3.6%Cu. (nominal compositions) The results are shown in Fig. 85.

Example 34

[00415] This example provides testing results for catalysts in which the temperature of copper deposition varied by approx.

10°C (approx. 25°C and approx. 35°C) while the heat treatment temperature after platinum deposition was substantially similar.

[00416] Catalysts: (1) 970°C/2%Pt/3.45%Cu/35°C and (2) 965°C/2%Pt/3.45%Cu/25°C. (nominal compositions)

[00417] As shown in Figs. 86 and 87, formaldehyde and formic acid generation were slightly lower for the catalyst prepared at the higher copper plating temperature.

[00418] The results shown in Fig. 88 indicate higher initial IDA generation for the catalyst prepared at the higher copper plating temperature, but similar results for each catalyst beginning with the third cycle.

[00419] As shown in Fig. 89, platinum leaching was lower for the catalyst prepared at the lower copper plating temperature. And Fig. 90 indicates reduced initial copper leaching for the catalyst prepared at the lower copper plating temperature.

Example 35

[00420] This example provides results for extended PMIDA oxidation testing over 30 reaction cycles.

[00421] The catalysts tested included:

(1) nominal 2%Pt/3.45%Cu/C prepared as described in Example 12;

(2) 5%Pt/0.1%Fe/0.4%Co;

(3) nominal 2%Pt/3.45%Cu/C prepared as described in Example 16;

(4) 5%Pt/0.5%Fe catalyst.

[00422] As shown in Figs. 91-94, the cycle time, total CO_2 generation, formaldehyde generation, and formic acid generation were substantially similar for each of (1)-(4). The catalyst loading was constant for each catalyst; thus, catalysts (1) and (3) provided similar results at reduced platinum loadings as compared to catalysts (2) and (4).

[00423] Fig. 95 provides Cu and Fe leaching data for catalysts (1), (3), and (4).

Example 36

[00424] This example provides PMIDA oxidation testing results for catalysts prepared at varying calcining temperatures and having varying copper contents. Catalysts: (1) 908°C/2%Pt/3.6%Cu; (2) 975°C/2%Pt/3.6%Cu; (3) 910°C/2%Pt/4%Cu; and (4) 970°C/2%Pt/3.45%Cu. (nominal compositions)

[00425] Fig. 96 provides IDA generation results.

[00426] Figs. 97 and 98 indicate substantially similar results for formaldehyde and formic acid generation.

Example 37

[00427] This example provides reactor testing data for 2%Pt/4%Cu/C catalysts prepared generally as described in Example 11. Each catalyst was tested over 9 PMIDA reaction cycles.

[00428] One catalyst was prepared by heating the metal-impregnated support to a maximum temperature of approximately 950°C in the presence of an inert argon atmosphere. A second catalyst was prepared by contacting the metal-impregnated support to a maximum temperature of approximately 950°C in the presence of a hydrogen/argon (2%/98%) (v/v) atmosphere.

[00429] Cycle time and CO_2 generation data are provided for the two catalysts in Table 11. Fig. 99 shows cycle time for each catalyst.

Table 11

Cycle	Calcined	Calcined	H_2-Reduced	H_2-Reduced
1	2220	38.75	1867	50.92
2	2226	37.67	2077	42.33
3	2181	37.58	2109	39.42
4	2181	38	2155	37.08
5	2179	37.25	2095	40.42
6	2094	39.25	2136	37.42
7	2078	39.75	2089	39
8	2075	39	2067	38.5
9	2034	40.33	2060	37.42

Example 38

[00430] This example provides reactor testing data for a 2%Pt/4%Cu/C catalyst and a 2%Pt/4%Cu/C metal-impregnated support (precursor) prepared generally as described in Example 11. The catalyst and metal-impregnated support were tested over 4 PMIDA reaction cycles. The catalyst was prepared by contacting a metal-impregnated support to a maximum temperature of approximately 950°C in the presence of a hydrogen/argon (2%/98%) (v/v) atmosphere.

[00431] Cycle time and CO_2 generation data are provided for the catalyst and metal-impregnated support in Table 12. Fig. 100 shows cycle time for each catalyst.

Table 12

Cycle	Precursor	Precursor	Catalyst	Catalyst
1	2003.4	36.92	1866.6	50.92
2	1912.5	39.17	2076.8	42.33
3	1841	41.58	2109.2	39.42

Example 39

[00432] This example provides a comparison of 2%Pt/4%Cu/C catalysts prepared using different sources of platinum. Each

catalyst was prepared generally as described in Example 11, including heating of a metal-impregnated support to a maximum temperature of approximately 950°C. Platinum was deposited by displacement deposition onto copper-impregnated supports using platinum sources of: (1) K_2PtCl_4 (i.e., Pt^{+2} ions) and (2) $H_2PtCl_6 \bullet H_20$ (i.e., Pt^{+4} ions).

[00433] Table 13 provides cycle time, CO_2 generation data, and difference in activity (based on cycle time) for each catalyst over 9 reaction cycles. Figs. 101 and 102 provide cycle time and activity difference data.

Table 13

Cycle	K_2PtCl_4	K_2PtCl_4	H_2PtCl_6	H_2PtCl_6	delta t	% Activity
1	1866.6	50.92	1640.8	58.5	7.58	0.87
2	2076.8	42.33	1879.8	50.58	8.25	0.84
3	2109.2	39.42	1989.6	46.42	7	0.85
4	2155.1	37.08	1980.4	45.33	8.25	0.82
5	2095.1	40.42	1982	44.08	3.66	0.92
6	2135.9	37.42	1994.7	44.25	6.83	0.85
7	2089	39	1954.2	45.75	6.75	0.85
8	2066.8	38.5	1973.4	44.75	6.25	0.86
9	2059.6	37.42	1962.1	45.08	7.66	0.83
	Total CO_2	Cycle time	Total CO_2	Cycle time		avg. 0.846 excluding the 5th cycle

Example 40

[00434] This example provides CO chemisorption data (i.e., platinum site density) for catalysts of varying platinum content prepared generally as described in Examples 8, 11, 14, and 15. Table 14 provides the CO chemisorption (determined generally in accordance with the method described in Example 67) and Fig. 103 provides a plot of platinum loading versus platinum site density. The catalysts were tested in PMIDA oxidation for 10 reaction cycles prior to CO chemisorption analysis.

Table 14

Pt loading	Chemisorption Cycle 2 Pt site density (μmol CO/g catalyst)
2	20.24
2.5	30.1
3	34.9
4	58

[00435] These results show a linear relationship between platinum loading and site density. Based on these results, it is currently believed that a significant portion of the platinum incorporated in the catalyst is present in the form of a relatively thin shell. Conversely, a non-liner relationship between platinum loading and site density has been observed for conventional platinum-containing catalysts. This is currently believed to be due to the fact that a greater portion of the platinum is distributed throughout metal particles. Thus, beyond certain level of platinum, loading platinum site density does not increase since the portion of platinum distributed throughout the particles does not contribute to exposed platinum surface area.

Example 41

[00436] Catalysts containing nominal metal contents of approximately 2%Pt and 4%Cu were prepared generally as described in Examples 11 and 12. The metal deposition bath was maintained under a nitrogen atmosphere during copper deposition. Reaction testing results comparing the Pt/Cu catalysts to a 5%Pt/0.5% Fe

catalyst are shown in Fig. 104. As shown, all catalysts provided comparable activity.

Example 42

[00437] This example details reaction testing of nominal 3%Pt/6%Cu catalysts prepared as described in Example 14 at varying catalyst loadings. One catalyst was tested at a catalyst loading of approximately 0.25 g and another was tested at a loading of approximately 0.17 g. The performance of each catalyst was compared to a 5%Pt/0.5%Fe catalyst prepared generally as described in U.S. Patent No. 6,417,133 at a loading of 0.25 g. Total catalyst and platinum loadings are summarized in Table 15. Total CO_2 generation results and cycle time results are shown in Figs. 105 and 106, respectively. As compared to the 5%Pt/0.5%Fe catalyst, these results indicate improved activity for the 3%Pt catalyst at equivalent catalyst loading and at least comparable activity at reduced catalyst loading. Accordingly, 3%Pt catalysts of the present invention, or other similar catalysts, may be utilized to provide an improvement in catalyst activity, or a reduction in working metal capital.

Table 15

	Cat. Loading	Reduction	Pt loading	Reduction in Pt loading
Condition One	0.25 g	0%	0.0075 g	40%
Condition Two	0.167 g	33%	0.005 g	60%
Control	0.25 g	0%	0.0125 g	0%

III. Additional Embodiments

Disodiumiminodiacetic acid (DSIDA) Preparation

Example 43

[00438] This example details analysis and testing of: (1) a carbon-supported palladium and copper-containing catalyst (CuPdC) of the type described in U.S. Patent No. 5,916,840, 5,689,000, and/or 5,627,125; and (2) a CuPdC catalyst prepared as described in U.S. Patent No. 5,916,840, 5,689,000, and/or 5,627,125 that was treated by contact with a mixture containing 1,4-cyclohexane dione and ethylene glycol as described in Example 1 (mechanism 2).

[00439] The treated and un-treated catalysts were analyzed to determine their Langmuir surface areas and to provide comparisons of the micropore and macropore surface areas prior to and after treatment.

Table 16

Sample	Dione	Diol	% of original micropore SA	% of original macropore SA
Carbon A	1,4-disubstituted	Ethylene Glycol	22.6	75.8
Carbon A	1,3-disubstituted	Ethylene Glycol	58.4	84
Carbon B	1,4-disubstituted	Ethylene Glycol	55.6	78.7
Carbon B	1,3-disubstituted	Ethylene Glycol	32.2	39.8
Carbon C	1,4-disubstituted	Ethylene Glycol	17.9	76.8
Carbon C	1,3-disubstituted	Ethylene Glycol	45	75.6
Carbon C	1,4-disubstituted	1,2-Propanediol	14.4	67.5
Carbon C	1,3-disubstituted	1,2-Propanediol	56.1	80.7

[00440] As shown in Table 16, treatment of the catalyst provided a 75% reduction in micropore surface area of the catalyst, while providing a reduction in macropore surface area of less than 20% (i.e., a preferential reduction in micropore surface area approximately 4 times greater than the reduction in macropore surface area).

[00441] The treated and untreated catalysts were also tested for the conversion of diethanolamine to disodiumiminodiacetic acid. Mixtures including water, the (original or modified) catalyst (2 wt.%), diethanolamine (1.8 wt.%), sodium hydroxide (2.4 wt.%), and disodiumiminodiacetic acid (DSIDA) (12.5 wt.%) were heated to temperatures ranging from 150-160°C over the course of 5 hours and under a pressure of approximately 135 psig. These conditions were selected to determine the performance of the modified and unmodified catalysts with regard to oxalate and glycine formation. The results are shown in Fig. 107. The modified catalyst provided an approximately 8-10 fold reduction in oxalate formation and an approximately 4 fold reduction in glycine generation. These results suggest that the modified catalyst provided reduced exposed noble metal believed to contribute to glycine and oxalate formation.

Example 44

[00442] This example details testing of palladium and copper-containing carbon-supported (CuPdC) catalysts in preparation of DSIDA by dehydrogenation of DEA. The catalysts were prepared as described in U.S. Patent No. 5,916,840, 5,689,000, and/or 5,627,125 and tested generally under the conditions described therein. Two CuPdC catalysts were prepared generally in accordance with the method described in one or more of these patents. Each catalyst was prepared to include 24wt.% Cu. One catalyst was prepared using an untreated carbon support; this resulted in a catalyst including 3wt.%Pd (i.e., 24%Cu/3%Pd/C). The second catalyst was prepared using a carbon support treated by the present method as described in Example 1 by contact with 1,4-CHDM; this resulted in a catalyst including

approx. 2.4wt.% Pd (i.e., 24%Cu/2.4%Pd/C). Thus, it is believed that use of the modified support resulted in reduced palladium deposition.

[00443] Each catalyst was tested in conversion of DEA to DSIDA generally in accordance with the conditions set forth in U.S. Patent No. 5,916,840, 5,689,000, and/or 5,627,125. The results are shown in Fig. 108 and Table 17.

[00444] As shown in Fig. 108, beginning with the second cycle, cycle time was reduced for the catalyst including 2.4% Pd on the treated carbon support. That is, the catalyst prepared using the treated carbon support provided an increase in activity of approx. 15-20% at a lower noble metal content.

Table 17

Cycle	24%Cu on 2.4%Pd/ modified MC-10			24%Cu on 3%Pd/MC-10		
mol %	Glycine	Oxalic Acid	Hydroxyethyl Glycine	Glycine	Oxalic Acid	Hydroxyethyl Glycine
1	1.08	0.49	0.46	1.69	0.73	0.56
2	0.9	0.38	0.46	1.28	0.45	0.42
3	0.88	0.35	0.49	1.22	0.44	0.43
4	0.9	0.34	0.58	1.3	0.43	0.4
5	0.9	0.34	1.01	1.25	0.42	0.42
6	0.94	0.34	0.87	1.31	0.44	0.41
7	0.96	0.34	0.89	1.3	0.43	0.39
8	0.97	0.34	0.76	1.35	0.43	0.36
9	1.01	0.34	0.71	1.35	0.43	0.38
10	1.01	0.35	0.61	1.38	0.43	0.36

[00445] As shown in Table 17, use of the 2.4%Pd catalyst on the modified carbon support provided reduced oxalic acid generation and glycine generation as compared to the 3%Pd

catalyst on the unmodified carbon support (e.g., an improvement in oxalic acid and glycine selectivities of approx. 15% and 25%, respectively).

IV. Platinum-Iron

Example 45

[00446] This example details preparation of a catalyst having a nominal platinum content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00447] Activated carbon (approximately 10.458 g) and degassed water (approximately 90 g) were mixed in a baffled beaker under a nitrogen atmosphere. $FeCl_3 \bullet xH_2O$ (2.007 g) was dissolved in degassed water (40 g) and this solution was pumped into the baffled beaker over a period of one hour. The pH of the slurry within the baffled beaker was maintained at 4 by introduction of 2.5N degassed NaOH, as necessary. After addition of the $FeCl_3$ solution was completed, the pH of the slurry was raised to approximately 4.5 and the slurry was allowed to mix at room temperature for approximately 15 minutes. The slurry was then heated to a temperature of approximately 60°C over a period of approximately 48 minutes, during which time the pH of the slurry was maintained at approximately 4.5 by addition of 2.5N NaOH.

[00448] The pH of the slurry was then raised to approximately 10.5 over a period of approximately 30 minutes at a temperature of approximately 60°C, and at a rate of 0.5 pH units per 5 minutes. After pH adjustment, the slurry was allowed to mix for approximately 10 minutes.

[00449] Sodium borohydride ($NaBH_4$) (approximately 0.686 g) was dissolved in degassed water (approximately 20 g); seven drops of 2.5N degassed NaOH were added to stabilize the $NaBH_4$ solution, and the resulting $NaBH_4$ solution was introduced to the baffled beaker at approximately 60°C over a period of 20 minutes. The slurry was then allowed to mix for ten additional minutes at approximately 60°C. The slurry was then filtered and the wet cake was then re-slurried in the baffled beaker in degassed deionized water (approx. 90 g). The pH of the resulting slurry was then lowered to approximately 5 by introduction of degassed 2M HCl.

[00450] K_2PtCl_4 (approximately 0.456 g) was dissolved in degassed water (approximately 20 g) and the resulting Pt solution was then added to the baffled beaker over a period of three minutes. The resulting slurry was then allowed to mix at ambient conditions (approximately 22°C) for approximately 60 minutes, and then heated to a final temperature of 65°C over a period of 30 minutes, and then allowed to mix at 60°C. The resulting slurry was then filtered and washed twice by contact with degassed water (approximately 100 g) at a temperature of approximately 65°C. The washed sample was then dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

[00451] The catalyst precursor was then heated at elevated temperatures up to approximately 900°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 120 minutes.

[00452] The 2%Pt/4%Fe finished catalyst was tested in PMIDA oxidation under the conditions set forth in Example 7. Inductively Coupled Plasma (ICP) analysis was used to determine platinum and iron leached from the catalyst and present in the

reaction mixture. ICP was conducted using a VG PQ ExCell Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)(commercially available from Thermo Jarrell Ash Corp., Thermo Elemental, Franklin, MA). The results are set forth in Table 18.

[00453] Fig. 109 provides results of XRD analysis (conducted as set forth in Example 69) for the finished catalyst (i.e., before reactor testing).

Table 18

Cycle	1	2	3	4	5	6	7	8	9	10
Total CO_2 (cc)	1766.6	1871.4	1966.5	1946.8	1935.5	1957.5	1940.7	1947.9	1932.0	1600.6
End point(min)	45.00	39.75	38.08	39.92	40.25	38.83	39.25	40.00	39.83	40.00
Maximum CO_2 Concentration (%)	35.7	37.9	38.8	36.9	36.7	37.4	37.0	36.7	36.5	36.5
PMIDA (wt.%)	0.008		0.010		0.010		0.010		0.010	0.034
Glyphosate(wt.%)	5.293		5.378		5.400		5.393		5.392	5.563
IDA(wt.%)	0.099		0.065		0.051		0.045		0.040	0.039
CH_2O(ppm)	2421		1990		1838		1660		1737	2309
HCOOH(ppm)	6696		6555		6143		6220		5716	6635
Pt(ppm)	<0.01		<0.01		<0.01		<0.01		<0.01	<0.01
Fe(ppm)	1.484		0.494		<0.1		<0.1		<0.1	<0.1

Example 46

[00454] This example details preparation of a catalyst having a nominal platinum content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00455] Activated carbon (approximately 10.455 g) and degassed water (approximately 90 g) were mixed in a baffled beaker under a nitrogen atmosphere. $Fe_2(SO_4)_3 \bullet xH_2O$ (2.990 g) was dissolved in degassed water (40 g) and this solution was pumped into the baffled beaker over a period of one hour. The pH of the slurry within the baffled beaker was maintained at 4 by introduction of 2.5N degassed NaOH, as necessary.

[00456] Mixing of the components of the slurry within the baffled beaker occurred for a total of approximately 20 minutes at a pH of approximately 4. The pH of the slurry was then raised to 4.5 by addition of NaOH. The slurry was then heated to a temperature of approximately 60°C over a period of 30 minutes. During the heating, the pH was maintained at 4.5 by introduction of 2.5N degassed NaOH (as necessary). At this elevated temperature, the pH of the slurry was raised to approximately 6.5 over a period of 20 minutes, via increases in pH at a rate of approximately 0.5 pH units per 5 minutes.

[00457] Sodium borohydride ($NaBH_4$) (approximately 0.681 g) was dissolved in degassed water (approximately 20 g) and then pumped into the baffled beaker at approximately 60°C over a period of 20 minutes. The slurry was then allowed to mix for ten additional minutes at 60°C. The slurry was then allowed to cool to 45°C, and then filtered. The wet cake was then re-slurried in the baffled beaker in degassed deionized water (90 g). The pH

of the resulting slurry was then lowered to approximately 5 by introduction of degassed 2M HCl.

[00458] K_2PtCl_4 (approximately 0.460g) was dissolved in degassed water (approximately 20g) and the resulting Pt solution was then added to the baffled beaker over a period of five minutes. The resulting slurry was then allowed to mix under ambient conditions (approximately 22°C) for approximately 60 minutes, and then heated to a final temperature of 65°C over a period of 30 minutes, and then allowed to mix at 65°C for an additional 10 minutes. The resulting slurry was then filtered and washed twice by contact with degassed water (approximately 100g) at a temperature of approximately 65°C. The washed sample was then dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

[00459] The catalyst precursor was then heated at elevated temperatures up to approximately 900°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 120 minutes.

[00460] Table 19 sets forth PMIDA reaction testing results, platinum leaching data, and iron leaching data for the 2%Pt/4%Fe finished catalyst.

Table 19

Cycle	1	2	3	4	5	6	7	8	9	10
Total CO_2 (cc)	1912.0	1933.8	1951.2	1978.7	1944.0	1943.9	1956.3	1891.4	1864.9	1602.2
End point(min)	38.17	37.33	36.75	35.67	37.75	37.50	37.67	39.50	40.83	40.17
Maximum CO_2 Concentration (%)	40.5	39.6	39.9	41.3	38.8	39.6	39.0	37.8	36.7	37.2
PMIDA (wt.%)	ND		0.006		0.006		0.007		0.007	0.009
Glyphosate(wt.%)	5.184		5.249		5.382		5.349		5.393	5.497
IDA(wt.%)	0.139		0.055		0.040		0.038		0.032	0.032
CH_2O(ppm)	2586		2212		2203		2149		2300	2983
HCOOH(ppm)	5387		5525		6021		5843		5623	5958
Pt(ppm)	0.019		0.024		0.027		0.025		0.027	0.032
Fe(ppm)	16.420		0.629		0.222		0.077		<0.05	<0.05

Example 47

[00461] This Example provides the results of X-Ray Diffraction (XRD) analysis for the catalyst prepared as described in Example 46. XRD analysis was conducted as set forth in Example 69.

[00462] The results are shown in Figs. 110 and 111. These results indicate the presence of Fe_3Pt bimetallic alloy.

Example 48

[00463] This example details preparation of a catalyst having a nominal Pt content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00464] Activated carbon (approximately 10.455 g) and degassed water (approximately 90 g) were mixed in a baffled beaker under a nitrogen atmosphere.

[00465] $FeCl_3 \cdot 6H_2O$ (approximately 2.009g) was dissolved in degassed water (40 g) and this solution was pumped into the baffled beaker over a period of one hour. The pH of the slurry within the baffled beaker was maintained at 4 by introduction of 2.5N degassed NaOH, as necessary. After addition of the $FeCl_3 \cdot 6H_2O$ solution to the beaker was completed, the pH of the slurry was raised to approximately 4.5 by addition of NaOH and the slurry was allowed to mix at ambient conditions (approximately 22°C) for approximately 20 minutes.

[00466] The slurry was then heated to a temperature of approximately 60°C over a period of approximately 50 minutes. During the heating, the pH was maintained at 4.5 with addition of 2.5N degassed NaOH. At this elevated temperature, the pH of the slurry was raised to approximately 10.5 over a period of 30

minutes, via increases in pH at a rate of approximately 0.5 pH units per 5 minutes.

[00467] Sodium borohydride ($NaBH_4$) (approximately 0.69 g) was dissolved in degassed water (approximately 20 g); 7 drops of 2.5N NaOH was added to stabilize the $NaBH_4$ solution. The sodium borohydride solution was then pumped into the baffled beaker at approximately 60°C over a period of 20 minutes. The slurry was then filtered and the wet cake was then re-slurried in the baffled beaker in degassed deionized water (90 g). The pH of the resulting slurry was then lowered to approximately 5 by introduction of degassed 2M HCl.

[00468] K_2PtCl_4 (approximately 0.460 g) was dissolved in degassed water (approximately 20 g) and the resulting Pt solution was then added to the baffled beaker over a period of three minutes. The resulting slurry was then allowed to mix at ambient conditions (approximately 22°C) for approximately 60 minutes, and then heated to a final temperature of approximately 65°C.

[00469] The resulting slurry was then filtered and washed twice by contact with degassed water (approximately 100 g) at a temperature of approximately 65°C. The washed sample was then dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

[00470] The catalyst precursor was then heated at elevated temperatures up to approximately 900°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 120 minutes.

[00471] Table 20 sets forth PMIDA reaction testing results, platinum leaching data, and iron leaching data for the 2%Pt/4%Fe finished catalyst.

Table 20

Cycle	1	2	3	4	5	6	7	8	9	
Total CO_2 (cc)	1738.2	1826.0	1846.2	1857.1	1866.1	1872.0	1878.0	1862.4	1875.6	1(
End point(min)	46.75	42.50	42.08	41.67	41.50	41.58	41.50	42.25	42.00	
Maximum CO_2 Concentration (%)	34.4	35.3	35.6	35.7	35.7	35.6	35.9	35.3	35.4	
PMIDA (wt.%)	0.007		0.010		0.009		0.009		0.009	0.060
Glyphosate(wt.%)	5.339		5.371		5.441		5.389		5.298	5.245
IDA(wt.%)	0.083		0.054		0.046		0.045		0.042	0.041
CH_2O(ppm)	2158		1857		1669		1706		1682	1831
HCOOH(ppm)	7454		7161		6919		6648		6487	6941
Pt(ppm)	0.011		0.013		0.015		0.015		0.015	0.019
Fe(ppm)	3.114		0.543		0.178		0.124		0.053	0.062

Cycle	11	12	13	14	15	16	17	18	19	20	21
Total CO_2 (cc)	1875.8	1868.2	1878.2	1868.5	1855.9	1890.5	1872.9	1837.5	1854.1	1845.7	1830.5
End point(min)	41.33	42.33	42.25	42.67	43.58	42.08	43.83	44.33	44.25	44.25	45.25
Maximum CO_2 Concentration (%)	35.7	35.9	35.5	35.0	34.6	35.5	34.4	34.1	34.1	34.4	33.9
PMIDA (wt.%)	0.009		0.010		0.009		0.010		0.010	0.010	0.010
Glyphosate(wt.%)	5.315		5.405		5.406		5.382		5.371	5.477	5.424
IDA(wt.%)	0.043		0.041		0.038		0.039		0.037	0.036	0.037
CH_2O(ppm)	1898		2086		2067		2111		2173	2107	1853

HCOOH(ppm)	6159		6287		6199		6302		5805	6582	
Pt(ppm)	0.023		0.024		0.024		0.023		0.024	0.024	
Fe(ppm)	<0.05		<0.05		0.054		<0.05		<0.05	<0.05	<0

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[00472] Fig. 111A includes platinum leaching data for the catalysts of Examples 46 and 48, as compared to a (Reference) 5%Pt/0.5%Fe catalyst prepared as described by Wan et al. in International Publication No. WO 2006/031938.

Example 49

[00473] The following preparation was conducted under nitrogen protection.

[00474] Activated carbon (approximately 10.456 g) and degassed water (approximately 90 g) were placed in a baffled beaker and allowed to mix for 20 minutes. $FeCl_3 \bullet 6H_2O$ (2.009 g) was dissolved in degassed water (approx. 40 g) and this solution was pumped into the baffled beaker over a period of 30 minutes while the pH of the slurry was maintained at 4 by addition of 2.5N NaOH. After addition of the $FeCl_3 \bullet 6H_2O$ solution, the pH was raised to 4.5 and allowed to mix for 10 minutes. The slurry was then heated to approximately 50°C over a period of 30 minutes, while the pH was maintained at pH 4.5. The pH of the slurry was then raised to 8 over a period of 15 minutes, and allowed to mix for approximately 10 minutes. Ethylene glycol (approx. 1.386 g) was then added to the slurry, and allowed to mix at approximately 60°C for approximately 20 minutes. After mixing was complete, the slurry was allowed to cool to 30°C.

[00475] The pH of the solution was then lowered to 5 by addition of 0.5M degassed HCl. K_2PtCl_4 (0.460 g) was dissolved in degassed water (20 g). The Pt solution was then added to the baffled beaker over a period of three minutes. The slurry was then allowed to mix at ambient conditions (approximately 22°C) room temperature for 30 minutes, and then heated to a temperature of 60°C over a period of 10 minutes.

[00476] The slurry was then filtered, and the wet cake was hot washed twice at 60°C with approximately 100 mL of degassed water. The resulting sample was then dried in a vacuum oven at 110°C for 12 hours with a small nitrogen stream.

Example 50

[00477] The following preparation was conducted under nitrogen protection.

[00478] Activated carbon (10.456 g) and degassed water (approximately 90 g) were placed in a baffled beaker and allowed to mix for 20 minutes. $FeCl_3 \bullet 6H_2O$ (2.011 g) was dissolved in degassed water (approximately 40 g) and this solution was pumped into the baffled beaker over a period of 34 minutes while the pH of the slurry was maintained at 4 by addition of 2.5N NaOH.

[00479] Upon the complete addition of the $FeCl_3 \bullet 6H_2O$ solution, the pH was raised to 4.5, and allowed to mix for 10 minutes. The slurry was then heated to approximately 60°C over a period of 34 minutes, while the pH was maintained at 4.5. The pH of the slurry was then raised to 11 over a period of 30 minutes, and then allowed to mix for 10 minutes. Ethylene glycol (1.385 g) was then added to the slurry, and allowed to mix at 60°C for approximately 10 minutes.

[00480] The pH of the solution was then lowered to 5 by addition of 1M degassed HCl. K_2PtCl_4 (0.459 g) was dissolved in degassed water (20 g). The Pt solution was then added to the baffled beaker over a period of three minutes. The slurry was then allowed to mix at ambient conditions (approximately 22°C) for 30 minutes, and then heated to a temperature of approximately 60°C over a period of 10 minutes.

[00481] The slurry was then filtered, and the wet cake was hot washed twice at 60°C with approximately 100 ml of degassed

water. The resulting sample was then dried in a vacuum oven at 110°C for 12 hours with a small nitrogen stream.

[00482] Four 2%Pt/4%Fe catalysts were prepared from a precursor prepared as described that was heated at elevated temperatures in the presence of a hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes. Maximum heating temperatures were:

(1) 900°C;

(2) 750°C;

(3) 650°C;

(4) 550°C.

[00483] Fig. 112 provides results of XRD analysis of catalyst (1); these results indicate the presence of a Fe_3Pt phase.

[00484] Fig. 113 provides results of XRD analysis of catalyst (2); these results indicate the presence of a Fe_3Pt phase.

[00485] Fig. 114 provides results of XRD analysis of catalyst (3); these results indicate the presence of a Fe_3Pt phase.

[00486] Fig. 115 provides results of XRD analysis of catalyst (4); these results indicate the presence of a FePt phase.

[00487] Reaction testing data, platinum leaching data, and iron leaching data for the 900°C/2%Pt/4%Fe catalyst are set forth in Table 21.

Table 21

Cycle	1	2	3	4	5	6	7	8
Total CO_2 (cc)	1751.9	1793.3	1863.9	1930.6	1931.1	1946.4	1926.7	1602.3
End point(min)	44.08	43.00	41.67	40.75	41.00	41.25	41.08	42.90
Maximum CO_2 Concentration (%)	36.2	35.2	35.3	35.5	35.7	35.2	36.1	34.4
PMIDA (wt.%)	0.003		0.006		0.006		0.006	0.104
Glyphosate(wt.%)	5.243		5.398		5.486		5.376	5.539
IDA(wt.%)	0.079		0.040		0.035		0.034	0.032
CH_2O(ppm)	3032		2513		2072		2156	2596
HCOOH(ppm)	6300		6615		6554		6358	6488
Pt(ppm)	0.011		0.014		0.014		0.013	0.017
Fe(ppm)	24.050		3.309		0.494		0.462	0.409

[00488] Reaction testing data, platinum leaching data, and iron leaching data for the 750°C/2%Pt/4%Fe catalyst are set forth in Table 22.

Table 22

Cycle	1	2	3	4	5	6	7	8	9
Total CO_2 (cc)	1812.9	1786.8	1854.8	1901.3	1864.6	1906.0	1921.1	1913.3	1601.9
End point(min)	39.92	42.58	41.42	40.25	42.58	41.83	41.50	42.00	42.55
Maximum CO_2 Concentration (%)	39.2	35.8	35.7	36.3	34.5	34.9	35.6	35.0	35.2
PMIDA (wt.%)	ND		0.009		0.006		0.010		0.064
Glyphosate(wt.%)	5.275		5.357		5.464		5.471		5.528
IDA(wt.%)	0.098		0.037		0.033		0.035		0.030
CH_2O(ppm)	2901		2398		2105		2010		2550
HCOOH(ppm)	6151		6628		6634		6640		6553
Pt(ppm)	0.013		0.015		0.016		0.016		0.019
Fe(ppm)	24.870		3.516		0.686		0.476		0.356

[00489] Reaction testing data, platinum leaching data, and iron leaching data for the 650°C/2%Pt/4%Fe catalyst are set forth in Table 23.

Table 23

Cycle	1	2	3	4	5	6	7	8	9	10
Total CO_2 (cc)	1782.0	1849.5	1908.8	1897.5	1957.4	1947.6	1878.0	1901.6	1913.4	1602.7
End point(min)	41.42	40.67	39.33	39.75	39.08	38.00	42.25	41.50	41.08	42.23
Maximum CO_2 Concentration (%)	38.7	36.7	37.2	36.8	37.7	39.7	34.9	35.5	36.1	35.3
PMIDA (wt.%)	ND		0.005		0.006		0.005		0.005	0.067
Glyphosate(wt.%)	5.229		5.373		5.394		5.413		5.394	5.490
IDA(wt.%)	0.099		0.045		0.040		0.037		0.036	0.036
CH_2O(ppm)	3042		2485		2357		2358		2395	2754
HCOOH(ppm)	6185		6634		6461		6521		6372	6512
Pt(ppm)	0.014		0.016		0.015		0.015		0.015	0.019
Fe(ppm)	25.230		2.754		0.493		0.395		0.422	0.332

[00490] Reaction testing data, platinum leaching data, and iron leaching data for the 550°C/2%Pt/4%Fe catalyst are set forth in Table 24.

Table 24

Cycle	1	2	3	4	5	6	7	8	9
Total CO_2 (cc)	1834.2	1842.8	1885.9	1881.2	1876.2	1891.8	1887.9	1842.3	1839.5
End point(min)	38.17	39.58	38.58	39.08	40.25	39.67	40.17	42.00	42.08
Maximum CO_2 Concentration (%)	41.0	38.1	38.6	38.0	36.7	37.5	37.3	35.8	35.8
PMIDA (wt.%)	0.003		0.007		0.006		0.007		0.009
Glyphosate(wt.%)	5.197		5.376		5.379		5.339		5.341
IDA(wt.%)	0.095		0.049		0.044		0.041		0.037
CH_2O(ppm)	2670		2306		2018		2236		2425
HCOOH(ppm)	6221		7076		7141		7100		7033
Pt(ppm)	0.015		0.015		0.015		0.016		0.016
Fe(ppm)	27.940		2.972		0.594		0.315		0.406

Example 51

[00491] The following preparation was conducted under nitrogen protection.

[00492] Activated carbon (approximately 10.456 g) and degassed water (approx. 90 g) were placed in a baffled beaker and allowed to mix for approximately 20 minutes.

[00493] $FeCl_3 \bullet 6H_2O$ (2.009 g) was dissolved in degassed water (approx. 40 g) and this solution was then pumped into the baffled beaker over a period of 30 minutes while the pH of the slurry was maintained at 4 by addition of 2.5N NaOH. Upon complete addition of the $FeCl_3 \bullet 6H_2O$ solution, the pH was raised to 4.5 and the slurry was allowed to mix for 10 minutes. The slurry was then heated to 60°C over a period of 30 minutes, while the pH was maintained at pH 4.5. The pH of the slurry was then raised to 6.5 over a period of 10 minutes, and allowed to mix for 10 minutes. Ethylene glycol (approx. 1.384 g) was then added to the slurry, and allowed to mix at approximately 60°C for approximately 10 minutes. The slurry was then filtered, and the wet cake was then re-slurried in degassed deionized water (90 g) and introduced into the baffled beaker.

[00494] The pH of the solution was then lowered to 5 by addition of degassed 1M HCl (0.841g). K_2PtCl_4 (0.459 g) was dissolved in degassed water (20 mL). The resulting Pt solution was then added to the baffled beaker over a period of three minutes. The slurry was then allowed to mix at ambient conditions (approximately 22°C) for 30 minutes, and then heated to a temperature of 60°C over a period of 10 minutes.

[00495] The slurry was filtered, and the wet cake was hot washed twice at 60°C with approximately 100 mL of degassed water. The resulting sample was then dried in a vacuum oven at 110°C for 12 hours with a small nitrogen stream.

[00496] The catalyst precursor was then heated at elevated temperatures up to approximately 755°C in the presence of a hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes.

Example 52

[00497] The following preparation was conducted under nitrogen protection.

[00498] Activated carbon (approximately 10.456 g) and degassed water (approximately 90 g) were placed in a baffled beaker and allowed to mix for 20 minutes. $FeCl_3 \bullet 6H_2O$ (2.411 g) was dissolved in degassed water (approximately 41 g) and this solution was then pumped into the baffled beaker over a period of 30 minutes while the pH of the slurry was maintained at 4 by addition of 2.5N NaOH. Upon complete addition of the $FeCl_3 \bullet 6H_2O$ solution, the pH was raised to 4.5, and allowed to mix for 10 minutes. The slurry was then heated to 60°C over a period of 25 minutes while the pH was maintained at pH 4.5. The pH of the slurry was then raised to 11 over a period of 30 minutes, and then allowed to mix for 10 minutes.

[00499] Ethylene glycol (1.382 g) was then added to the slurry, and allowed to mix at approximately 60°C for approximately ten minutes. The slurry was then filtered, and the wet cake was then re-slurried in degassed deionized water (90 g) and introduced into the baffled beaker.

[00500] The pH of the solution was then lowered to 5 by addition of degassed 1M degassed HCl (3.7 g). K_2PtCl_4 (0.552 g) was dissolved in degassed water (20 g) and the Pt solution was then introduced into the baffled beaker over a period of three minutes. The slurry was then allowed to mix at ambient

conditions (approximately 22°C) for 30 minutes and then heated to a temperature of 60°C over a period of 10 minutes.

[00501] The slurry was then filtered, and the wet cake was hot washed twice at 60°C with approximately 100 mL of degassed water. The sample was then dried in a vacuum oven at 110°C for 12 hours with a small nitrogen stream.

[00502] The catalyst precursor was then heated at elevated temperatures up to approximately 650°C in the presence of a hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes.

Table 24A

Cycle	1	2	3	4	5	6	7	8	9	
Total CO_2 (cc)	1944.2	1977.4	2048.3	2044.4	2055.9	2058.7	2054.7	2065.8	2037.7	1(
End point(min)	33.58	34.92	34.08	35.58	35.50	35.58	35.42	35.25	35.83	3
Maximum CO_2 Concentration (%)	44.5	41.3	41.8	39.8	39.5	40.0	40.2	41.0	40.6	37.8
PMIDA (wt.%)	ND		0.005		0.005		0.007		0.007	0.106
Glyphosate(wt.%)	5.121		5.341		5.410		5.378		5.433	5.538
IDA(wt.%)	0.155		0.057		0.048		0.042		0.041	0.039
CH_2O(ppm)	2625		2077		1897		1897		1659	2602
HCOOH(ppm)	5320		5891		5858		5800		5817	6283
Pt(ppm)	0.019		0.018		0.018		0.018		0.018	0.022
Fe(ppm)	30.170		2.713		0.577		0.372		0.331	0.541

Example 53

[00503] The following preparation was conducted under nitrogen protection.

[00504] Activated carbon (10.456 g) and degassed water (approximately 90 g) were placed in a baffled beaker and allowed to mix for 20 minutes. $FeCl_3 \bullet 6H_2O$ (2.009 g) was dissolved in degassed water (approximately 41 g) and the resulting solution was pumped into the baffled beaker over a period of 30 minutes while the pH of the slurry was maintained at 4 by addition of 2.5N NaOH. After addition of the $FeCl_3 \bullet 6H_2O$ solution, the pH was raised to 4.5, and allowed to mix for 10 minutes. The slurry was then heated to approximately 50°C over a period of 32 minutes, while the pH was maintained at pH 4.5. The pH of the slurry was then raised to 8 over a period of 15 minutes, and then allowed to mix for 10 minutes. Ethylene glycol (1.386 g) was then added to the slurry, and allowed to mix at 60°C for ten minutes. The slurry was then filtered, and the wet cake was then re-slurried in degassed deionized water (90 g) and introduced into the baffled beaker.

[00505] The pH of the solution was then lowered to 5 by addition of degassed 0.5M HCl (2.17 g). K_2PtCl_4 (0.460 g) was dissolved in degassed water (20 g) and the Pt solution was then introduced into the baffled beaker over a period of three minutes. The slurry was then allowed to mix at room temperature for 30 minutes, and then heated to a temperature of 60°C over a period of 10 minutes. The slurry was then filtered, and the wet cake hot washed twice at 60°C with approximately 100mL of degassed water. The sample was then dried in a vacuum oven at 110°C for 12 hours with a small nitrogen stream.

[00506] The catalyst precursor was then heated at elevated temperatures up to approximately 550°C in the presence of a

hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes.

Example 54

[00507] This example details preparation of a catalyst having a nominal Pt content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00508] Activated carbon (approximately 10.458 g) and degassed water (approximately 90 g) were mixed in a baffled beaker under a nitrogen atmosphere.

[00509] $FeCl_3 \bullet 6H_2O$ (approximately 2.028 g) was dissolved in degassed water (20 g) and this solution was pumped into the baffled beaker over a period of approximately 25 minutes. The pH of the slurry within the baffled beaker was maintained at 4 by introduction of 2.5N degassed NaOH, as necessary. After addition of the $FeCl_3 \bullet 6H_2O$ solution to the beaker was completed, the pH of the slurry was raised to approximately 4.5 by addition of NaOH and the slurry was allowed to mix at ambient conditions (approximately 22°C) for approximately 10 minutes.

[00510] The slurry was then heated to a temperature of approximately 60°C over a period of approximately 40 minutes. During the heating, the pH was maintained at 4.5 with addition of 2.5N degassed NaOH.

[00511] The pH of the slurry was then raised to approximately 7.5 over a period of approximately 15 minutes at a temperature of approximately 60°C, via increases in pH at a rate of approximately 0.5 pH units per 5 minutes. The slurry was then allowed to mix at pH of approximately 7.5 for approximately

10 minutes, and then cooled to ambient conditions (approximately 22°C).

[00512] K_2PtCl_4 (approximately 0.460 g) was dissolved in degassed water (approximately 20 g) and the resulting Pt solution was then added to the baffled beaker over a period of approximately 20 minutes. The resulting slurry was allowed to mix for approximately 30 minutes. The thus mixed slurry was then cooled to approximately 60°C over a period of 45 minutes, and then allowed to mix at 60°C for 15 minutes.

[00513] The resulting slurry was then filtered and then dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

[00514] The catalyst precursor was then heated at elevated temperatures up to approximately 950°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 120 minutes.

[00515] Table 25 sets forth PMIDA reaction testing results, platinum leaching data, and iron leaching data for the 2%Pt/4%Fe finished catalyst.

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Table 25

Cycle	1	2	3	4	5
Total CO_2 (cc)	2169.6	2196.5	2147.3	2122.5	2062.5
End point(min)	36.42	36.08	37.83	38.42	40.00
Maximum CO_2 Concentration (%)	40.5	39.7	37.8	37.5	36.4
PMIDA (wt.%)	ND		0.008		0.008
Glyphosate(wt.%)	5.363		5.520		5.461
IDA(wt.%)	0.087	0.030	0.021		0.017
CH_2O(ppm)	1408		1143		1247
HCOOH(ppm)	5283		5733		5993
Pt(ppm)	0.122		0.153		0.155
Fe(ppm)	33.310		0.941		0.491

Example 55

[00516] This example provides microscopy results (conducted in accordance with Protocol B described in Example 68) for the catalyst precursor prepared as described in Example 54.

[00517] Fig. 116 is a scanning transmission electron microscopy (STEM) micrograph of a portion of the surface of the precursor, including points 1 and 2. Figs. 117 and 118 are results of energy dispersive x-ray (EDX) spectroscopy analysis for points 1 and 2, respectively. As shown, these portions of the precursor surface included iron well-dispersed throughout, but not all iron had platinum deposited thereon.

[00518] Figs. 119 and 120 are STEM photomicrographs of a portion of the precursor surface indicating spatial distribution of metal throughout the carbon particle.

[00519] Figs. 121 and 122 are an STEM micrograph and EELS line scan for a portion of the precursor surface, 1, identified in the micrograph. Figs. 123 and 124, and 125 and 126 are also pairs of STEM micrographs and EELS line scan analysis. These STEM and EELS results indicate the presence of iron throughout the carbon particle.

Example 56

[00520] This example details preparation of a catalyst having a nominal Pt content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00521] Activated carbon support (approximately 10.457 g) was introduced into a baffled beaker under a nitrogen atmosphere. $FeCl_3 \bullet 6H_2O$ (approximately 2.013 g) and sucrose (approximately 4.550 g) were dissolved in degassed water

(approximately 85 g). 50 wt.% NaOH (approximately 5.225 g) of was added to and mixed with the $FeCl_3 \bullet 6H_2O$ - sucrose solution. The $FeCl_3 \bullet 6H_2O$ - sucrose solution was then poured into the baffled beaker, and allowed to mix. The resulting slurry was then heated to approximately 60°C over a period of approximately 10 minutes.

[00522] Ethylene glycol (approximately 1.263 g) was added to the baffled beaker and allowed to mix with the slurry for approximately ten minutes at approximately 60°C. The slurry was then filtered, and the wet cake was then re-slurried in the baffled beaker in degassed deionized water (approximately 90 g). The pH of the resulting slurry was then lowered to approximately 7 by addition of degassed 2M HCl.

[00523] K_2PtCl_4 (0.462 g) was dissolved in degassed water (approximately 20 g) to form a platinum solution that was pumped into the baffled beaker over a period of approximately 20 minutes. The resulting slurry was then allowed to mix at ambient conditions (approximately 22°C) for approximately 30 minutes, and then heated to a temperature of approximately 60°C over a period of approximately 60 minutes. The final slurry was then filtered and the wet cake was dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

[00524] The catalyst precursor was then heated at elevated temperatures up to approximately 900°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 120 minutes.

[00525] Table 26 sets forth PMIDA reaction testing results, platinum leaching data, and iron leaching data for the 2%Pt/4%Fe catalyst.

Table 26

Cycle	1	2	3	4	5	6	7	8	9	
Total CO_2 (cc)	1765.8	1812.5	1881.3	1908.2	1926.6	1877.7	1891.9	1878.2	1871.1	160
End point(min)	44.08	43.50	41.92	42.25	41.58	43.67	43.08	43.83	43.67	43
Maximum CO_2 Concentration (%)	36.3	34.7	35.4	34.8	35.6	33.9	34.6	33.8	34.3	33.9
PMIDA (wt.%)	0.005		0.009		0.010		0.009		0.011	0.074
Glyphosate(wt.%)	5.326		5.397		5.348		5.448		5.423	5.568
IDA(wt.%)	0.081		0.038		0.032		0.028		0.028	0.027
CH_2O(ppm)	3191		2588		2311		2559		2620	2915
HCOOH(ppm)	6079		6290		6124		6123		6018	6223
Pt(ppm)	<0.01		0.014		0.016		0.014		0.015	0.018
Fe(ppm)	55.230		3.238		0.694		0.751		0.457	0.454

Example 57

[00526] This Example details the results of microscopy analysis (conducted in accordance with Protocol B described in Example 68) for the finished catalyst prepared as described in Example 56.

[00527] Figs. 127-132 include microscopy results for the catalyst after use in PMIDA oxidation testing as described in Example 56.

[00528] Fig. 127 includes four high resolution electron photomicrographs (HREM) for various portions of the spent catalyst surface. These indicate formation of graphite and iron oxide on the outer regions of metal particles. Fig. 128 includes three STEM micrographs, which indicate the presence of nanoporous platinum regions.

[00529] Fig. 129 is an STEM micrograph showing various portions of the spent catalyst surface that were analyzed by EDX analysis. The results of the EDX analysis are shown in Fig. 130, which indicates the presence of a platinum-rich composition.

[00530] Fig. 131 is also an STEM micrograph and Fig. 132 the results of EDX analysis for the portions of the spent catalyst surface. These results indicate the presence of varying metal compositions.

[00531] Figs. 133-137 include microscopy results for the finished catalyst prepared as described in Example 56, but prior to reaction testing.

[00532] Fig. 133 is an STEM photomicrograph identifying a particle to be analyzed by EELS line scan analysis, the results of which are shown in Fig. 134. As shown in Fig. 134, a partial shell of iron oxide was detected.

[00533] Fig. 135 is an HREM photomicrograph highlighting Pt lattice regions. As shown in Fig. 135, the particle identified included no more than about 4 Pt lattice fringes. It is currently believed that each lattice fringe corresponds to a layer of platinum atoms. That is, the particle identified included a layer of platinum no more than about 4 platinum atoms thick.

[00534] Figs. 136 and 137 are HREM photomicrographs identifying two layers of platinum atoms.

[00535] Fig. 138 provides XRD analysis results, which indicate formation of an $Fe_{0.75}Pt_{0.25}$ phase.

Example 58

[00536] This example details preparation of a catalyst precursor having a nominal Pt content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00537] Activated carbon support (approximately 10.456 g) was introduced into a baffled beaker under a nitrogen atmosphere. $FeCl_3 \bullet 6H_2O$ (approximately 2.011 g) and sucrose (approximately 4.511 g) were dissolved in degassed water (approximately 91.1 g). 50 wt.% NaOH (approximately 5.214 g) was added to and mixed with the $FeCl_3 \bullet 6H_2O$ - sucrose solution. The $FeCl_3 \bullet 6H_2O$ - sucrose solution was then poured into the baffled beaker, and allowed to mix with the activated carbon support. The resulting slurry was then heated to approximately 40°C over a period of approximately 10 minutes.

[00538] Ethylene glycol (approximately 1.309 g) was added to the baffled beaker and allowed to mix with the slurry for approximately ten minutes at approximately 40°C. The slurry was

then filtered, and the wet cake was then re-slurried in the baffled beaker in degassed deionized water (90 g). The pH of the resulting slurry was then adjusted/lowered to approximately 7 by addition of degassed 2M HCl (1.52 g).

[00539] K_2PtCl_4 (approximately 0.461 g) was dissolved in degassed water (20 g) to form a platinum solution that was introduced into the baffled beaker over a period of 3 minutes. The resulting slurry was then allowed to mix at approximately 25°C for approximately 30 minutes, and then heated to a temperature of approximately 60°C over a period of approximately 40 minutes.

[00540] The final slurry was then filtered and the wet cake was washed twice by contact with degassed water (approximately 100 g) at a temperature of approximately 60°C. The wet cake was dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

Example 59

[00541] This example details preparation of a catalyst having a nominal Pt content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00542] Activated carbon support (approximately 10.456 g) was introduced into a baffled beaker under a nitrogen atmosphere. $FeCl_3 \bullet 6H_2O$ (approximately 2.011 g) and sucrose (approximately 4.513 g) were dissolved in degassed water (approximately 91 g). 50 wt.% NaOH (approximately 5.25 g) was added to and mixed with the $FeCl_3 \bullet 6H_2O$ - sucrose solution. The

$FeCl_3 \bullet 6H_2O$ - sucrose solution was then poured into the baffled beaker, and allowed to mix with the activated carbon support.

[00543] Ethylene glycol (approximately 1.31 g) was added to the baffled beaker and the resulting slurry was heated to a temperature of approximately 30°C over a period of approximately 15 minutes. The slurry was then filtered, and the wet cake was then re-slurried in the baffled beaker in cold degassed deionized water (90 g) at a temperature of approximately 12°C. The pH of the resulting solution was then lowered to approximately 7 by addition of degassed 2M HCl (approximately 0.645 g) and 1M HCl (approximately 0.461g).

[00544] K_2PtCl_4 (approximately 0.461g) was dissolved in cold degassed water (approximately 20 g) at a temperature of approximately 12°C. The platinum solution was then pumped into the baffled beaker over a period of approximately 20 minutes.

[00545] The final slurry was then filtered and the wet cake was dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

[00546] The catalyst precursor was then heated at elevated temperatures up to approximately 755°C in the presence of a hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes.

[00547] Table 27 sets forth PMIDA reaction testing results, platinum leaching data, and iron leaching data for the 2%Pt/4%Fe finished catalyst.

Table 27

Cycle	1	2	3	4	5	6	7	8	9	10
Total CO_2 (cc)	1776.6	1830.6	1877.3	1898.8	1846.8	1868.2	1853.1	1825.1	1827.8	1600.2
End point(min)	44.75	44.92	43.67	44.00	46.25	45.75	46.25	47.42	47.00	48.50
Maximum CO_2 Concentration (%)	35.6	33.5	33.7	33.7	32.5	32.8	32.6	32.0	32.7	31.7
PMIDA (wt.%)	ND		0.003		0.005		0.004		0.006	0.057
Glyphosate(wt.%)	5.278		5.463		5.489		5.450		5.508	5.516
IDA(wt.%)	0.079		0.036		0.031		0.029		0.029	0.029
CH_2O(ppm)	3702		2914		2366		2434		2422	2756
HCOOH(ppm)	5549		6036		5987		5882		5850	5842
Pt(ppm)	0.016	0.016	0.018		0.019		0.017		0.017	0.022
Fe(ppm)	36.130	11.570	2.818		0.552		0.456		0.423	0.375

Example 60

[00548] Figs. 139-148 include microscopy results (conducted in accordance with Protocol B described in Example 68) for the finished catalyst prepared as described in Example 59.

[00549] Fig. 139 is an STEM micrograph identifying the particle analyzed by EELS line scan analysis, the results of which are shown in Fig. 140. As shown in Fig. 139, the Fe:Pt atomic ratio of the particle analyzed was 85.99/14.01. The line scan results of Fig. 140 indicate formation of an iron oxide outer layer.

[00550] Fig. 141 is an STEM micrograph indicating the particle that was analyzed by EDX line scan analysis, the results of which are shown in Fig. 142. The line scan results indicate a relatively constant platinum signal, suggesting a very thin platinum shell, i.e., varying by no more than about 25% during the scan across the particle (e.g., from about 17.5 nm to about 46 nm along the scanning line. As also shown in Fig. 142, the variation in the magnitude of the iron signal during the scan across the particle is proportionally greater than the variation in the platinum signal during the scan across the particle (i.e., on the order of at least about 1.5:1).

[00551] Fig. 143 is an STEM micrograph and Figs. 144 and 145 the corresponding EELS line scan analysis and EDX line scan analysis, respectively. The EELS line scan results indicate the presence of an iron oxide layer. The EDX line scan results indicate the presence of a thin platinum shell.

[00552] Fig. 146 is an STEM micrograph and Fig. 147 the corresponding EDX line scan analysis. The line scan results indicate a relatively constant platinum signal, i.e., ranging by no more than about 25% during the scan across the particle from about 9 nm to about 35 nm along the scanning line and a greater

variation in the magnitude of the iron signal as compared to the variation in the platinum signal (i.e., on the order of about 1.5:1).

[00553] Fig. 148 provides XRD results of analysis conducted as described in Example 69. These results indicate formation of an $Fe_{0.75}Fe_{0.25}$ phase.

[00554] Figs. 149-153 are microscopy results for the spent catalyst (i.e., after testing in PMIDA oxidation).

[00555] Fig. 149 is an STEM micrograph showing various porous metal particles at the spent catalyst surface.

[00556] Fig. 150 is an STEM micrograph and Fig. 151 the corresponding EDX line scan analysis results. Fig. 152 is an STEM micrograph and Fig. 153 the corresponding EDX line scan analysis results. These results indicate a platinum-rich composition throughout the particles analyzed due to leaching of iron from the core, i.e., inner regions of the particles to form porous platinum-rich particles.

Example 61

[00557] This example details preparation of a catalyst precursor having a nominal Pt content of 2 wt.% and a nominal iron content of 3.5 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00558] Activated carbon support (approximately 10.457 g) was introduced into a baffled beaker under a nitrogen atmosphere. $FeCl_3 \bullet 6H_2O$ (approximately 1.753 g) and sucrose (approximately 4.455 g) were dissolved in degassed water (approximately 90 g). 50 wt.% NaOH (approximately 4.613 g) was added to and mixed with the $FeCl_3 \bullet 6H_2O$ - sucrose solution. The $FeCl_3 \bullet 6H_2O$ - sucrose solution was then poured into the baffled

beaker, and allowed to mix with the activated carbon support. The slurry was then heated a temperature of approximately 60°C over a period of 10 minutes.

[00559] Ethylene glycol (approximately 1.200 g) was added to the baffled beaker and allowed to mix with the slurry for approximately ten minutes at approximately 60°C. The slurry was then filtered, and the wet cake was then re-slurried in degassed deionized water (90 g) and introduced into the baffled beaker. The pH of the resulting slurry was then lowered to approximately 6 by addition of degassed 1M HCl (3.6 g).

[00560] K_2PtCl_4 (approximately 0.452 g) was dissolved in degassed water (approximately 20 g) to form a platinum solution that was introduced into the baffled beaker over a period of approximately 3 minutes. The resulting slurry was then allowed to mix at ambient conditions (approximately 22°C) for approximately 15 minutes, and then heated to a temperature of approximately 40°C over a period of approximately 12 minutes.

[00561] The final slurry was then filtered and the wet cake was hot washed twice by contact with degassed water (approximately 100g) at a temperature of approximately 60°C. The resulting sample was then dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream.

[00562] The catalyst precursor was then heated at elevated temperatures up to approximately 755°C in the presence of a hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes.

[00563] Fig. 154 provides XRD analysis results for the finished 2%Pt/3.5%Fe catalyst, which indicate formation of a Fe_3Pt phase.

[00564] Table 28 sets forth PMIDA reaction testing results, platinum leaching data, and iron leaching data for the finished catalyst. Fig. 155 provides XRD analysis results for the catalyst after reaction testing (i.e., the spent catalyst). These results indicate formation of a Pt phase.

Table 28

Cycle	1	2	3	4	5	6	7	8	9	1(
Total CO_2 (cc)	1785.7	1841.8	1913.6	1928.1	1970.6	1956.8	1956.0	1947.8	1967.6	1602.(
End point(min)	43.83	41.67	39.83	40.17	40.42	40.75	40.58	41.83	41.67	42.7!
Maximum CO_2 Concentration (%)	35.4	36.0	36.9	36.9	36.2	35.7	36.2	35.1	35.4	34.7
PMIDA (wt.%)	ND		0.003		0.004		0.004		0.004	0.143
Glyphosate(wt.%)	5.169		5.405		5.405		5.343		5.446	5.430
IDA(wt.%)	0.085		0.045		0.039		0.038		0.036	0.036
CH_2O(ppm)	3172		2624		2341		2272		2068	2612
HCOOH(ppm)	6258		6539		6489		6391		6313	6465
Pt(ppm)	0.011		0.013		0.014		0.016		0.016	0.022
Fe(ppm)	24.680		2.502		0.584		0.487		0.363	0.362

Example 61A

[00565] This example details preparation of a catalyst having a nominal Pt content of 2 wt.% and a nominal iron content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00566] Activated carbon (approximately 10.456 g) and degassed water (approximately 90 g) were mixed in a baffled beaker and allowed to mix for 20 minutes.

[00567] $FeCl_3 \bullet 6H_2O$ (approx. 2.009 g) was dissolved in degassed water (40 g) and this solution was then pumped into the baffled beaker over a period of 30 minutes while maintaining the pH of the slurry at 4 with 2.5N NaOH, as necessary. After addition of the $FeCl_3 \bullet 6H_2O$ solution to the beaker was completed, the pH of the slurry was raised to 4.5 and allowed to mix for 10 minutes.

[00568] The slurry was then heated to approximately 60°C over a period of approximately 30 minutes. During the heating, the pH was maintained at 4.5. The pH of the slurry was then raised to 11 over a period of 30 minutes, and then allowed to mix for 10 minutes. Ethylene glycol (1.388 g) was then added to the slurry, and allowed to mix at approximately 60°C for approximately 10 minutes. The slurry was then filtered, and the wet cake was then re-slurried in the baffled in degassed deionized water (approx. 90 g).

[00569] The pH of the solution was then lowered to 7 by addition of 0.5M degassed HCl. K_2PtCl_4 (0.460 g) was dissolved in 20 mL of degassed water. The Pt solution was then pumped into the baffled beaker over a period of 30 minutes. The resulting slurry was then allowed to mix at ambient conditions (approx. 20°C) for approximately 30 minutes, and then heated to a temperature of approximately 60°C over a period of 10 minutes.

[00570] The resulting slurry was then filtered and washed twice by contact with degassed water (approx. 100 g) at a temperature of approximately 60°C. The sample was then dried in a

vacuum oven at approximately 110°C for 12 hours with a small nitrogen stream to form a Pt/Fe catalyst precursor.

[00571] The catalyst precursor was then heated at elevated temperatures up to approximately 650°C in the presence of a hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes.

V. Platinum-Cobalt

Example 62

[00572] This example details preparation of a catalyst having a nominal platinum content of approximately 2 wt.% and a nominal cobalt content of approximately 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00573] $CoCl_2$ (1.686 g) and sucrose (4.499 g) were dissolved in degassed water (89.4 mL) in a screw top jar that had been flushed with nitrogen. To this mixture was added 50 wt.% sodium hydroxide (5.209 g), the jar was flushed with nitrogen, and the solution was then mixed for one minute.

[00574] Activated carbon support (10.458 g) was added to a 400 mL baffled beaker and the $CoCl_2$ solution was then poured into the baffled beaker, the beaker was flushed with nitrogen, and the components were allowed to mix at room temperature for approximately five minutes. The resulting solution was then heated to approximately 60°C over a period of approximately forty minutes. Ethylene glycol (approx. 1.272 g) was then added, and the resulting solution was allowed to mix at approximately 60°C for approximately twenty minutes.

[00575] The solution was then filtered on a fritted glass filter, the resulting wet cake was returned to the baffled beaker. The pH of the solution was reduced to approximately 4.7 by addition of HCl (2M).

[00576] K_2PtCl_4 (approx. 0.460g) was dissolved in degassed water (20 ml) and the platinum solution was added to the baffled beaker drop-wise over a period of approximately three minutes. The resulting solution was allowed to mix at approximately 25°C for approximately sixty minutes. The solution was then heated to approximately 60°C over a period of approximately twenty minutes. The resulting solution was then filtered, and the filtrate was hot washed twice with in degassed water (120 ml) at approximately 60°C. The sample was then dried in a vacuum oven at 110°C for 12 hours with a nitrogen stream.

[00577] The catalyst precursor was then heated at elevated temperatures up to approximately 900°C in the presence of a hydrogen/argon stream (4%/96%; v/v) for approximately 120 minutes.

Example 63

[00578] This example details preparation of a catalyst precursor having a nominal platinum content of 2 wt.% and a cobalt content of 4 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00579] Activated carbon (10.458 g) was placed in a baffled beaker. $CoCl_2 \cdot 6H_2O$ (1.685 g) and sucrose (4.566 g) were mixed with degassed water (89.2 ml) and allowed to dissolve. 5.154 g of 50 wt.% sodium hydroxide was added to the cobalt solution and allowed to mix. The resulting $CoCl_2 \cdot 6H_2O$ solution was then poured into the baffled beaker with carbon, and allowed to mix.

[00580] The resulting slurry was then heated to approximately 60°C over a period of twenty minutes. Sodium borohydride (approx. 0.558 g) was dissolved in degassed water (20 ml) to which 2.5N degassed NaOH (0.329 g) was then added. The sodium borohydride solution was added to the baffled beaker at approximately 60°C

over a period of approximately twenty minutes, and then allowed to mix for ten additional minutes. The slurry was then filtered, and the wet cake was washed twice at approximately 60°C. The resulting wet cake was then re-slurried in degassed deionized water (90 g).

[00581] The pH of the solution was reduced to approximately 5 by addition of degassed 2M HCl. K_2PtCl_4 (0.459 g) was dissolved in degassed water (20 ml). The Pt solution was then added to the baffled beaker over a period of approximately three minutes. The slurry was then allowed to mix at approximately 25°C for approximately 40 minutes, and then heated to a temperature of approximately 40°C.

[00582] The resulting slurry was then filtered, and the wet cake was washed twice with hot water (approx. 100 ml) at approx. 60°C. The resulting sample was then dried in a vacuum oven at approximately 110°C for 12 hours with a small nitrogen stream.

VI. Platinum-Tin

Example 64

[00583] The following preparation was conducted under nitrogen protection. Activated carbon (10.457 g) was placed in a baffled beaker and mixed with degassed water (100 ml).

[00584] $SnCl_4 \bullet 5H_2O$ (2.545 g) and K_2PtCl_4 (0.463 g) were dissolved in degassed water (20 ml). The Sn/Pt solution was then pumped into the baffled beaker over a period of approximately twenty-three minutes. The temperature and pH of the Sn/Pt solution were raised simultaneously to approximately 60°C and approximately 7, respectively, over a period of approximately forty five minutes. The solution was allowed to mix for approximately thirty minutes.

[00585] $NaBH_4$ (1.310 g) was dissolved in degassed water (10 ml) and this solution was added to the baffled beaker over a twenty minute period. The resulting slurry was then allowed to mix for approximately twenty minutes, the slurry filtered, and the wet cake was hot washed twice with approximately 100 ml of degassed water at approximately 60°C. The resulting sample was then dried in a vacuum oven at 110°C for 12 hours with a small nitrogen stream.

[00586] The catalyst precursor was then heated at elevated temperatures up to approximately 545°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 120 minutes.

VII. Platinum-Copper

Example 65

[00587] The following preparation was conducted under nitrogen protection.

[00588] Preparation of nominal 2%Pt4%Cu on activated carbon: The following was added to a baffled beaker including approx. 10g of activated carbon: 1.64 g of $CuSO_4 \cdot 5H_2O$ solution, 4.51 g of sucrose, 90 g of degassed deionized water, and 4.63 g of 50 wt.% NaOH. The mixture was heated to approx. 40°C and stirred for approx. 10 minutes with a mechanical agitator. To this slurry was added 1.71 g of 37% formaldehyde diluted to 17.1 g with degassed deionized water. The resulting slurry was heated to approx. 40°C along with continued stirring for approx. 30 minutes (or until solution became colorless). Then the slurry was filtered, washed once in the filter, and then re-slurried in water to pH 2.02 by adding 1M degassed HCl. A solution of 0.454g of K_2PtCl_4 in 10g of degassed water was then added to the slurry, along with continued stirring for approx. 30 minutes at ambient conditions. Then the slurry was heated to approx. 60°C and stirred for approx. 30 more

minutes. This slurry was then filtered and washed with water, and dried under vacuum at approx. 110°C under a small stream of nitrogen. A total of 11.720 g of dried material was recovered. During heat treatment to a maximum temperature of approximately 950°C in the presence of an argon/hydrogen atmosphere (2%/98%) (v/v) for approximately 120 minutes, the sample lost 13.5% weight.

[00589] Figs. 155A and 155B include microscopy results for the finished catalyst. Figs 155C - 155F include microscopy results for the catalyst after testing in PMIDA oxidation.

Example 66

[00590] This example details preparation of a catalyst having a nominal Pt content of 2 wt.% and a nominal copper content of 3.75 wt.% on an activated carbon support having a Langmuir surface area of approximately 1500 m^2/g. The following preparation was conducted under nitrogen protection.

[00591] Activated carbon support (approximately 10.457 g) was introduced into a baffled beaker under a nitrogen atmosphere. $CuSO_4 \bullet 5H_2O$ (approximately 1.540 g) and sucrose (approximately 4.225 g) were dissolved in degassed water (approximately 91 g). 50 wt.% NaOH (approximately 4.370 g) was added to and mixed with the $CuSO_4 \bullet 5H_2O$ - sucrose solution, and the resulting solution was then poured into the baffled beaker, and allowed to mix with the activated carbon support at a temperature of approximately 29°C for approximately 20 minutes.

[00592] Formaldehyde (37%) (approximately 1.604 g) was added to the baffled beaker and allowed to mix with the slurry for approximately eighty four minutes at approximately 29°C. The slurry was then filtered, and the wet cake was then re-slurried in degassed deionized water (90 g) and introduced into the beaker.

The pH of the resulting slurry was then lowered to approximately 4 by addition of degassed 1M HCl.

[00593] K_2PtCl_4 (approximately 0.427 g) was dissolved in degassed water (approximately 20 g) to form a platinum solution that was introduced into the baffled beaker over a period of approximately 3 minutes. The resulting slurry was then allowed to mix at ambient conditions (approximately 22°C) for approximately 30 minutes, and then heated to a temperature of approximately 60°C, and then mixed for approximately an additional 30 minutes.

[00594] The final slurry was then filtered and the wet cake was hot washed twice at 60°C by contact with degassed water (approximately 100g). The resulting sample was dried in a vacuum oven at approximately 110°C for approximately 12 hours with a small nitrogen stream.

[00595] The catalyst precursor was then heated at elevated temperatures up to approximately 950°C in the presence of a hydrogen/argon stream (2%/98%; v/v) for approximately 120 minutes.

[00596] Table 29 sets forth PMIDA reaction testing results, platinum leaching data, and iron leaching data for the finished catalyst.

Table 29

Cycle	1	2	3	4	5	6	7	8	9	
Total CO_2 (cc)	1916.9	2049.0	2048.7	2037.5	2010.9	1996.5	1995.9	1918.9	1920.4	1601
End point(min)	49.00	43.50	42.00	42.17	42.33	42.33	41.58	44.42	44.92	45.
Maximum CO_2 Concentration (%)	29.8	32.6	33.7	33.9	34.6	34.9	36.9	33.9	33.8	33.9
PMIDA (wt.%)	0.007		0.004		0.006		0.005		0.005	0.217
Glyphosate(wt.%)	5.476		5.553		5.492		5.511		5.474	5.443
IDA(wt.%)	0.051		0.021		0.018		0.019		0.019	0.018
CH_2O(ppm)	2208		2057		1905		2105		1876	2517
HCOOH(ppm)	4743		4945		5234		5567		5780	5802
Pt(ppm)	0.023		0.031		0.033		0.039		0.046	0.068
Fe(ppm)	16.930		0.953		0.553		0.387		0.284	0.247

VIII. Testing Protocols

Example 67: Protocol A

[00597] The following example details CO chemisorption analysis used to determine the exposed metal surface areas of catalysts prepared as described herein. The method described in this example is referenced in this specification and appended claims as "Protocol A."

[00598] This protocol subjects a single sample to two sequential CO chemisorption cycles.

[00599] Cycle 1 measures initial exposed noble metal at zero valence state. The sample is vacuum degassed and treated with oxygen. Next, residual, un-adsorbed oxygen is removed and the catalyst is then exposed to CO. The volume of CO taken up irreversibly is used to calculate initial noble metal (e.g., Pt^0) site density.

[00600] Cycle 2 measures total exposed noble metal. Without disturbing the sample after cycle 1, it is again vacuum degassed and then treated with flowing hydrogen, and again degassed. Next the sample is treated with oxygen. Finally, residual, non-adsorbed oxygen is removed and the catalyst is then again exposed to CO. The volume of CO taken up irreversibly is used to calculate total exposed noble metal (e.g., Pt^0) site density. See, for example, Webb et al., *Analytical Methods in Fine Particle Technology*, Micromeritics Instrument Corp., 1997, for a description of chemisoprtion analysis. Sample preparation, including degassing, is described, for example, at pages 129-130.

Equipment:

[00601] Micromeritics (Norcross, GA) ASAP 2010~ static chemisorption instrument; Required gases: UHP hydrogen; carbon monoxide; UHP helium; oxygen (99.998%); Quartz flow through sample tube with filler rod; two stoppers; two quartz wool plugs; Analytical balance.

Preparation:

[00602] Insert quartz wool plug loosely into bottom of sample tube. Obtain tare weight of sample tube with 1st wool plug. Pre-weigh approximately 0.25 grams of sample then add this on top of the 1st quartz wool plug. Precisely measure initial sample weight. Insert 2nd quartz wool plug above sample and gently press down to contact sample mass, then add filler rod and insert two stoppers. Measure total weight (before degas): Transfer sample tube to degas port of instrument then vacuum to <10 μm Hg while heating under vacuum to 150°C for approximately 8-12 hours. Release vacuum. Cool to ambient temperature and reweigh. Calculate weight loss and final degassed weight (use this weight in calculations).

Cycle 1:

[00603] Secure sample tube on analysis port of static chemisorption instrument. Flow helium (approximately 85 cm^3/minute) at ambient temperature and atmospheric pressure through sample tube, then heat to 150°C at 5°C/minute. Hold at 150°C for 30 minutes. Cool to 30°C.

[00604] Evacuate sample tube to <10 μm Hg at 30°C. Hold at 30°C for 15 minutes. Close sample tube to vacuum pump and run leak test. Evacuate sample tube while heating to 70°C at 5°C/min. Hold for 20 minutes at 70°C.

[00605] Flow oxygen (approximately 75 cm^3/minute) through sample tube at 70°C and atmospheric pressure for 50 minutes.

[00606] Evacuate sample tube at 70°C for 5 minutes.

[00607] Flow helium (approximately 85 cm^3/minute) through sample tube at atmospheric pressure and increase to 80°C at 5°C/minute. Hold at 80°C for 15 minutes.

[00608] Evacuate sample tube at 80°C for 60 minutes and hold under vacuum at 80°C for 60 minutes. Cool sample tube to 30°C and continue evacuation at 30°C for 30 minutes. Close sample tube to vacuum pump and run leak test.

[00609] Evacuate sample tube at 30°C for 30 minutes and hold under vacuum at 30°C for 30 minutes.

[00610] For a first CO analysis, CO uptakes are measured under static chemisorption conditions at 30°C and starting manifold pressures of 50, 100, 150, 200, 250, 300, 350 and 400 mm Hg (gauge) to determine the total amount of CO adsorbed (i.e., both chemisorbed and physisorbed).

[00611] Pressurize manifold to the starting pressure (e.g., 50 mm Hg). Open valve between manifold and sample tube allowing CO to contact the sample in the sample tube. Allow the pressure in the sample tube to equilibrate. The reduction in pressure from the starting manifold pressure to equilibrium pressure in the sample tube indicates the volume of CO uptake by the sample.

[00612] Close valve between the manifold and sample tube and pressurize the manifold to the next starting pressure (e.g., 100 mm Hg). Open valve between manifold and sample tube allowing CO to contact the sample in the sample tube. Allow the pressure in the sample tube to equilibrate to determine the volume of CO uptake by the sample. Perform for each starting manifold pressure.

[00613] Evacuate sample tube at 30°C for 30 minutes.

[00614] For a second CO analysis, CO uptakes are measured under static chemisorption conditions at 30°C and starting manifold pressures of 50, 100, 150, 200, 250, 300, 350 and 400 mm Hg (gauge) as described above for the first CO analysis to determine the total amount of CO physisorbed.

Cycle 2:

[00615] After the second CO analysis of Cycle 1, flow helium (approximately 85 cm^3/minute) at 30°C and atmospheric pressure through sample tube then heat to 150°C at 5°C/minute. Hold at 150°C for 30 minutes.

[00616] Cool to 30°C. Evacuate sample tube to <10 μm Hg at 30°C for 15 minutes. Hold at 30°C for 15 minutes.

[00617] Close sample tube to vacuum pump and run leak test.

[00618] Evacuate sample tube at 30°C for 20 minutes.

[00619] Flow hydrogen (approximately 150 cm^3/minute) through sample tube at atmospheric pressure while heating to 150°C at 10°C/min. Hold at 150°C for 15 minutes.

[00620] Evacuate sample tube at 150°C for 60 minutes. Cool sample tube to 70°C. Hold at 70°C for 15 minutes.

[00621] Flow oxygen (approximately 75 cm^3/minute) through sample tube at atmospheric pressure and 70°C for 50 minutes.

[00622] Evacuate sample tube at 70°C for 5 minutes.

[00623] Flow helium (approximately 85 cm^3/minute) through sample tube at atmospheric pressure and increase temperature to 80°C at 5°C/minute. Hold at 80°C for 15 minutes. Evacuate sample tube at 80°C for 60 minutes. Hold under vacuum at 80°C for 60 minutes.

[00624] Cool sample tube to 30°C and continue evacuation at 30°C for 30 minutes. Close sample tube to vacuum pump and run leak test.

[00625] Evacuate sample tube at 30°C for 30 minutes and hold for 30 minutes.

[00626] For a first CO analysis, CO uptakes are measured under static chemisorption conditions at 30°C and starting manifold pressures of 50, 100, 150, 200, 250, 300, 350 and 400 mm Hg (gauge) to determine the total amount of CO adsorbed (i.e., both chemisorbed and physisorbed).

[00627] Pressurize manifold to the starting pressure (e.g., 50 mm Hg). Open valve between manifold and sample tube allowing CO to

contact the sample in the sample tube. Allow the pressure in the sample tube to equilibrate. The reduction in pressure from the starting manifold pressure to equilibrium pressure in the sample tube indicates the volume of CO uptake by the sample.

[00628] Close valve between the manifold and sample tube and pressurize the manifold to the next starting pressure (e.g., 100 mm Hg). Open valve between manifold and sample tube allowing CO to contact the sample in the sample tube. Allow the pressure in the sample tube to equilibrate to determine the volume of CO uptake by the sample. Perform for each starting manifold pressure.

[00629] Evacuate sample tube at 30°C for 30 minutes.

[00630] For a second CO analysis, CO uptakes are measured under static chemisorption conditions at 30°C and starting manifold pressures of 50, 100, 150, 200, 250, 300, 350 and 400 mm Hg (gauge) as described above for the first CO analysis to determine the total amount of CO physisorbed.

Calculations:

[00631] Plot first and second analysis lines in each cycle: volume CO physically adsorbed and chemisorbed (1st analysis) and volume CO physically adsorbed (2nd analysis) (cm^3/g at STP) versus target CO pressures (mm Hg). Plot the difference between First and Second analysis lines at each target CO pressure. Extrapolate the difference line to its intercept with the Y-axis. In Cycle 1, total exposed Pt_0 (μmole CO/g) = Y-intercept of difference line/22.414 X 1000. In Cycle 2, total exposed Pt (μmole CO/g) = Y-intercept of difference line/22.414 X 1000.

Example 68 (Microscopy): Protocol B

[00632] This Example details microscopy analysis of catalyst samples of the present invention.

High Resolution Electron Micrographs (HREM):

[00633] HREM for various catalyst samples were generated using a Jeol 2100 field emission gun (FEG) transmission electron microscope (TEM) operated at an accelerating voltage of 200 keV. Samples were placed in the holder as-is without carbon interference (i.e., the samples were not microtomed and embedded in an organic-containing material such as an epoxy), and under conditions that identified lattice fringe rings.

Atomic Layer Measurements:

[00634] Lattice d spacings of catalyst particles identified by TEM were measured. These measurements were calibrated based on the known d spacing (3.84 A) of single crystal silicon (110) that was also analyzed using the Jeol 2100 FEG TEM at the same magnification and accelerating voltage (200 KeV). The measurements were recorded and analyzed using DigitalMicrograph software. The number of atomic layers of platinum for the particles analyzed was determined based from the number of repeating lattice fringe rings observed in the HREM micrographs.

Line Scan Analysis:

[00635] Energy dispersive x-ray spectroscopy (EDX) line scan analysis was conducted using the Jeol 2100 FEG TEM operated in scanning transmission electron microscopy (STEM) mode. The probe size was 1 nm.

[00636] Electron energy loss spectroscopy (EELS) line scan analysis was conducted using the Jeol 2100 FEG TEM operated in STEM mode with a probe size of 0.5 nm.

Example 69 (X-Ray Diffraction)

[00637] This example details the method utilized for X-Ray Diffraction (XRD) analysis for the results reported herein. Powder samples (less than approx. 0.2 g) were compacted using a pellet press to form sample pellets for analysis. The sample pellet was placed on a plastic sample holder for analysis in a Bruker D8 Discover Diffractometer.

[00638] CuKαX radiation ($\lambda_{CuK\alpha}$ = 1.5418 Å) was produced in a sealed Cu tube at 40 kV and 40 mA. Prior to the experiment, a korundum sample was used to adjust any peak misalignments.

[00639] The sample holder was placed on the XYZ stage and analyzed in locked coupled scan mode; the gun and detector angles were kept at the same value (i.e., $\theta_1 = \theta_2$). XRD data were collected using a LynxEye® Position Sensitive Detector (PSD) which is 10^3 times more sensitive than regular XRD. For each sample, an XRD spectrum was collected within the 0-90° 2θ range with a step size of 0.02° and a total collection time of approx. 3 hours.

Example 70 (Pore Volume and Surface Area Analysis)

[00640] Various metal-impregnated supports and catalysts were generally analyzed to determine surface area and pore volume data as reported herein using a Micromeritics 2010 Micropore analyzer with a one-torr transducer and a Micromeritics 2020 Accelerated Surface Area and Porosimetry System, also with a one-torr transducer. These analysis methods are described in, for example, Analytical Methods in fine Particle Technology, First Edition, 1997, Micromeritics Instrument Corp.; Atlanta, Georgia (USA); and Principles and Practice of Heterogeneous Catalysis, 1997, VCH Publishers, Inc; New York, NY (USA).

[00641] The present invention is not limited to the above embodiments and can be variously modified. The above description of the preferred embodiments, including the Examples, is intended only to acquaint others skilled in the art with the invention, its principles, and its practical application so that others skilled in the art may adapt and apply the invention in its numerous forms, as may be best suited to the requirements of a particular use.

[00642] With reference to the use of the word(s) comprise or comprises or comprising in this entire specification (including the claims below), unless the context requires otherwise, those words are used on the basis and clear understanding that they are to be interpreted inclusively, rather than exclusively, and

applicants intend each of those words to be so interpreted in construing this entire specification.

[00643] When introducing elements of the present invention or the preferred embodiments(s) thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[00644] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

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WHAT IS CLAIMED IS:

1. A process for oxidizing a substrate selected from the group consisting of N-(phosphonomethyl)iminodiacetic acid or a salt thereof, formaldehyde, and formic acid, the process comprising:

contacting the substrate with an oxidizing agent in the presence of an oxidation catalyst comprising a particulate carbon support, a first metal, and a second metal, the support having at its surface particles comprising the first metal and the second metal, wherein:

the second metal distribution within at least one of said particles as characterized by EDX line scan analysis produces a second metal signal that varies by no more than about 25% across a scanning region having a dimension that is at least about 70% of the largest dimension of the at least one particle.

2. An oxidation catalyst comprising a particulate carbon support, a first metal, and platinum, the support having at its surface particles comprising the first metal and platinum, wherein the first metal is selected from the group consisting of cobalt, copper, iron, and combinations thereof, and:

the platinum distribution within at least one of said first metal and platinum-containing particles as characterized by EDX line scan analysis produces a platinum signal that varies by no more than about 25% across a scanning region having a dimension that is at least about 70% of the largest dimension of the at least one particle and wherein first metal and platinum-containing particles at the surface of the carbon support comprise a core comprising the first metal and a shell at least partially surrounding the core and comprising platinum, the shell having a thickness of no more than three platinum atoms.

3. The process or catalyst as set forth in claim 1 or 2 wherein EDX line scan analysis is conducted in accordance with Protocol B.

4. The process or catalyst as set forth in any of claims 1 to 3 wherein the second metal signal or platinum signal varies by no more than about 20% across the scanning region.

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5. The process or catalyst as set forth in any of claims 1 to 3 wherein the second metal signal or platinum signal varies by no more than about 20% across a scanning region having a dimension that is at least about 60% of the largest dimension of the at least one particle.

6. The process or catalyst as set forth in claim 5 wherein the second metal signal or platinum signal varies by no more than about 15% across the scanning region.

7. The process or catalyst as set forth in any of claims 1 to 3 wherein the second metal signal or platinum signal varies by no more than about 15% across a scanning region having a dimension that is at least about 50% of the largest dimension of the at least one particle.

8. The process or catalyst as set forth in claim 7 wherein the second metal signal or platinum signal varies by no more than about 10% across the scanning region.

9. The process or catalyst as set forth in any of claims 1 to 8 wherein the atomic ratio of second metal or platinum to first metal of the at least one particle is less than 1:1.

10. The process or catalyst as set forth in any of claims 1 to 9 wherein the at least one particle has a largest dimension of at least about 6 nm.

11. The process or catalyst as set forth in any of claims 1 to 10 wherein the at least one particle constitutes at least about 1% of the metal particles at the surface of the carbon support.

12. The process or catalyst as set forth in any of claims 1 to 11 wherein the first metal distribution of the at least one metal particle as characterized by EDX line scan analysis produces a first metal signal, the ratio of the maximum first metal signal to the maximum second metal signal across the scanning region being at least about 1.5:1.

13. The process as set forth in any of claims 1 or 3 to 11, wherein the carbon support is porous, the second metal is a noble metal, the catalyst comprising one or more

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first metal regions at the surface of the carbon support and one or more noble metal regions at the surface of the one or more first metal regions, wherein the first metal has an electropositivity greater than the electropositivity of the noble metal, and wherein the oxidation catalyst is prepared by a process comprising contacting the carbon support having one or more first metal regions at its surface with a noble metal deposition bath comprising ions of the noble metal, thereby depositing the noble metal by displacement of the first metal from one or more of said regions.

14. The process of claim 13 wherein the weight ratio of the noble metal to the first metal is at least about 0.25:1.

15. The process as set forth in any of claims 1 or 3 to 11, wherein the second metal is a noble metal and wherein:

the metal particles comprise a core comprising the first metal and a shell at least partially surrounding the core and comprising the noble metal, wherein at least about 70% of the noble metal is present within the particle shell.

16. The process as set forth in any of claims 1 or 3 to 11, wherein the first metal is copper and the second metal is platinum, the support having at its surface metal particles comprising platinum and copper, wherein the atom percent of the platinum at the surface of the particles is at least about 40%.

17. The oxidation catalyst as set forth in any of claims 2 to 11, wherein the first metal is copper and the second metal is platinum, the support having at its surface metal particles comprising platinum and copper, wherein the atom percent of platinum at the surface of the particles is at least about 40% and wherein metal particles comprising platinum and copper at the surface of the carbon support comprise a core comprising copper and a shell at least partially surrounding the core and comprising platinum, the shell having a thickness of no more than three platinum atoms.

18. The process or catalyst as set forth in any of claims 1 or 3 to 15 wherein the first metal is selected from the group consisting of vanadium, tungsten, molybdenum, gold, osmium, iridium, tantalum, palladium, ruthenium, antimony, bismuth, arsenic, mercury,

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silver, copper, titanium, tin, lead, germanium, zirconium, cerium, nickel, cobalt, iron, chromium, zinc, manganese, aluminum, beryllium, magnesium, lithium, barium, cesium, and combinations thereof.

19. The process or catalyst as set forth in claim 18 wherein the first metal is selected from the group consisting of copper, tin, nickel, cobalt, and combinations thereof.

20. The process or catalyst as set forth in claim 18 wherein the first metal is selected from the group consisting of cobalt, copper, iron, and combinations thereof.

21. The process or catalyst as set forth in any of claims 1 to 15 or 18 to 20 wherein the first metal is copper.

22. The process or catalyst as set forth in any of claims 1 to 15 or 18 to 20 wherein the first metal is iron.

23. The process or catalyst as set forth in any of claims 1 to 15 or 18 to 20 wherein the first metal is cobalt.

24. The process or catalyst as set forth in any of claims 1 to 23 wherein the first metal or copper constitutes at least about 1% by weight of the catalyst.

25. The process or catalyst as set forth in any of claims 1 to 24 wherein the first metal or copper constitutes from about 1% to about 10% by weight of the catalyst.

26. The process or catalyst as set forth in any of claims 1, 3 to 12, or 18 to 25 wherein the second metal is a noble metal.

27. The process or catalyst as set forth in claim 26 wherein the noble metal is selected from the group consisting of platinum, palladium, ruthenium, rhodium, iridium, silver, osmium, gold, and combinations thereof.

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28. The process or catalyst as set forth in claim 26 wherein the noble metal comprises platinum, palladium, or platinum and palladium.

29. The process or catalyst as set forth in claim 26 wherein the noble metal is platinum.

30. The process or catalyst as set forth in any of claims 1 to 29 wherein the second metal, noble metal, or platinum constitutes at least about 1% by weight of the catalyst.

31. The process or catalyst as set forth in any of claims 1 to 30 wherein the second metal, noble metal, or platinum constitutes less than about 8% by weight of the catalyst.

32. The process or catalyst as set forth in any of claims 1 to 31 wherein the second metal, noble metal, or platinum constitutes from about 3% to about 6% by weight of the catalyst.

33. The process as set forth in any of claims 1, 3 to 16, or 18 to 32 wherein the second metal, noble metal, or platinum constitutes from about 1% to about 5% by weight of the catalyst.

34. The process as set forth in any of claims 1, 3 to 16, or 18 to 33 wherein the substrate is N-(phosphonomethyl)iminodiacetic acid or a salt thereof.

35. The process as set forth in claim 34 wherein said oxidation catalyst is effective for oxidation of byproduct formaldehyde and/or formic acid produced in the oxidation of N-(phosphonomethyl)iminodiacetic acid or a salt thereof.

FIG. 1A

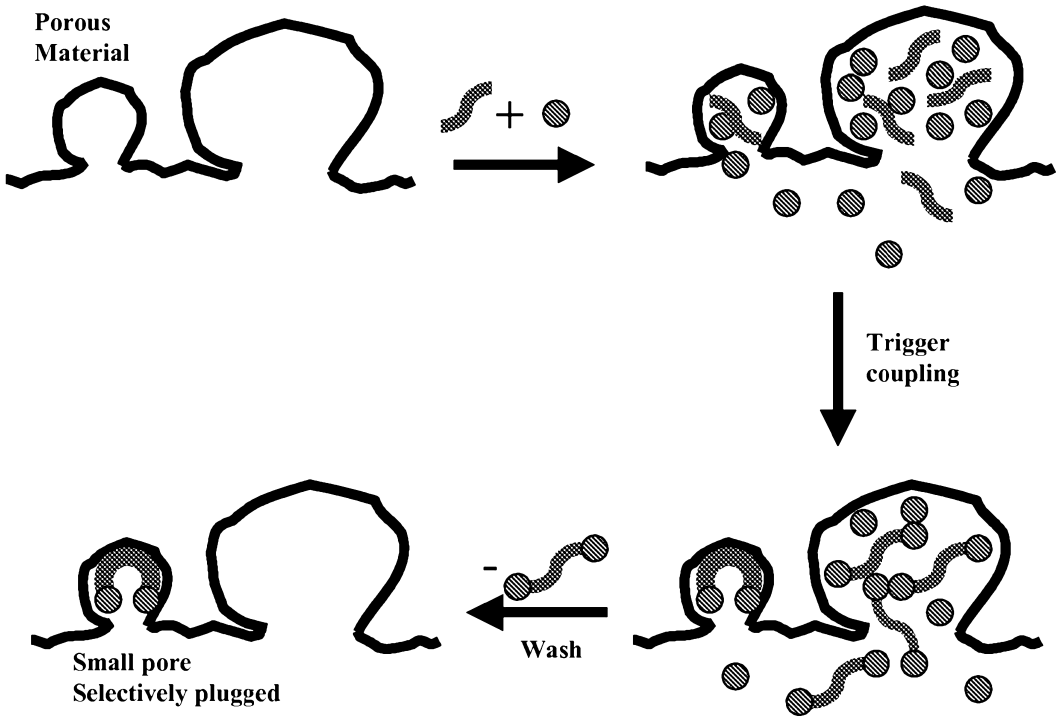

Mechanism One: *In-Situ* Coupling
Porous
Material
+
Trigger
coupling
-
Wash
Small pore
Selectively plugged

FIG. 1B

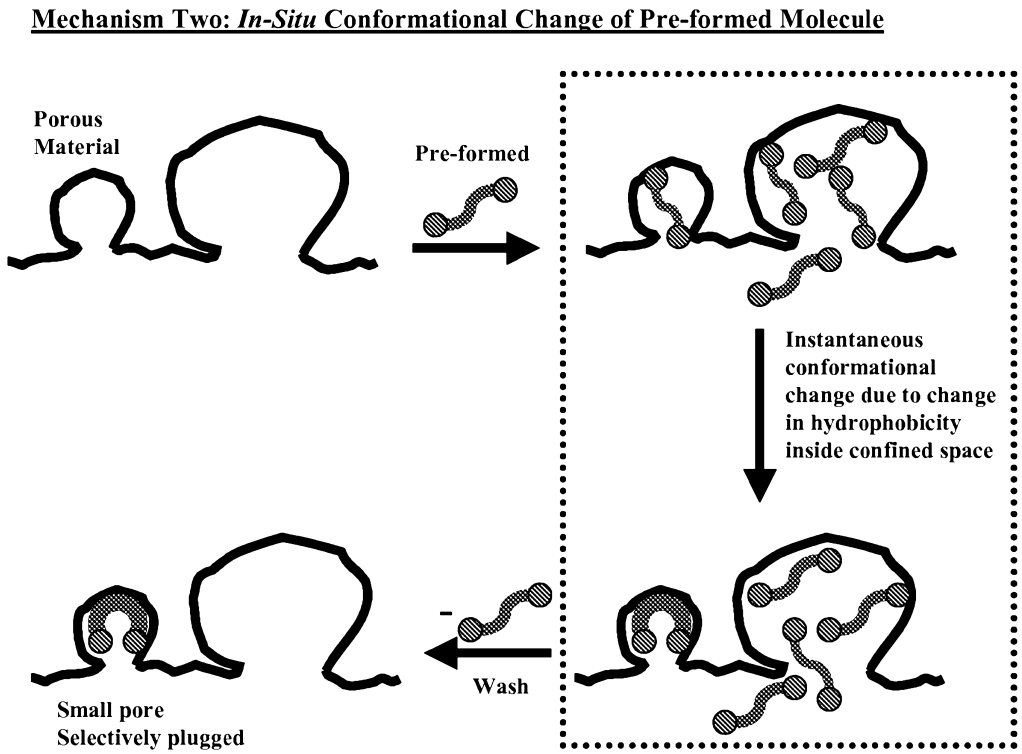

Mechanism Two: *In-Situ* Conformational Change of Pre-formed Molecule
Porous Material
Pre-formed
Instantaneous conformational change due to change in hydrophobicity inside confined space
Wash
Small pore Selectively plugged

FIG. 1C

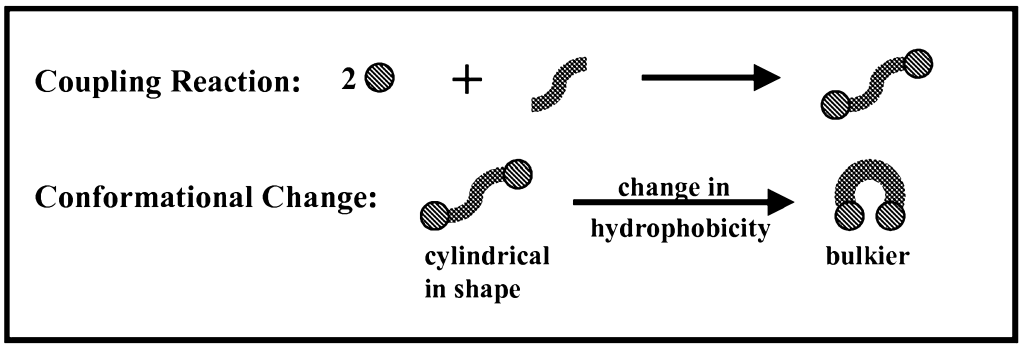

Coupling Reaction:
2
Conformational Change:
change in hydrophobicity
cylindrical in shape
bulkier

FIG. 1D

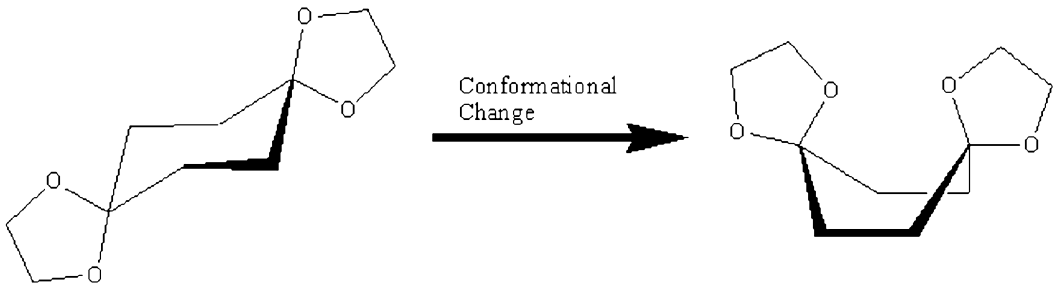


FIG.2

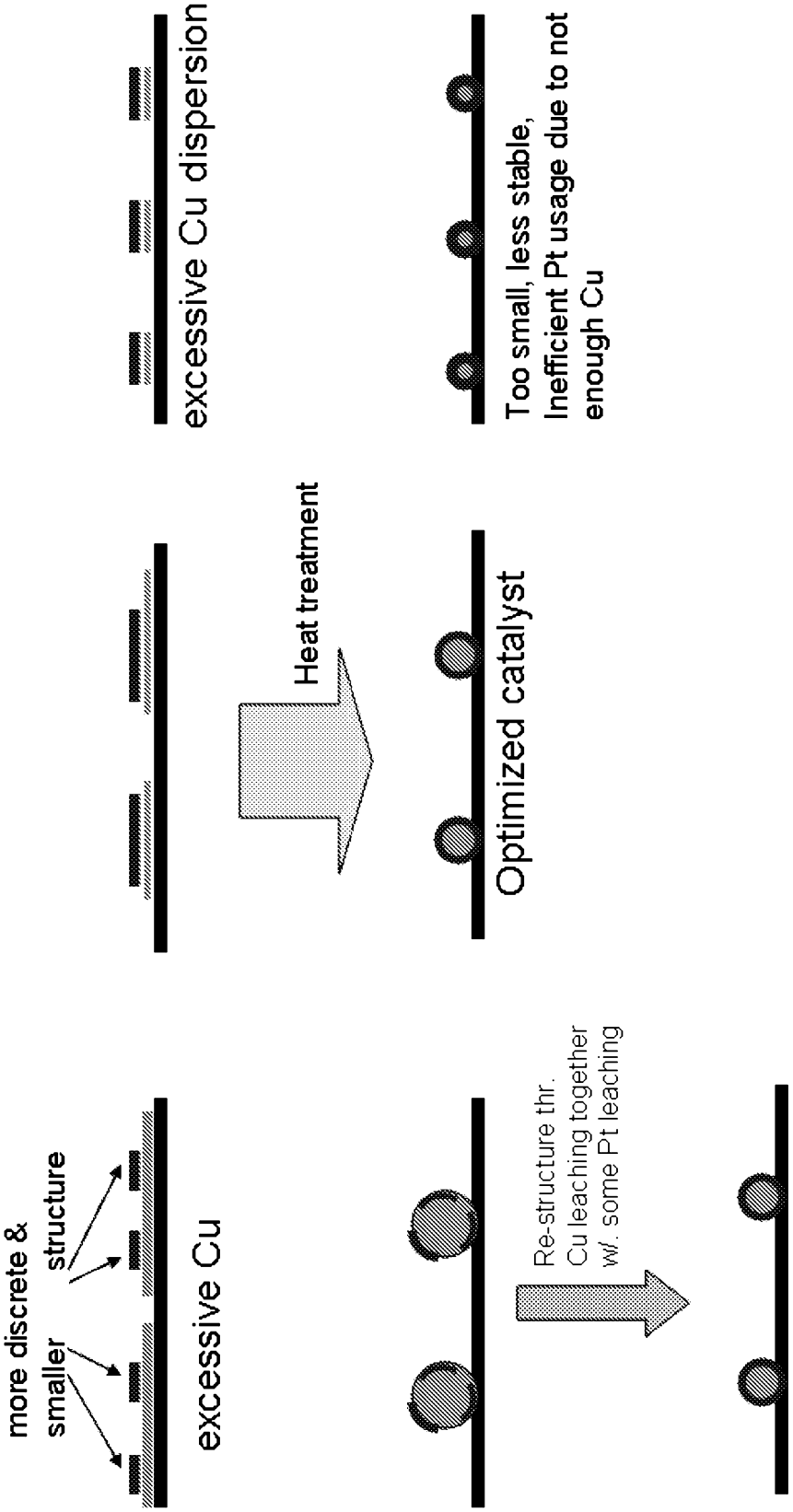

more discrete &
smaller
structure
excessive Cu
Heat treatment
excessive Cu dispersion
Too small, less stable,
Inefficient Pt usage due to not
enough Cu
Optimized catalyst
Re-structure thr.
Cu leaching together
w/. some Pt leaching

FIG. 3A

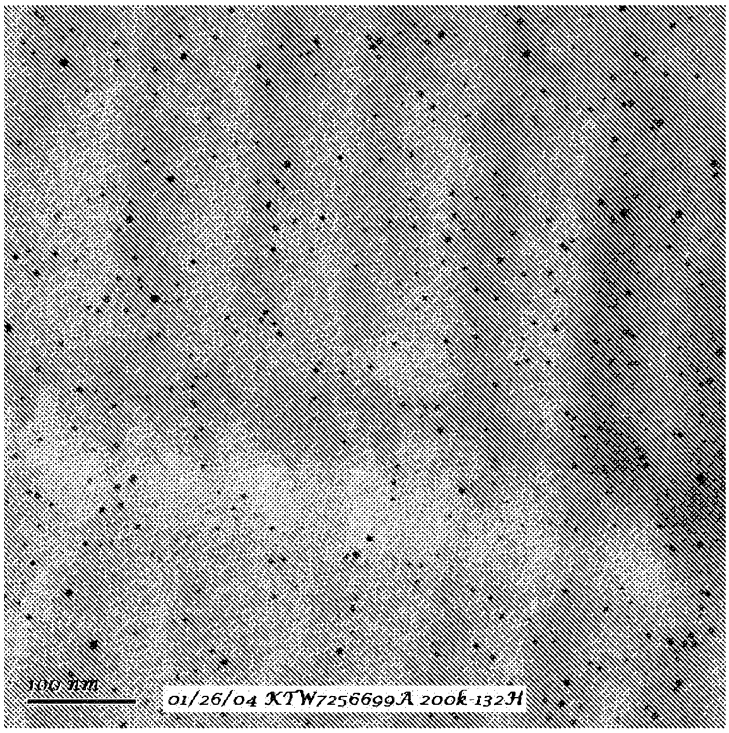

100 nm
01/26/04 KTW7256699A 200k 132H

FIG. 3B

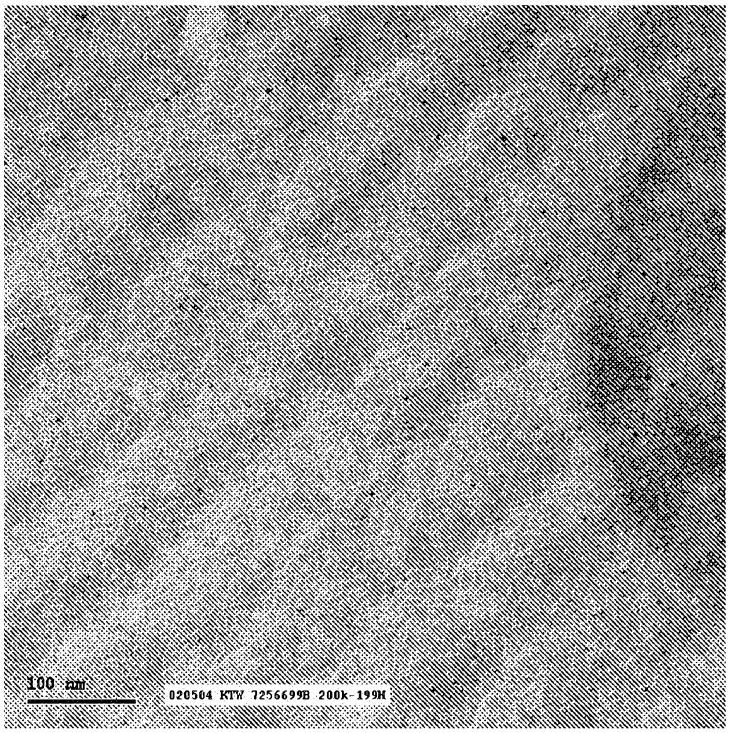

100 nm
020504 KTW 7256699B 200k-199H

FIG. 4A

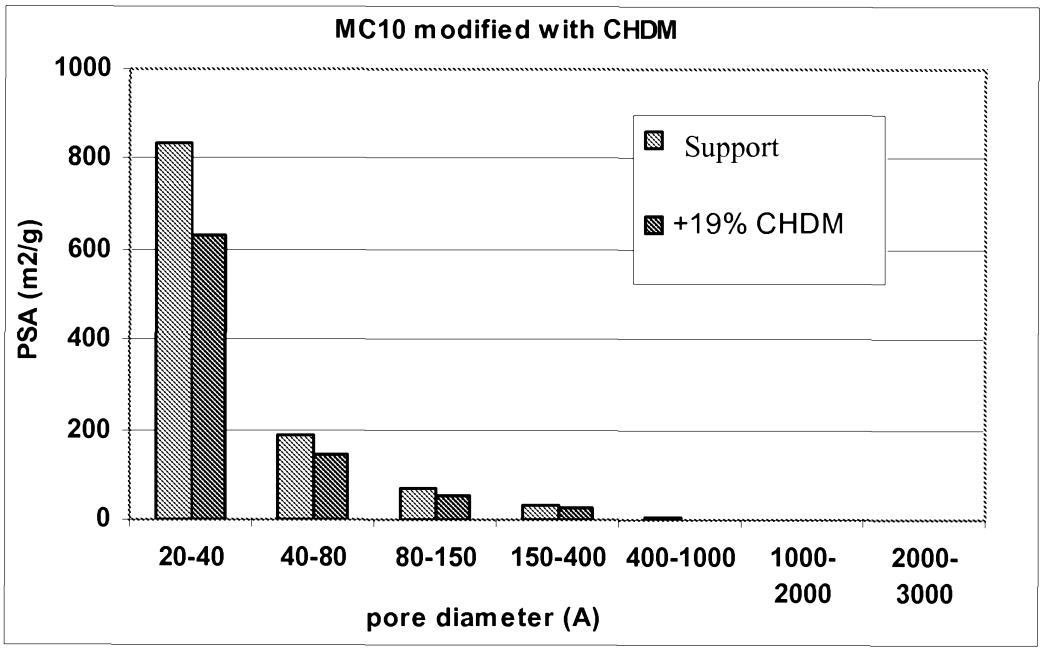

MC10 modified with CHDM
PSA (m2/g)
1000
800
600
400
200
0
Support
+19% CHDM
20-40
40-80
80-150
150-400
400-1000
1000-2000
2000-3000
pore diameter (A)

FIG. 4B

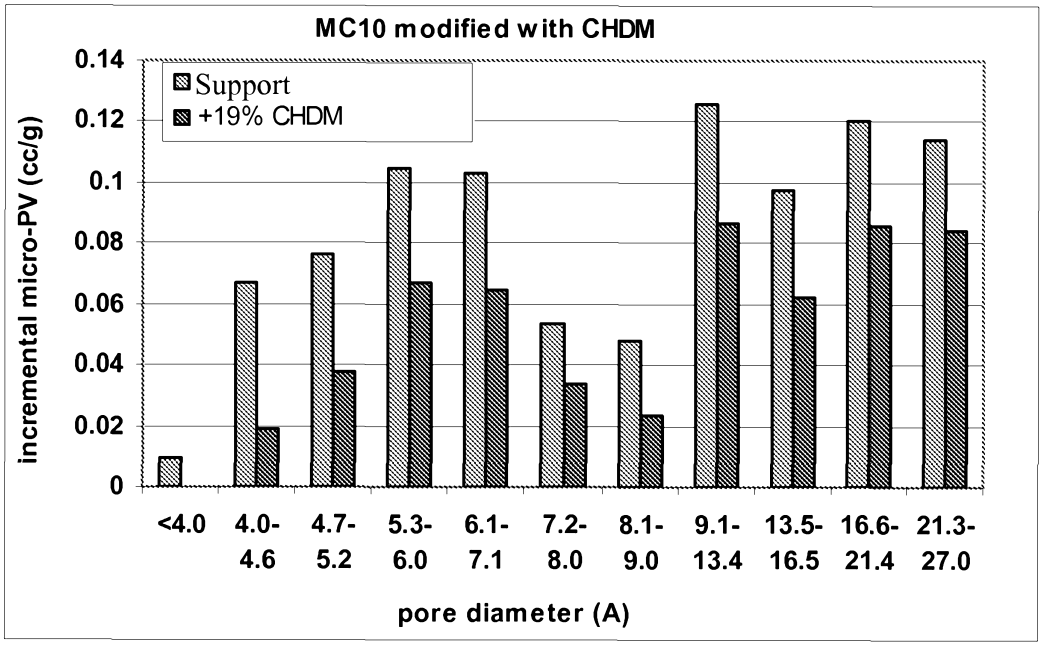

MC10 modified with CHDM
incremental micro-PV (cc/g)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Support
+19% CHDM
<4.0
4.0-4.6
4.7-5.2
5.3-6.0
6.1-7.1
7.2-8.0
8.1-9.0
9.1-13.4
13.5-16.5
16.6-21.4
21.3-27.0
pore diameter (A)

FIG. 5A

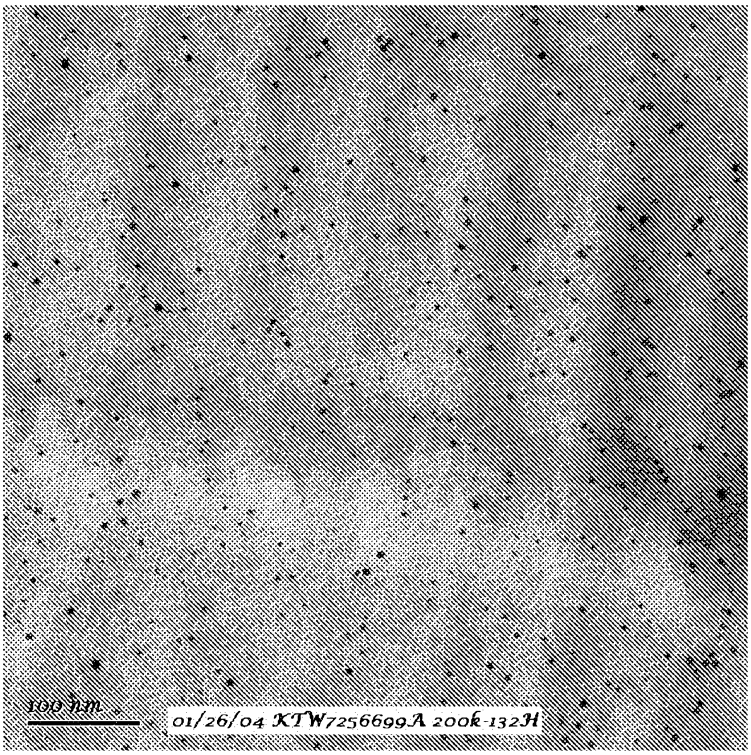

100 nm
01/26/04 KTW7256699A 200k-132H

FIG. 5B

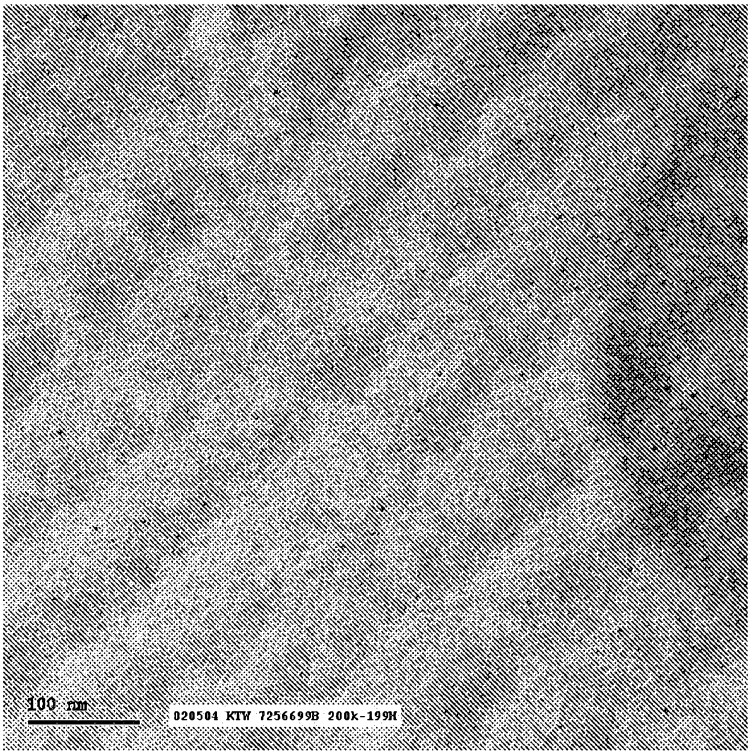

100 nm
020504 KTW 7256699B 200k-199H

FIG. 5C

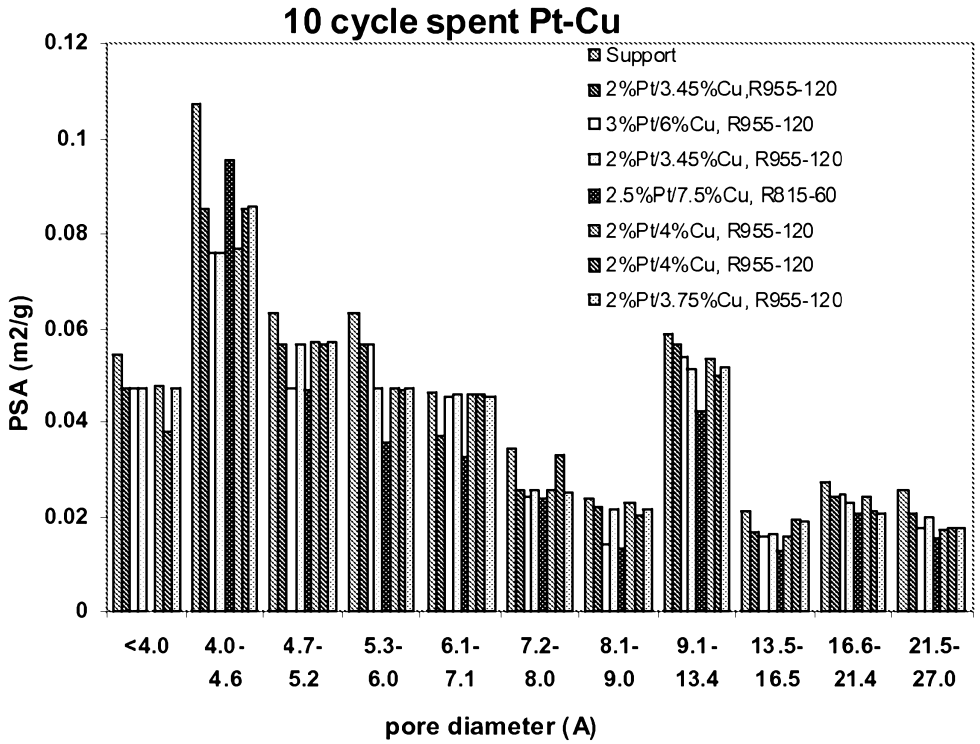

10 cycle spent Pt-Cu
Support
2%Pt/3.45%Cu,R955-120
3%Pt/6%Cu, R955-120
2%Pt/3.45%Cu, R955-120
2.5%Pt/7.5%Cu, R815-60
2%Pt/4%Cu, R955-120
2%Pt/4%Cu, R955-120
2%Pt/3.75%Cu, R955-120
PSA (m2/g)
0.12
0.1
0.08
0.06
0.04
0.02
0
<4.0
4.0-4.6
4.7-5.2
5.3-6.0
6.1-7.1
7.2-8.0
8.1-9.0
9.1-13.4
13.5-16.5
16.6-21.4
21.5-27.0
pore diameter (A)

FIG. 5D

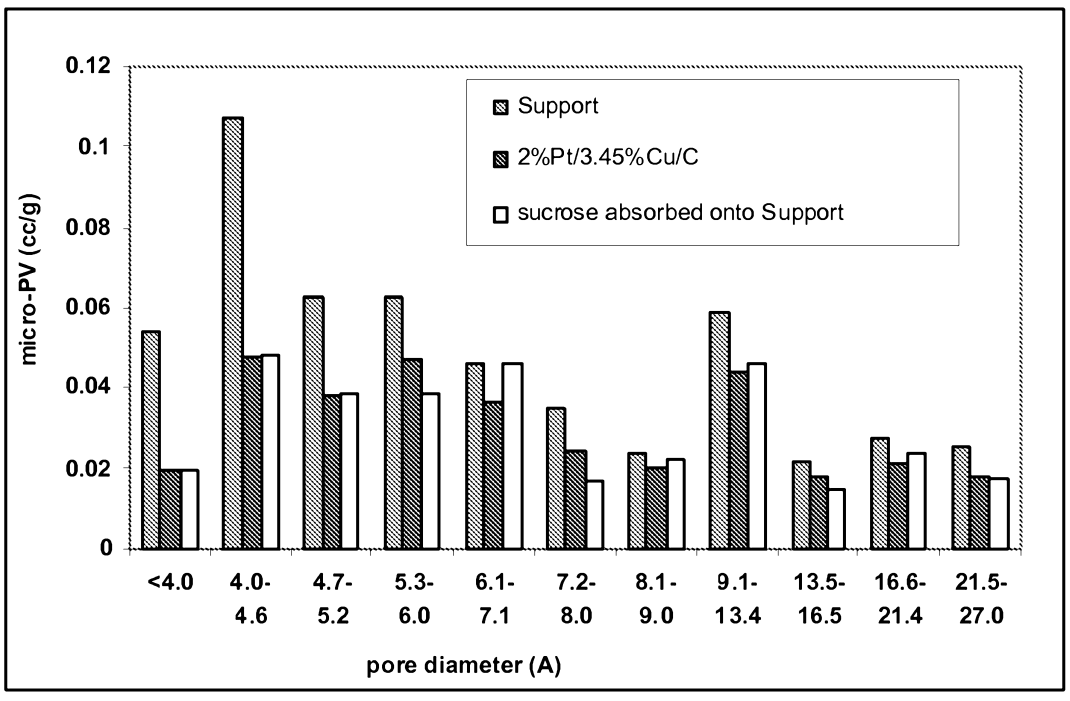

Support
2%Pt/3.45%Cu/C
sucrose absorbed onto Support
micro-PV (cc/g)
0.12
0.1
0.08
0.06
0.04
0.02
0
<4.0
4.0-4.6
4.7-5.2
5.3-6.0
6.1-7.1
7.2-8.0
8.1-9.0
9.1-13.4
13.5-16.5
16.6-21.4
21.5-27.0
pore diameter (A)

FIG. 6

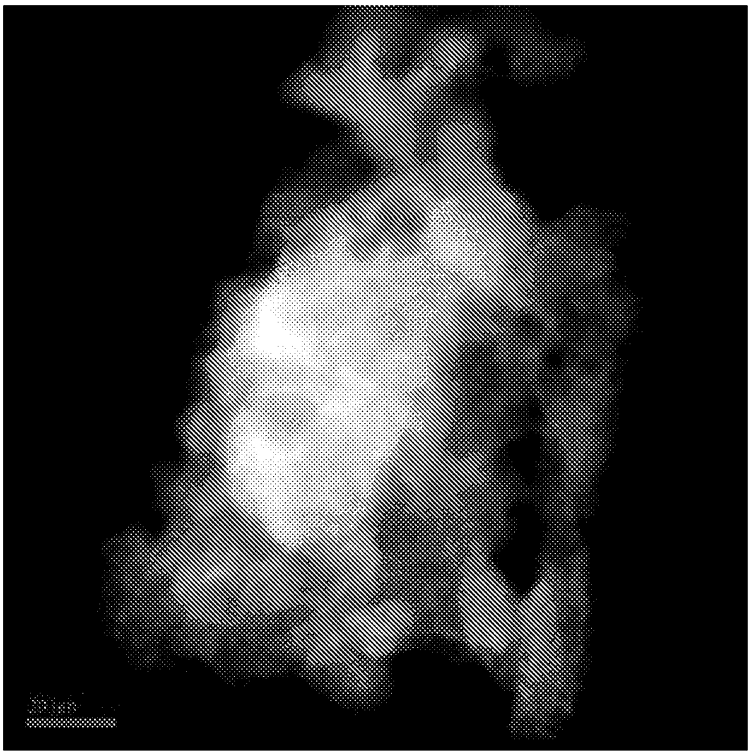


FIG. 7

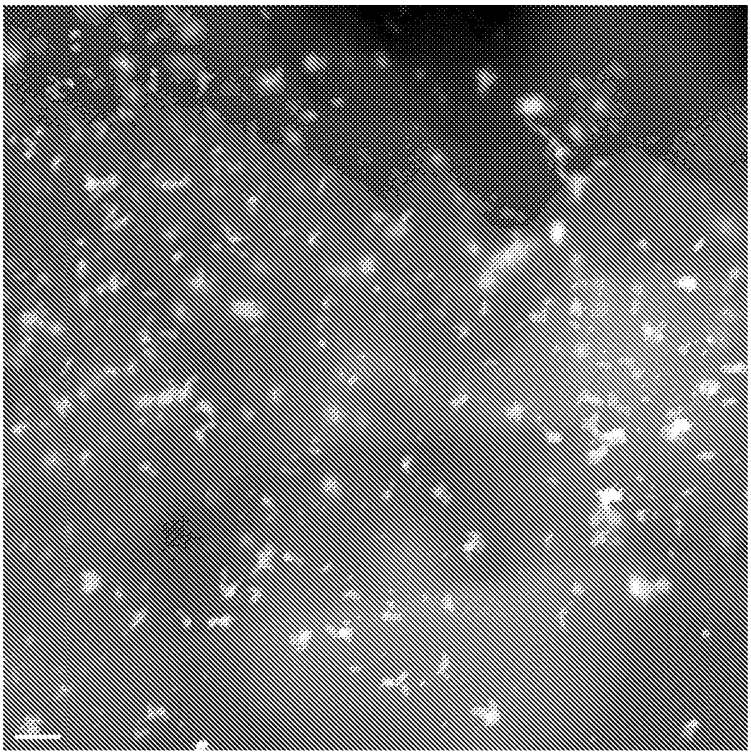


FIG. 8

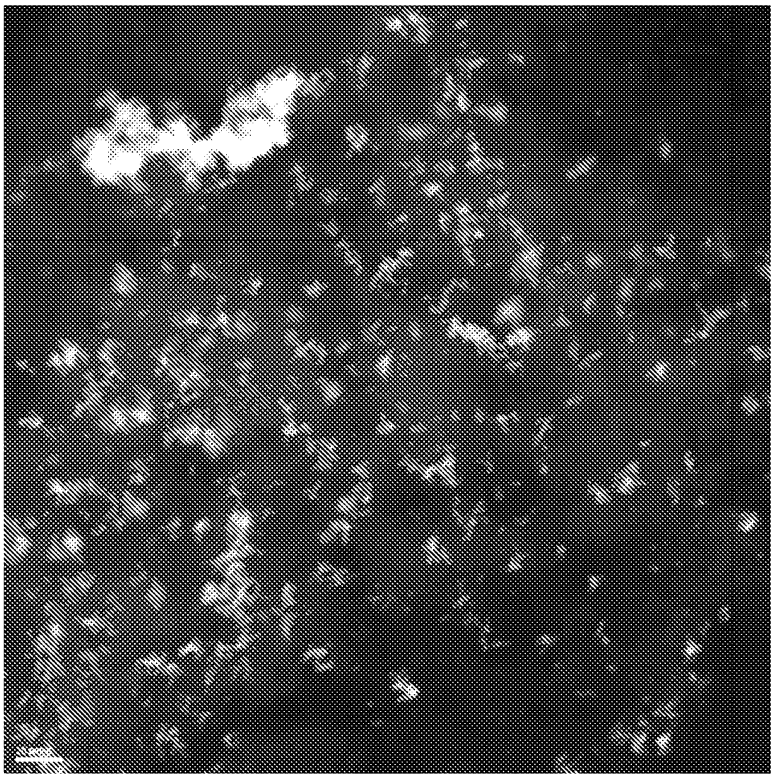


FIG. 9

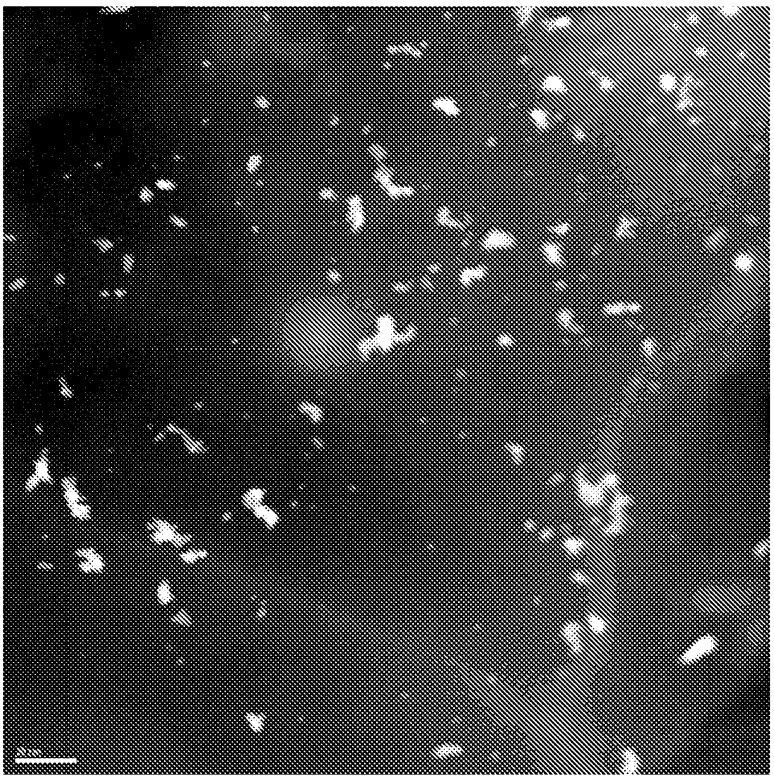


FIG. 10

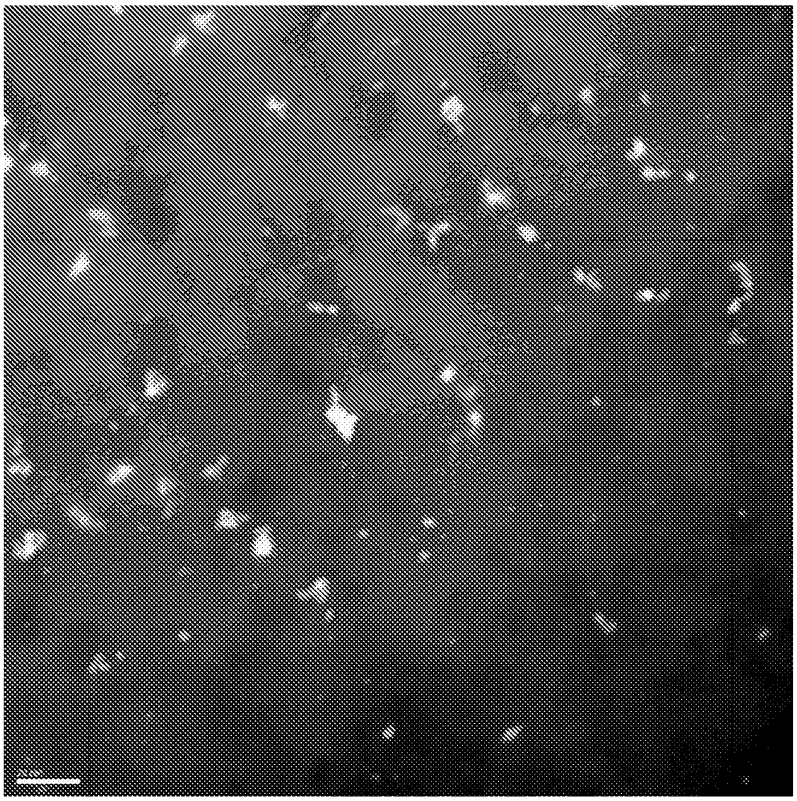


FIG. 11

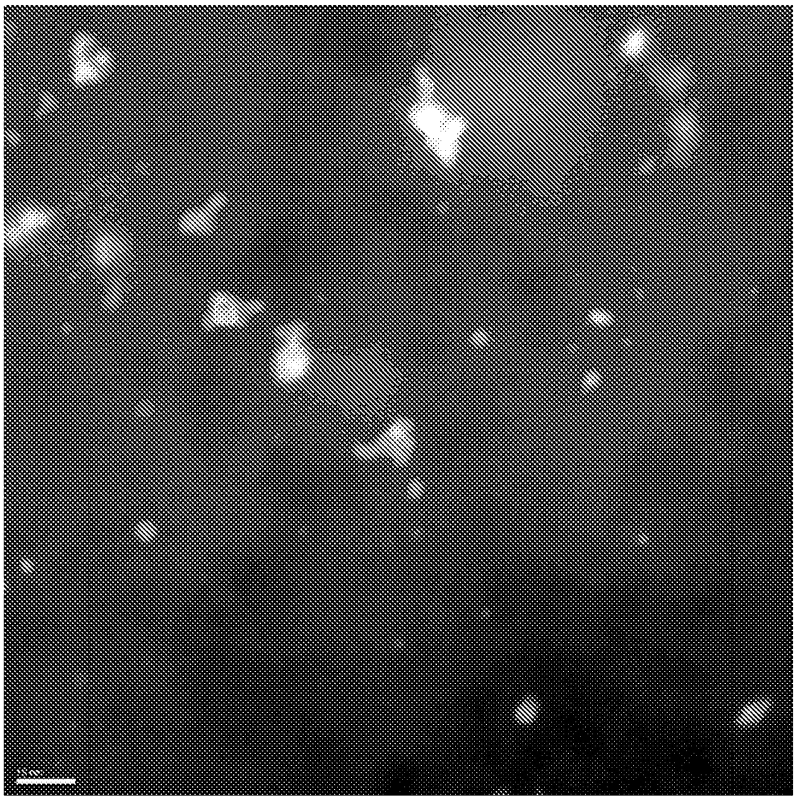


FIG. 12

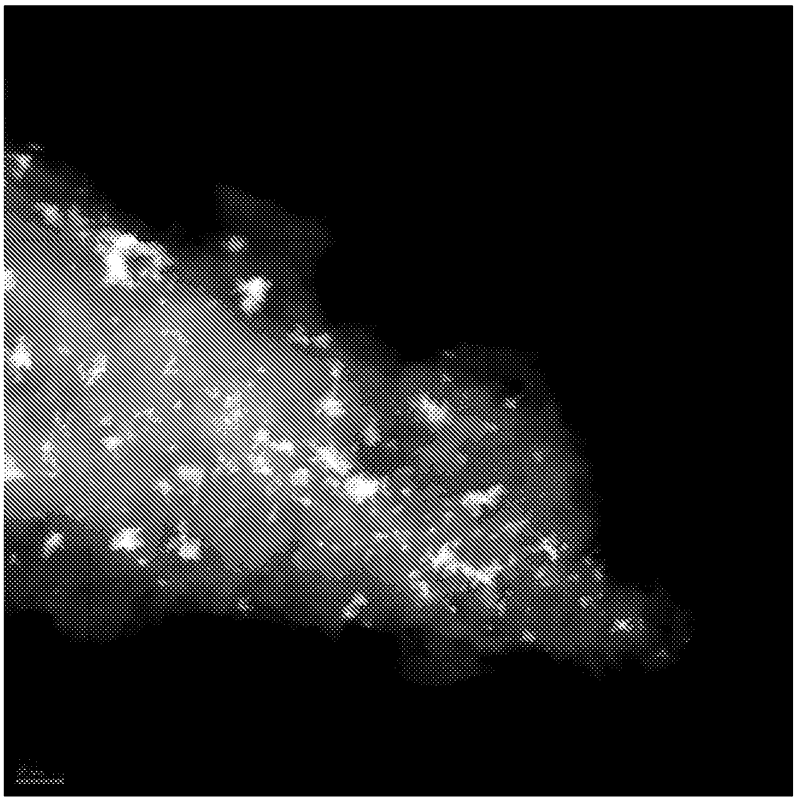


FIG. 13

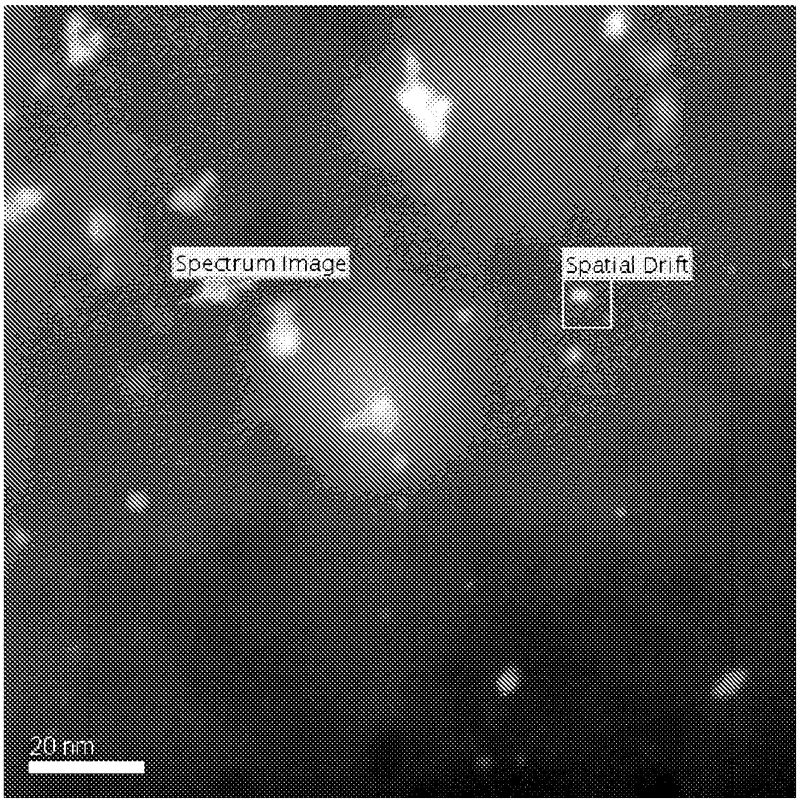


FIG. 14

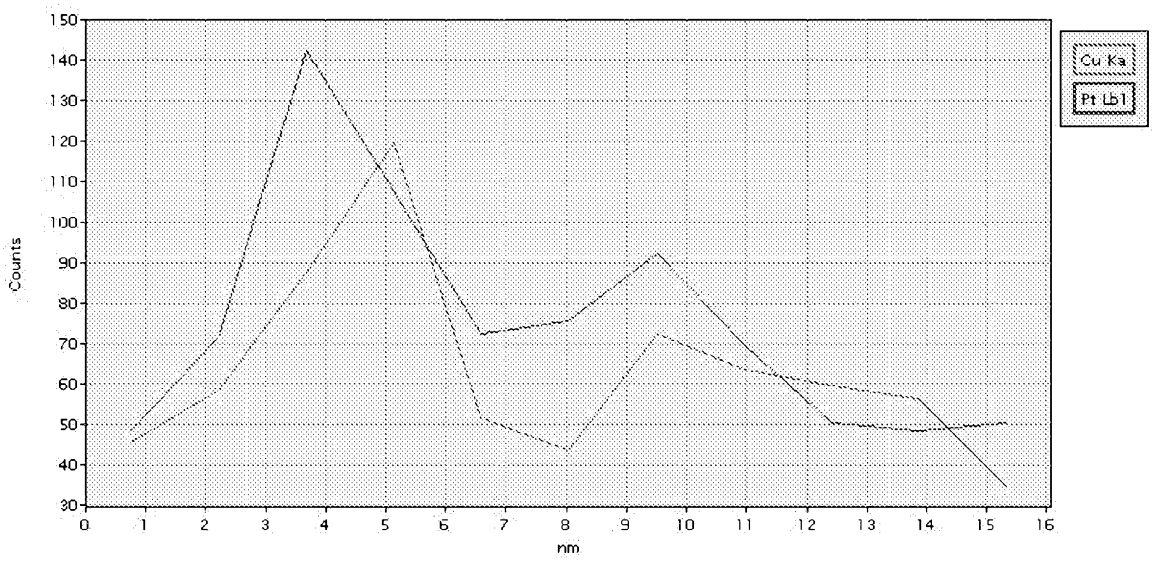


FIG. 15

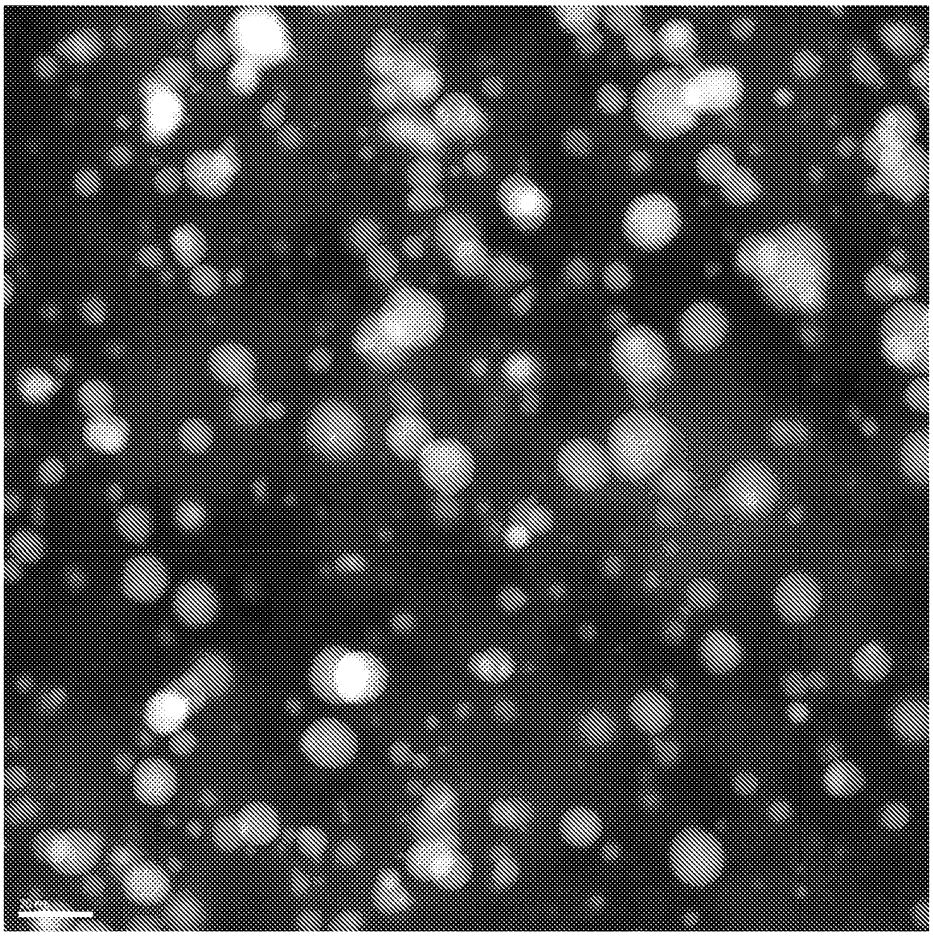


FIG. 16

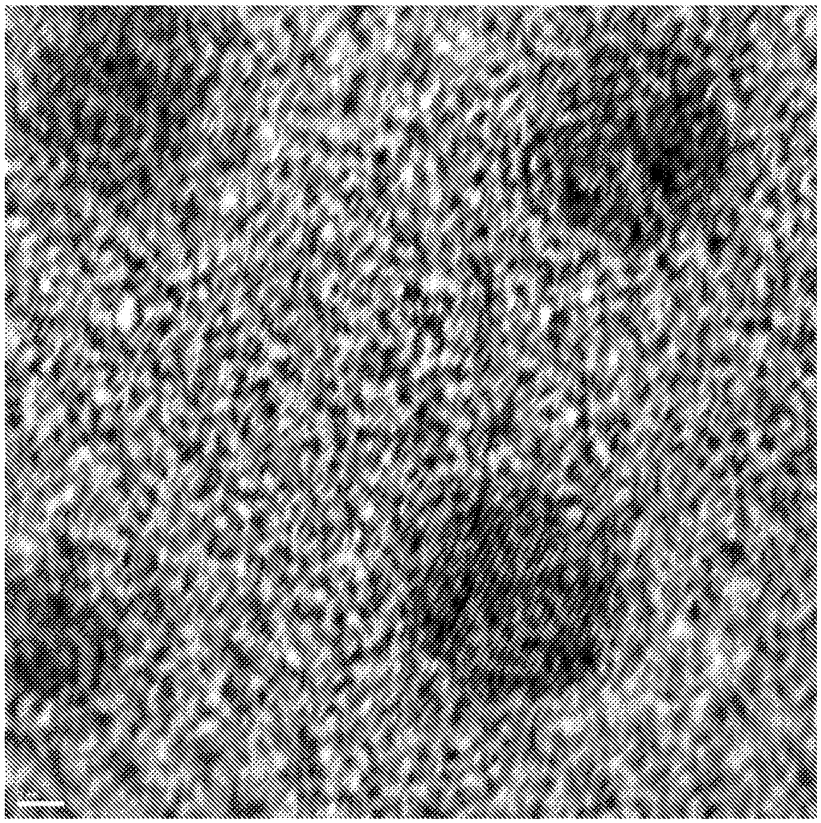


FIG. 17

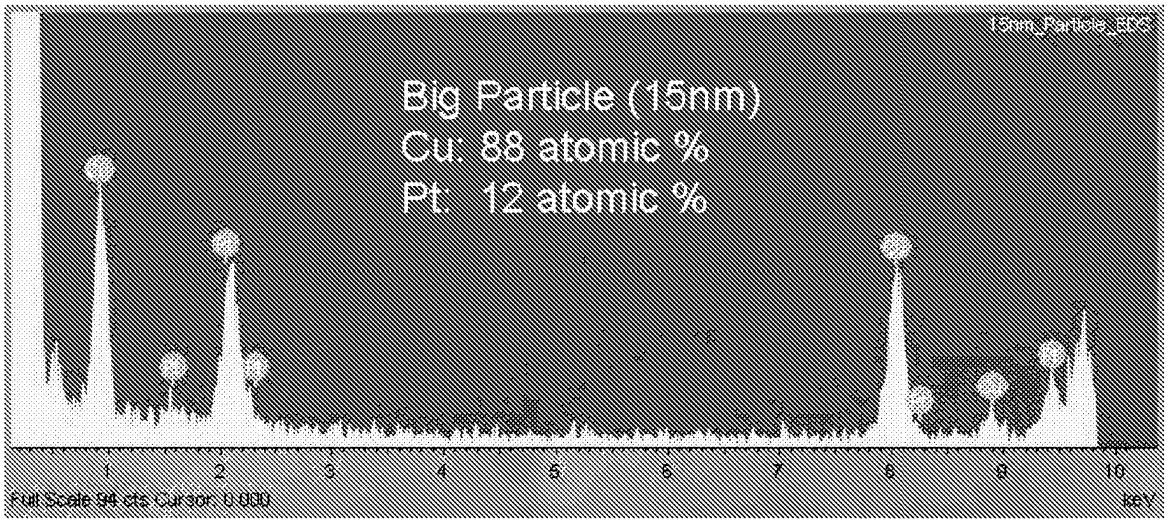

15nm_Particle_EDS
Big Particle (15nm)
Cu: 88 atomic %
Pt: 12 atomic %
1
2
3
4
5
6
7
8
9
10
Full Scale 94 cts Cursor: 0.000
keV

FIG. 18

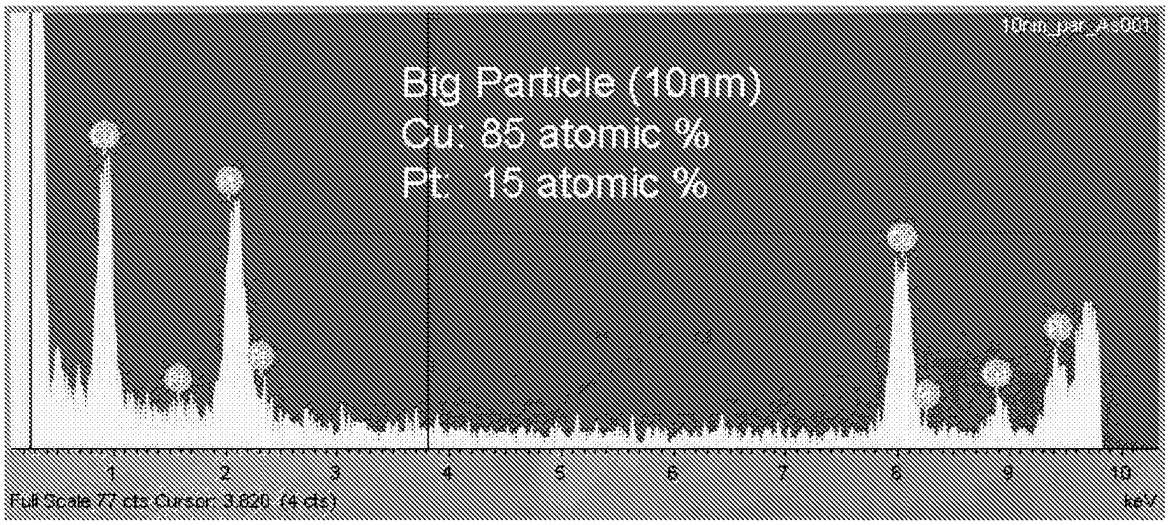


FIG. 19

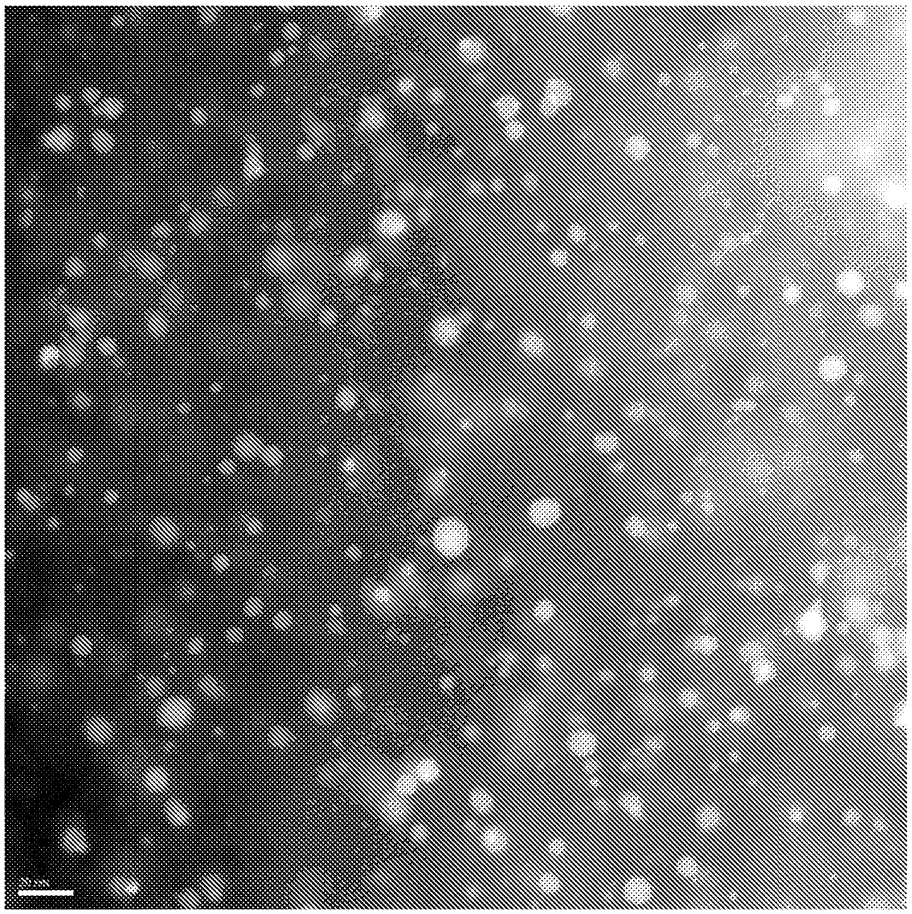


FIG. 20

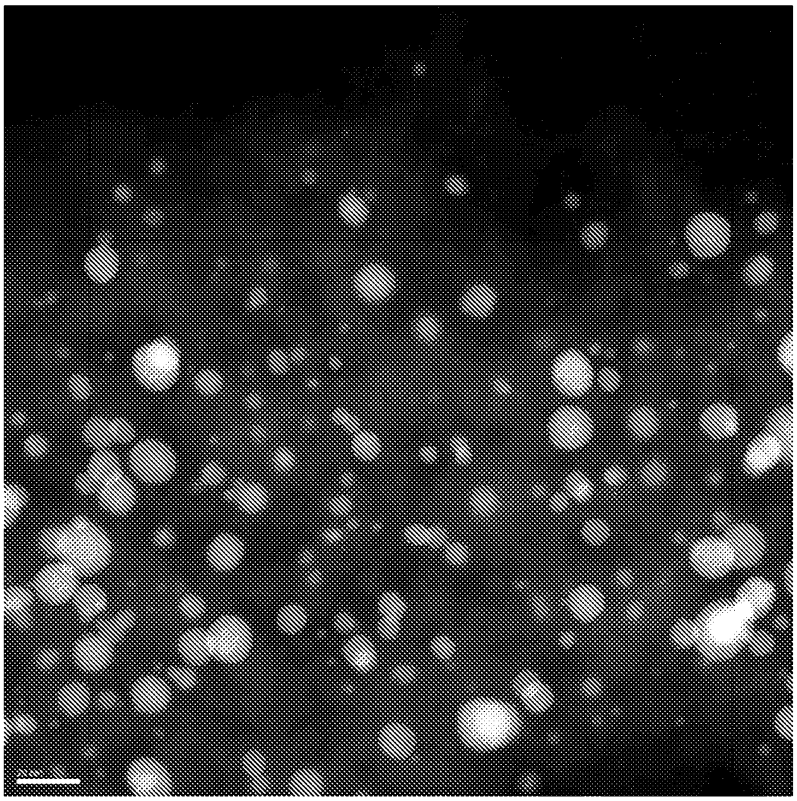


FIG. 21

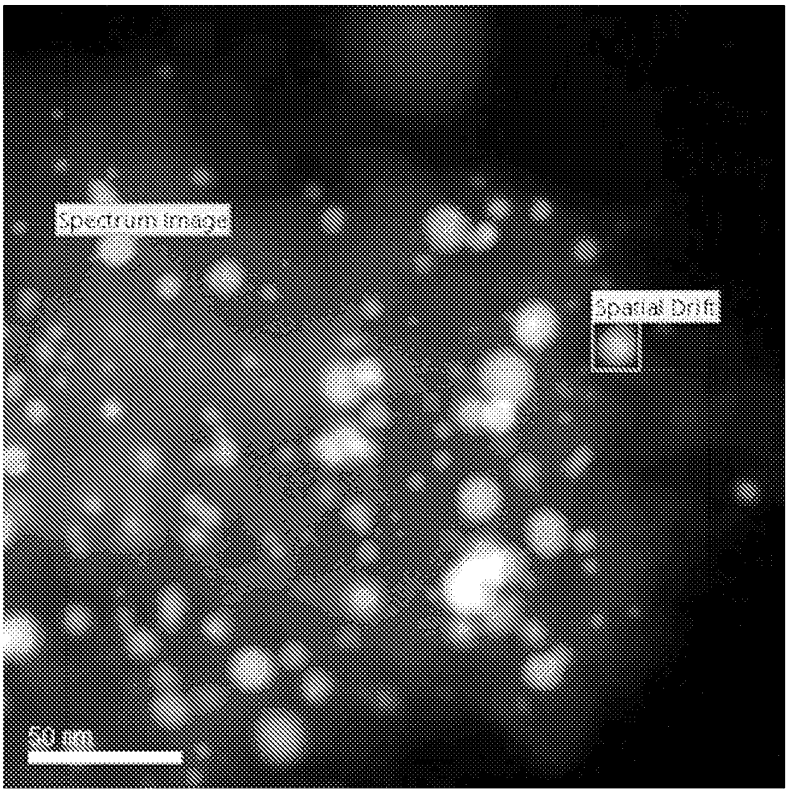


FIG. 22

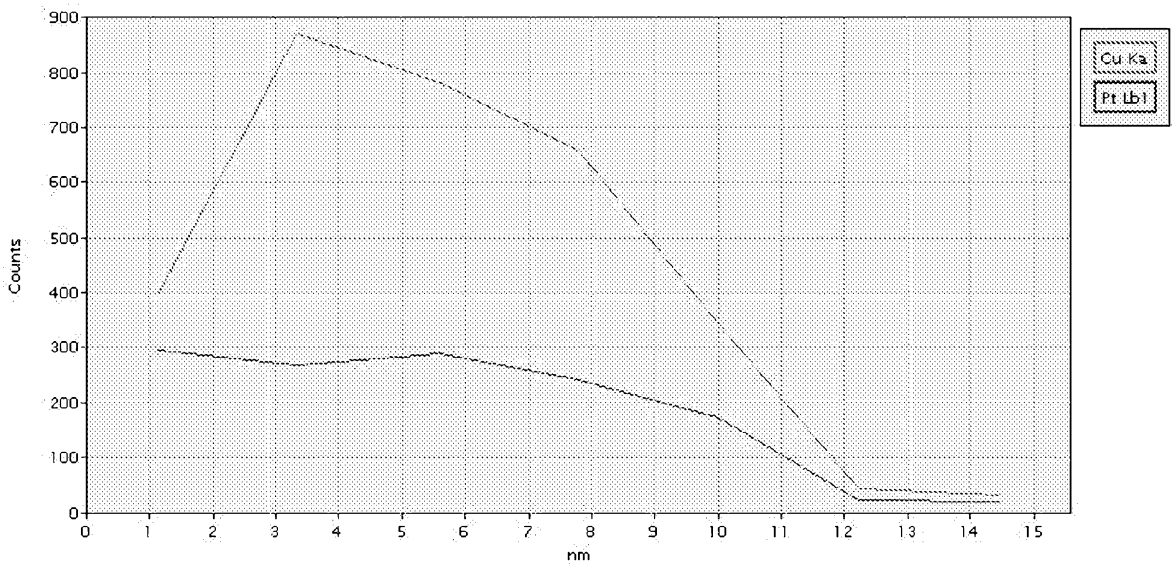


FIG. 23

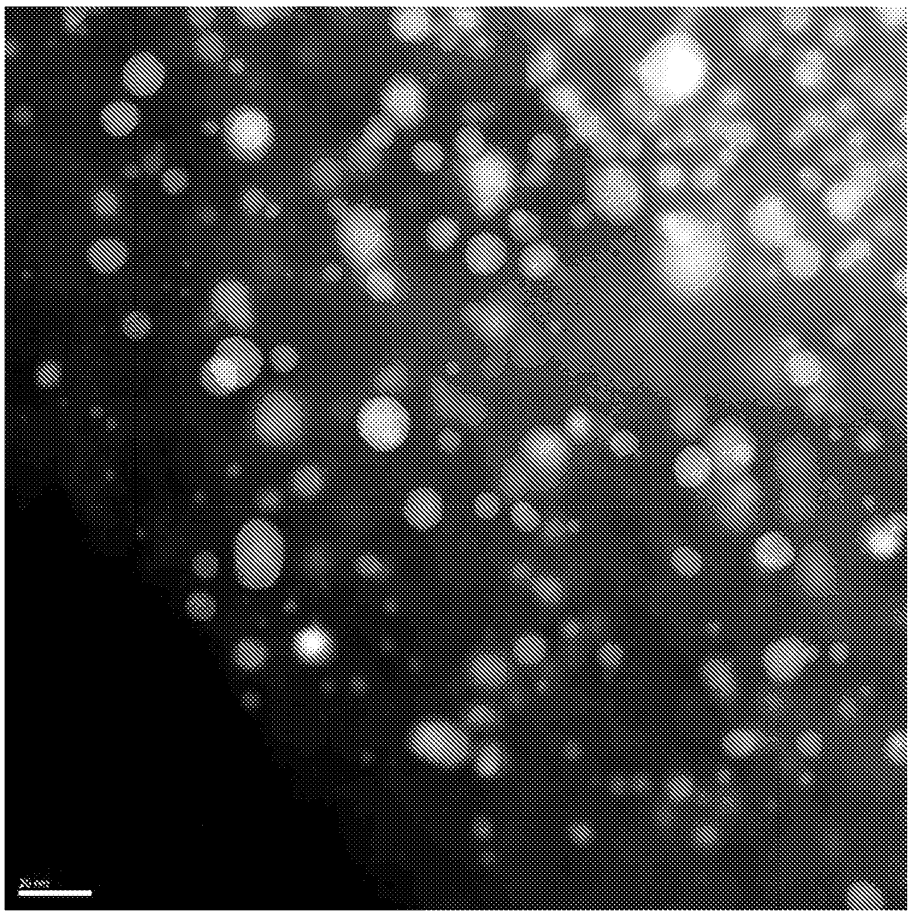


FIG. 24

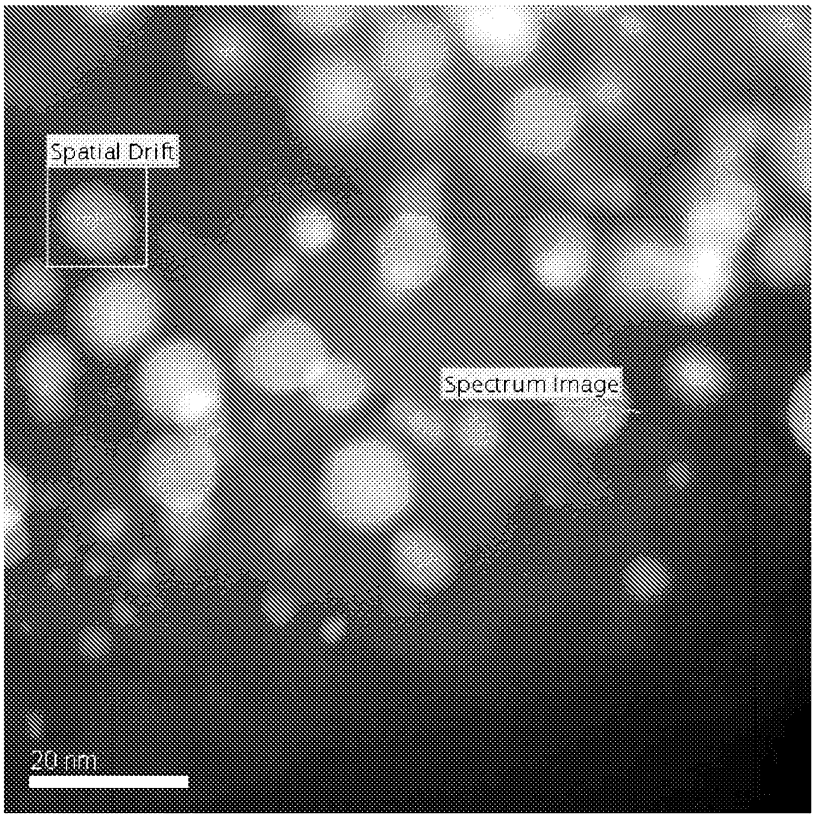

Spatial Drift
Spectrum Image
20 nm

FIG. 25

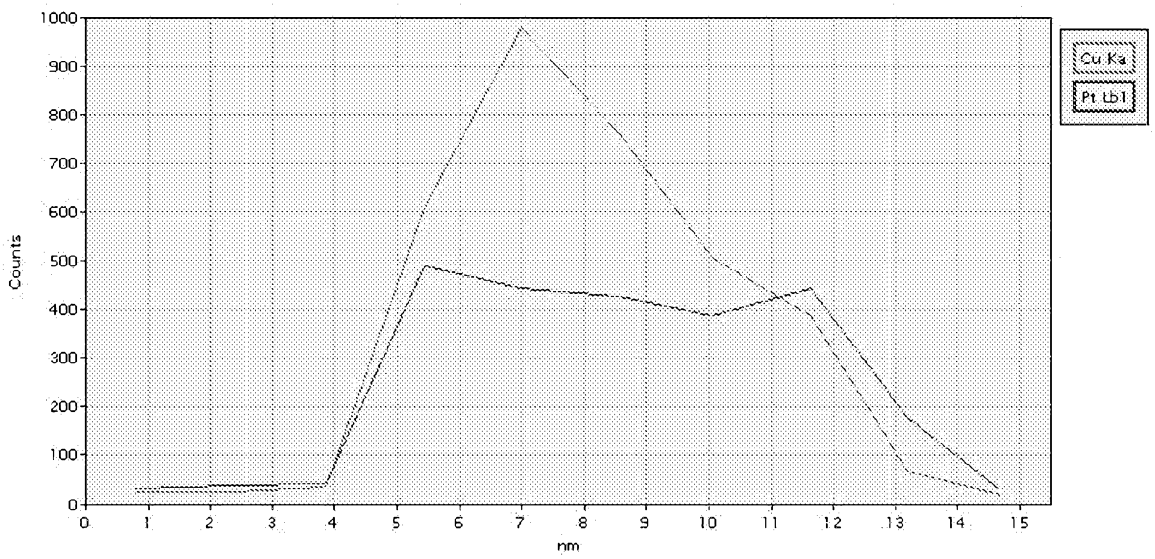

Cu Ka
Pt Lb1
Counts
nm
0
100
200
300
400
500
600
700
800
900
1000
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

FIG. 26

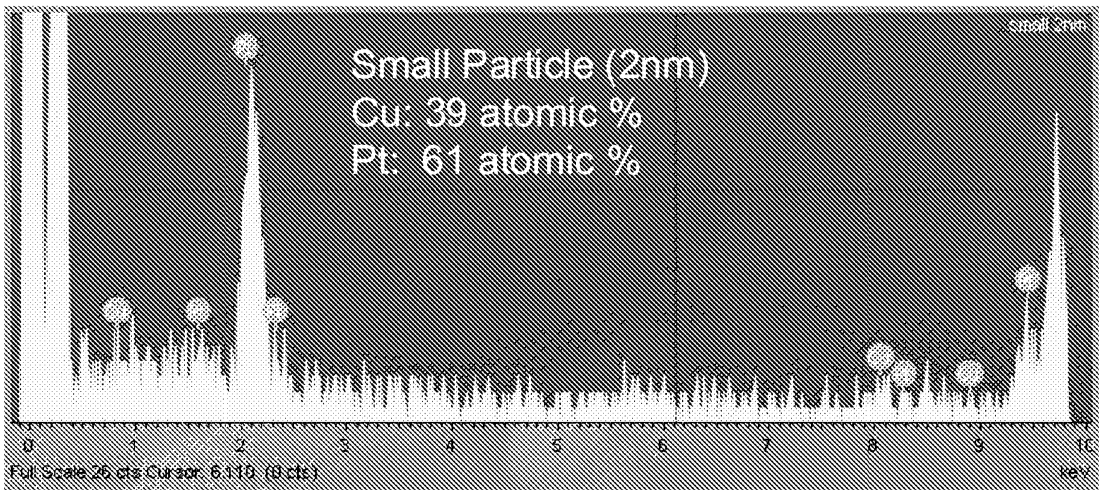

Small 2nm
Small Particle (2nm)
Cu: 39 atomic %
Pt: 61 atomic %
0 1 2 3 4 5 6 7 8 9 10
Full Scale 26 cts Cursor: 6.110 (0 cts)
keV

FIG. 27

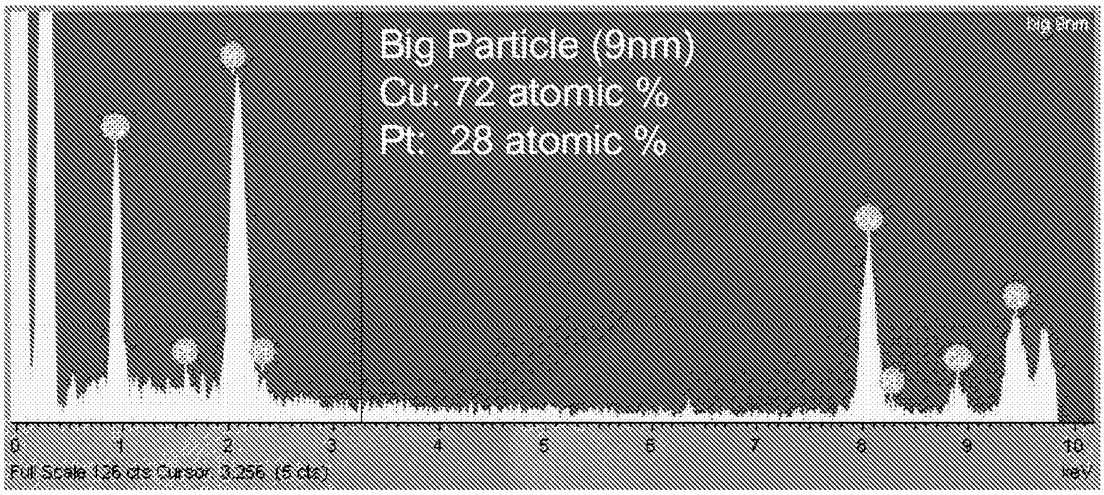

Big 9nm
Big Particle (9nm)
Cu: 72 atomic %
Pt: 28 atomic %
0 1 2 3 4 5 6 7 8 9 10
Full Scale 126 cts Cursor: 3.256 (5 cts)
keV

FIG. 28

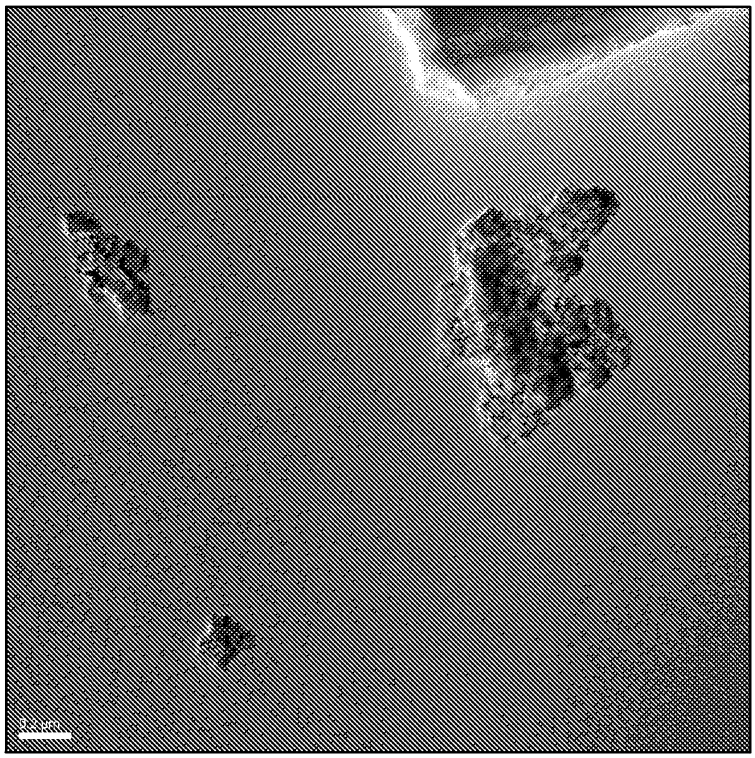


FIG. 29

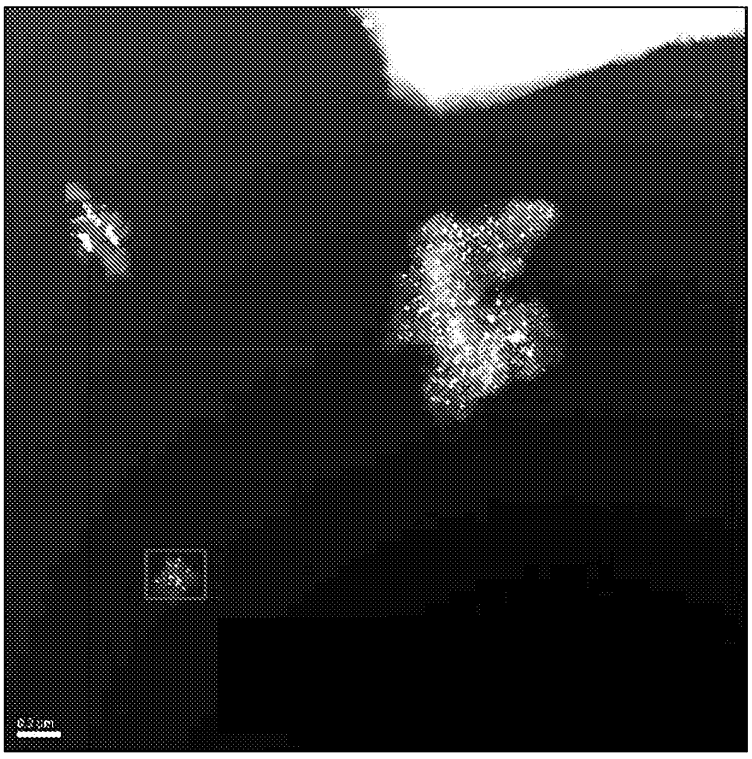


FIG. 30

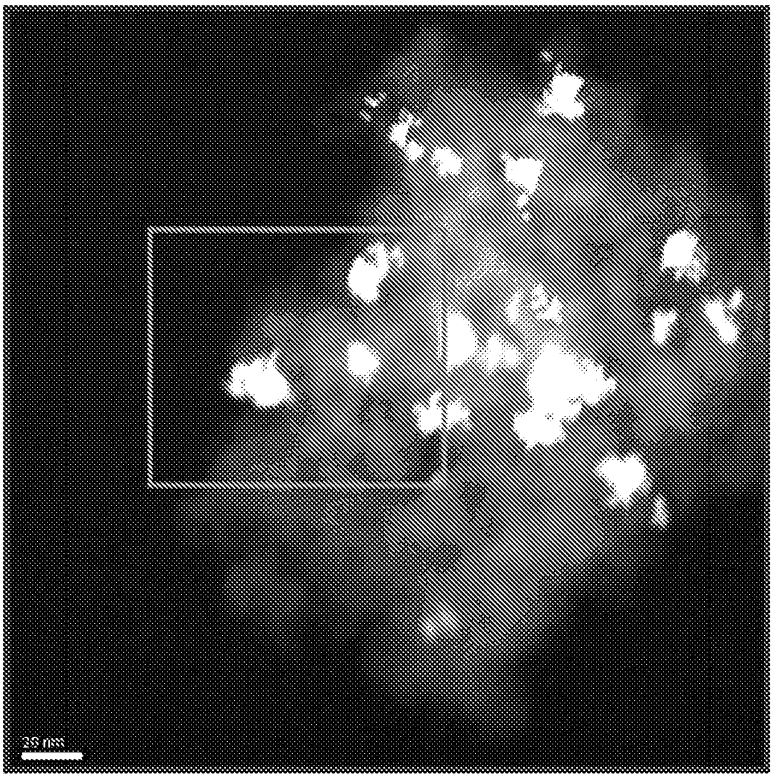

38 nm

FIG. 31

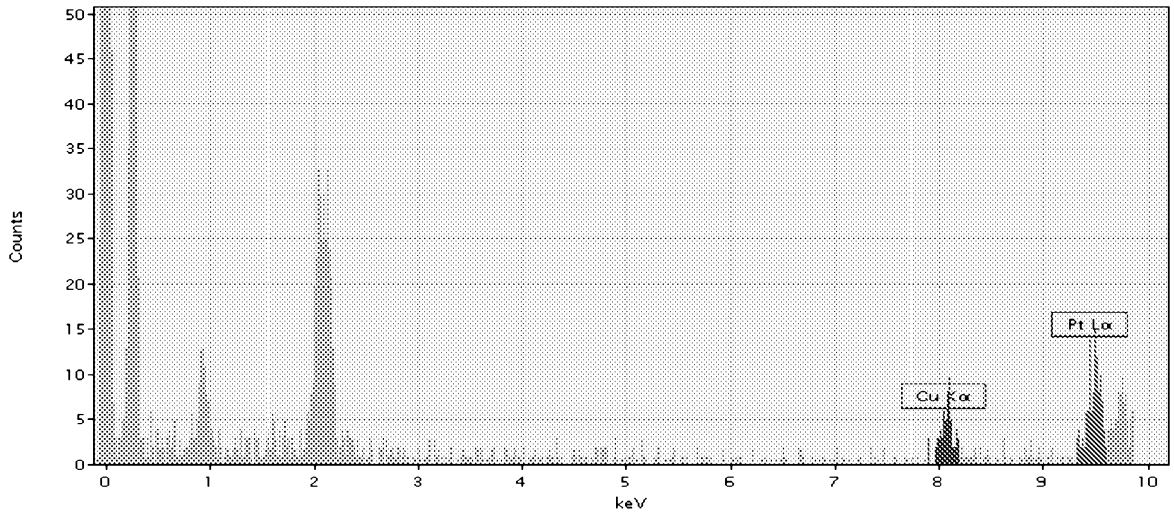

Counts
keV
Cu Kα
Pt Lα
0
5
10
15
20
25
30
35
40
45
50
0
1
2
3
4
5
6
7
8
9
10

FIG. 32

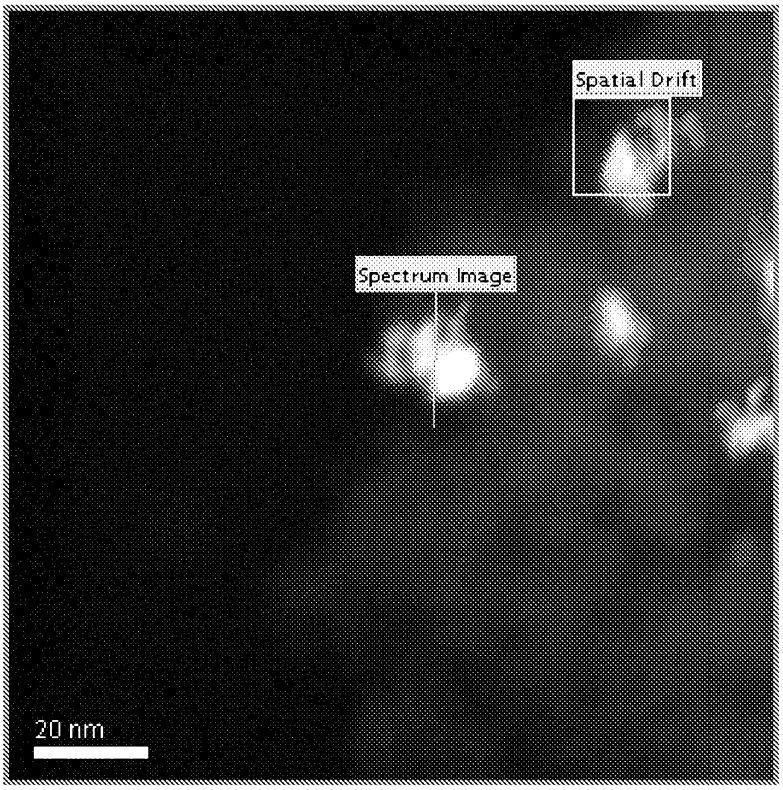

Spatial Drift
Spectrum Image
20 nm

FIG. 33

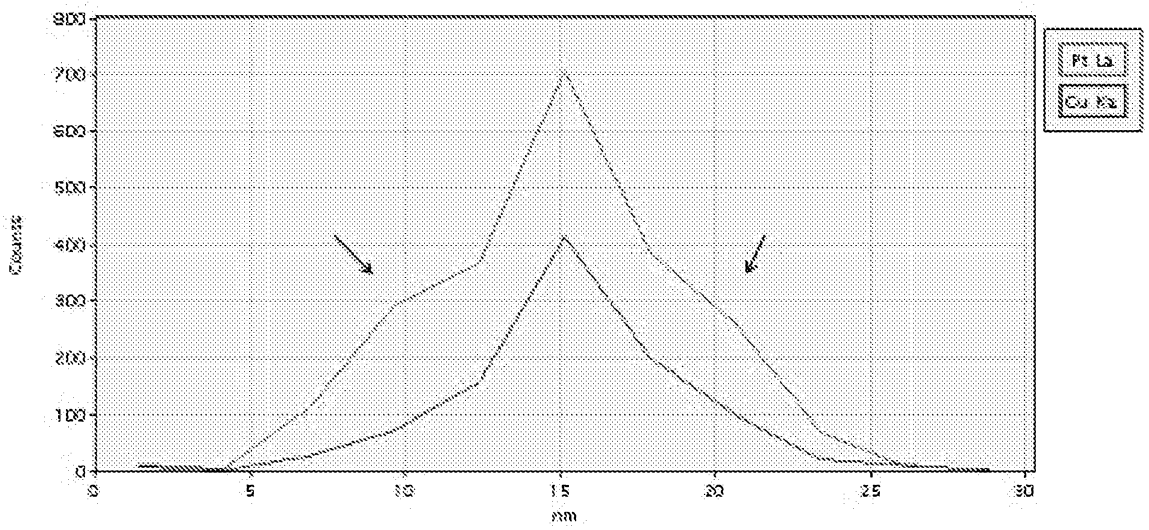

800
700
600
500
400
300
200
100
0
0
5
10
15
20
25
30
nm
Pt La
Cu Ka

FIG. 34

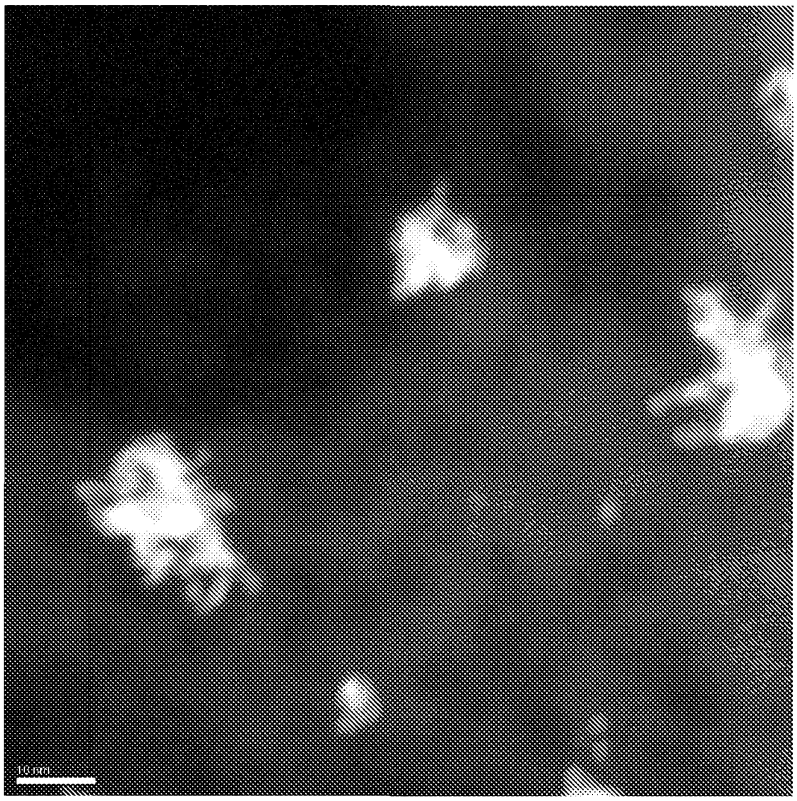

10 nm

FIG. 35

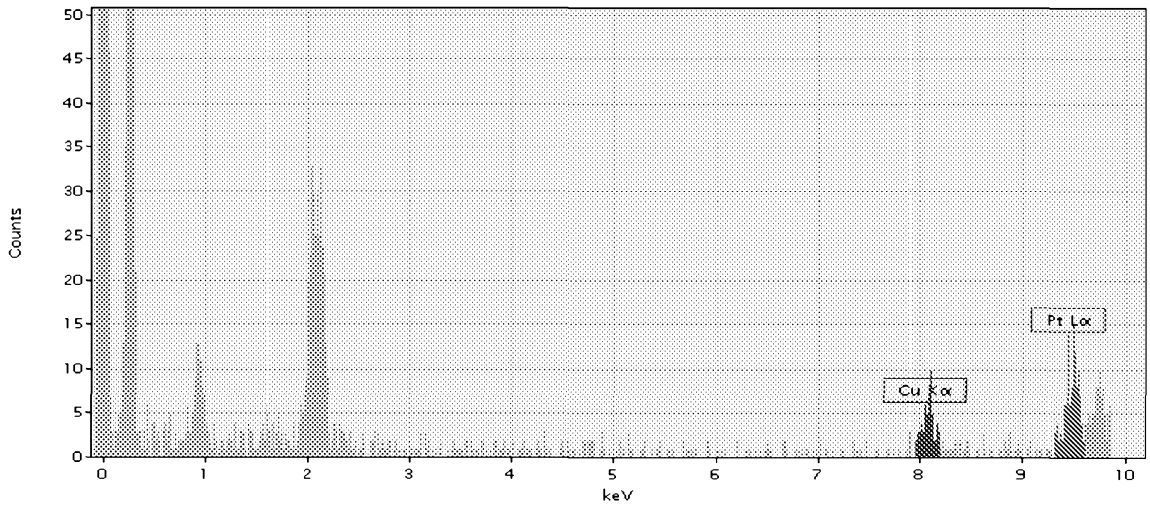

Counts
keV
Pt Lα
Cu Kα
0
5
10
15
20
25
30
35
40
45
50
0
1
2
3
4
5
6
7
8
9
10

FIG. 36

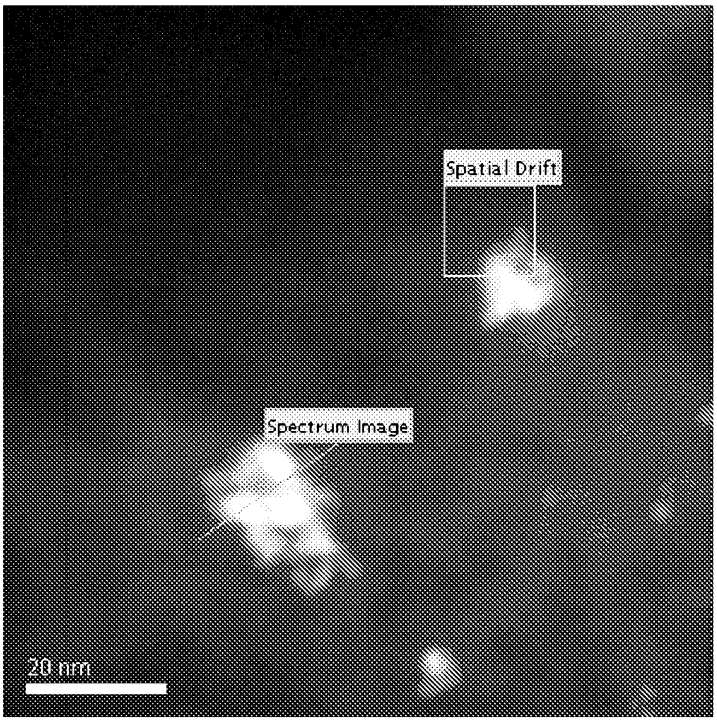

Spatial Drift
Spectrum Image
20 nm

FIG. 37

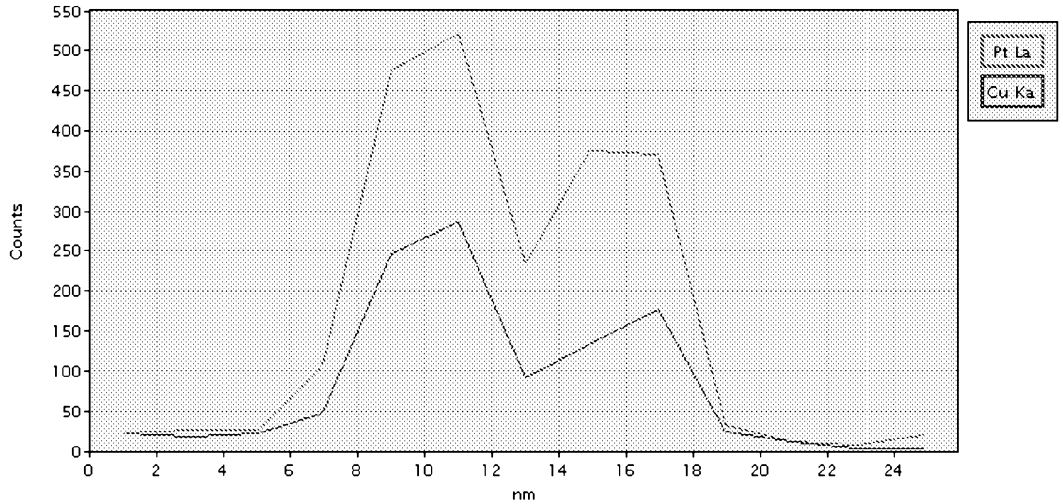

Counts
nm
Pt La
Cu Ka
0
50
100
150
200
250
300
350
400
450
500
550
0
2
4
6
8
10
12
14
16
18
20
22
24

FIG. 38

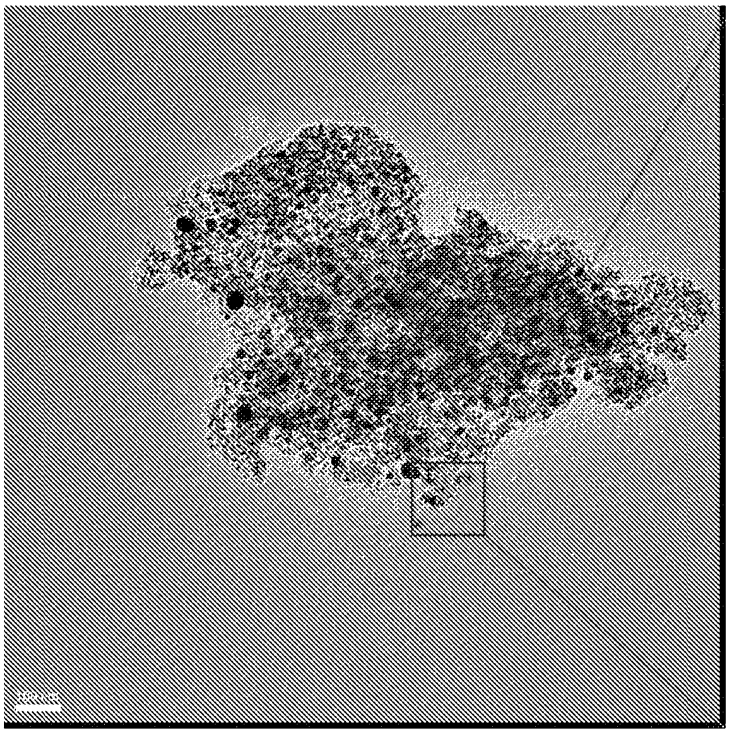


FIG. 39

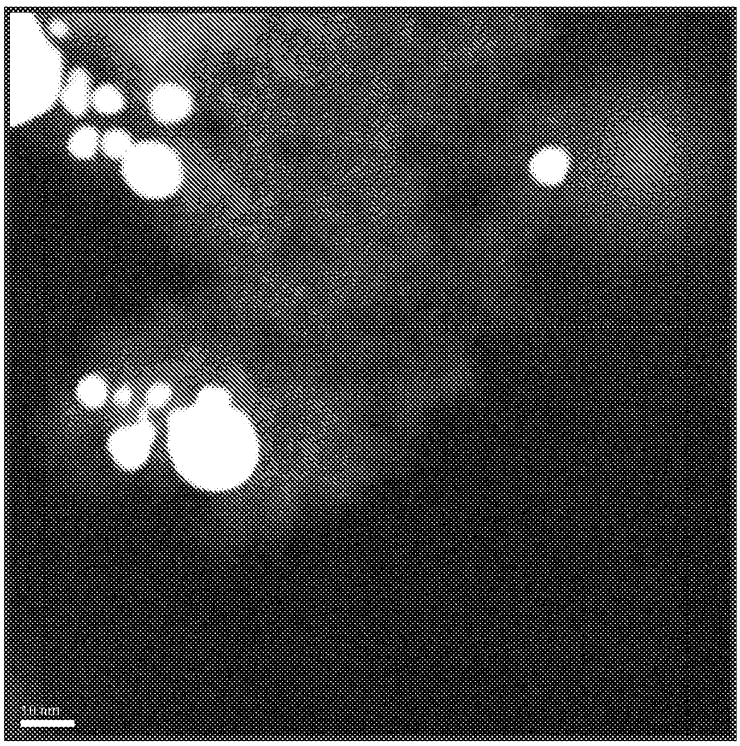


FIG. 40

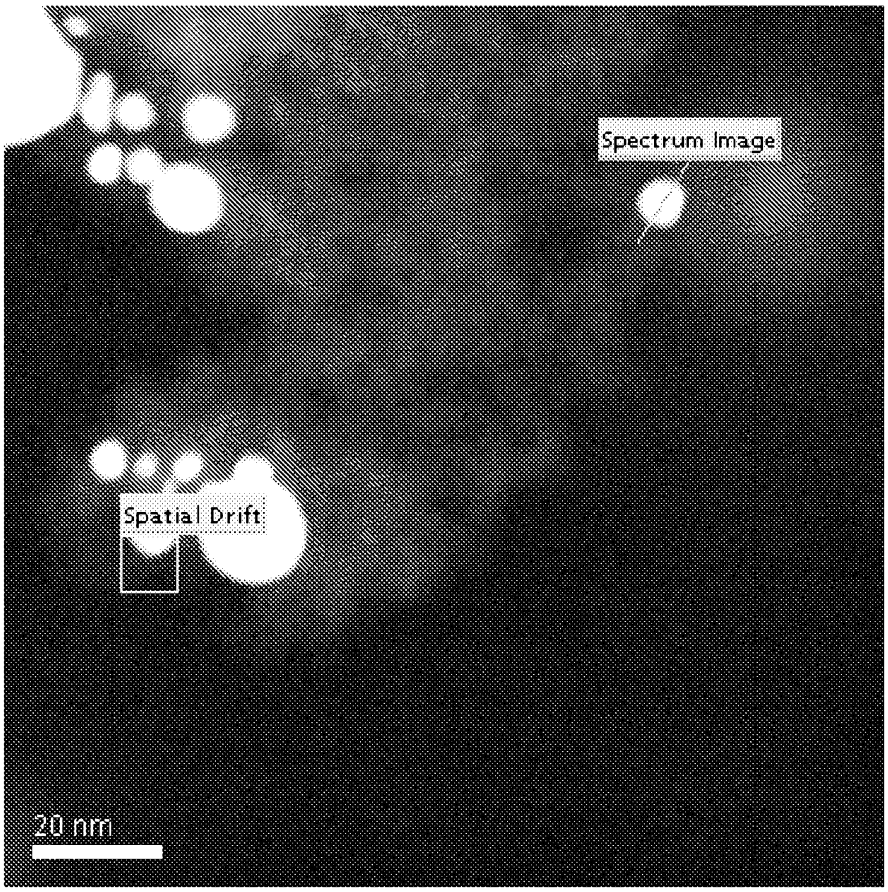


FIG. 41

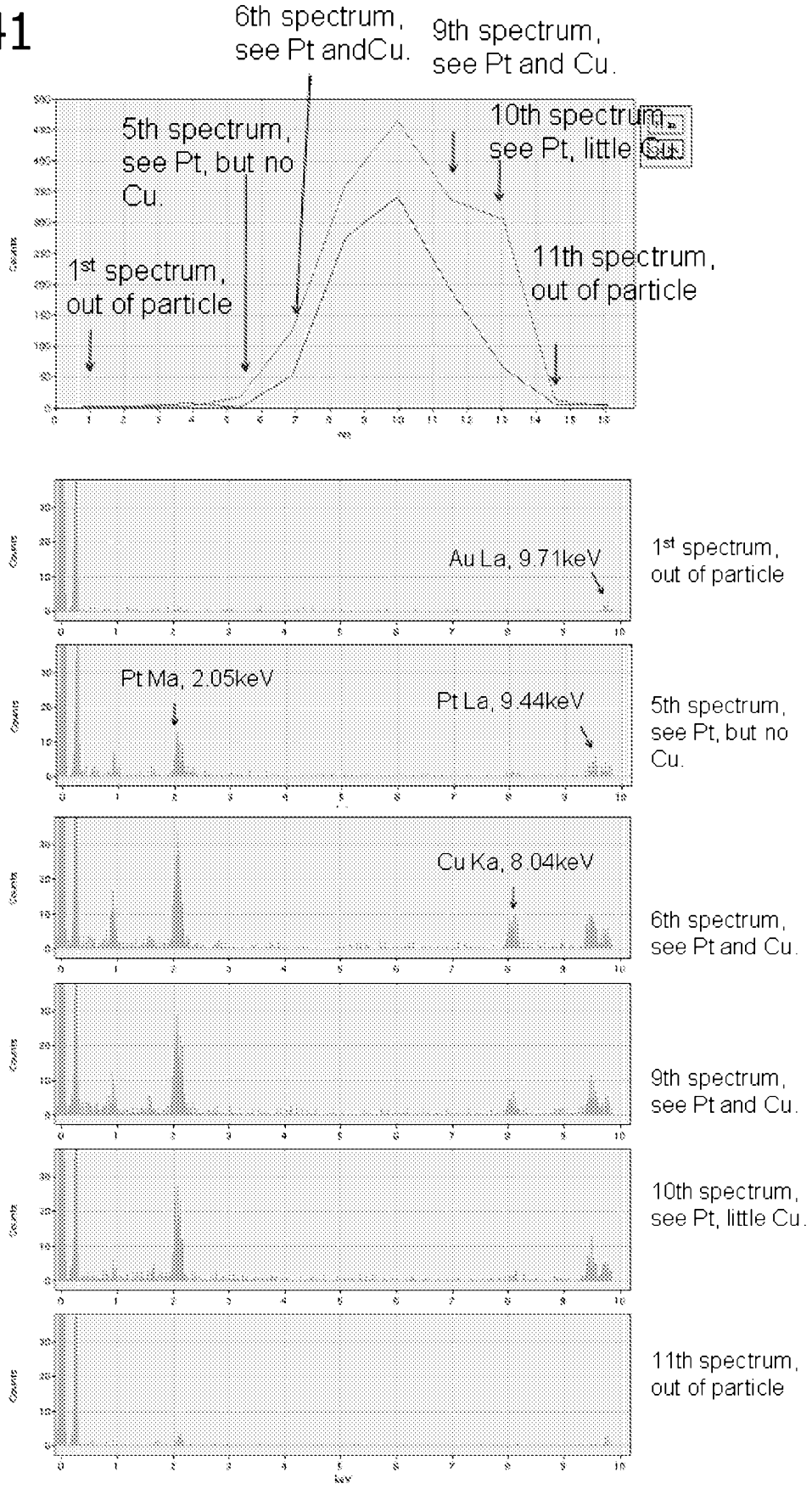

6th spectrum, see Pt andCu.
9th spectrum, see Pt and Cu.
5th spectrum, see Pt, but no Cu.
10th spectrum, see Pt, little Cu.
1st spectrum, out of particle
11th spectrum, out of particle
Au La, 9.71keV
1st spectrum, out of particle
Pt Ma, 2.05keV
Pt La, 9.44keV
5th spectrum, see Pt, but no Cu.
Cu Ka, 8.04keV
6th spectrum, see Pt and Cu.
9th spectrum, see Pt and Cu.
10th spectrum, see Pt, little Cu.
11th spectrum, out of particle

FIG. 42

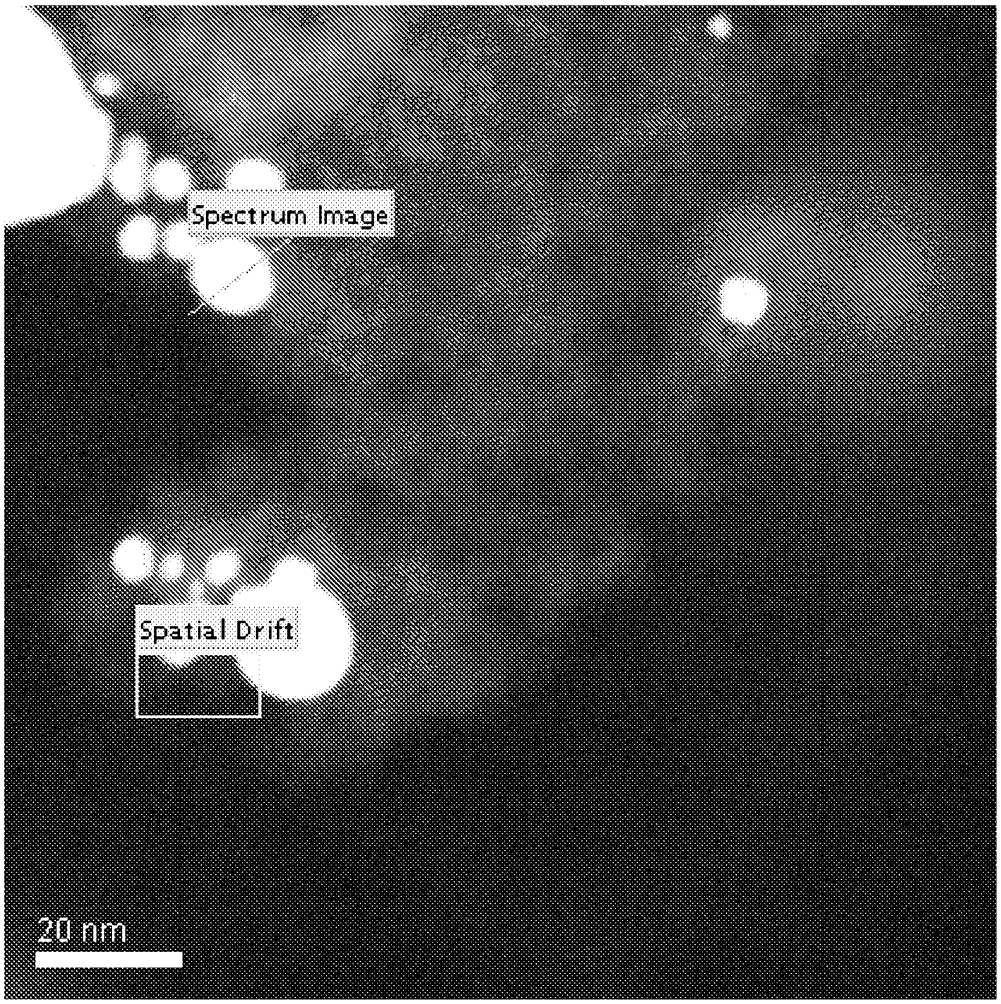


FIG. 43

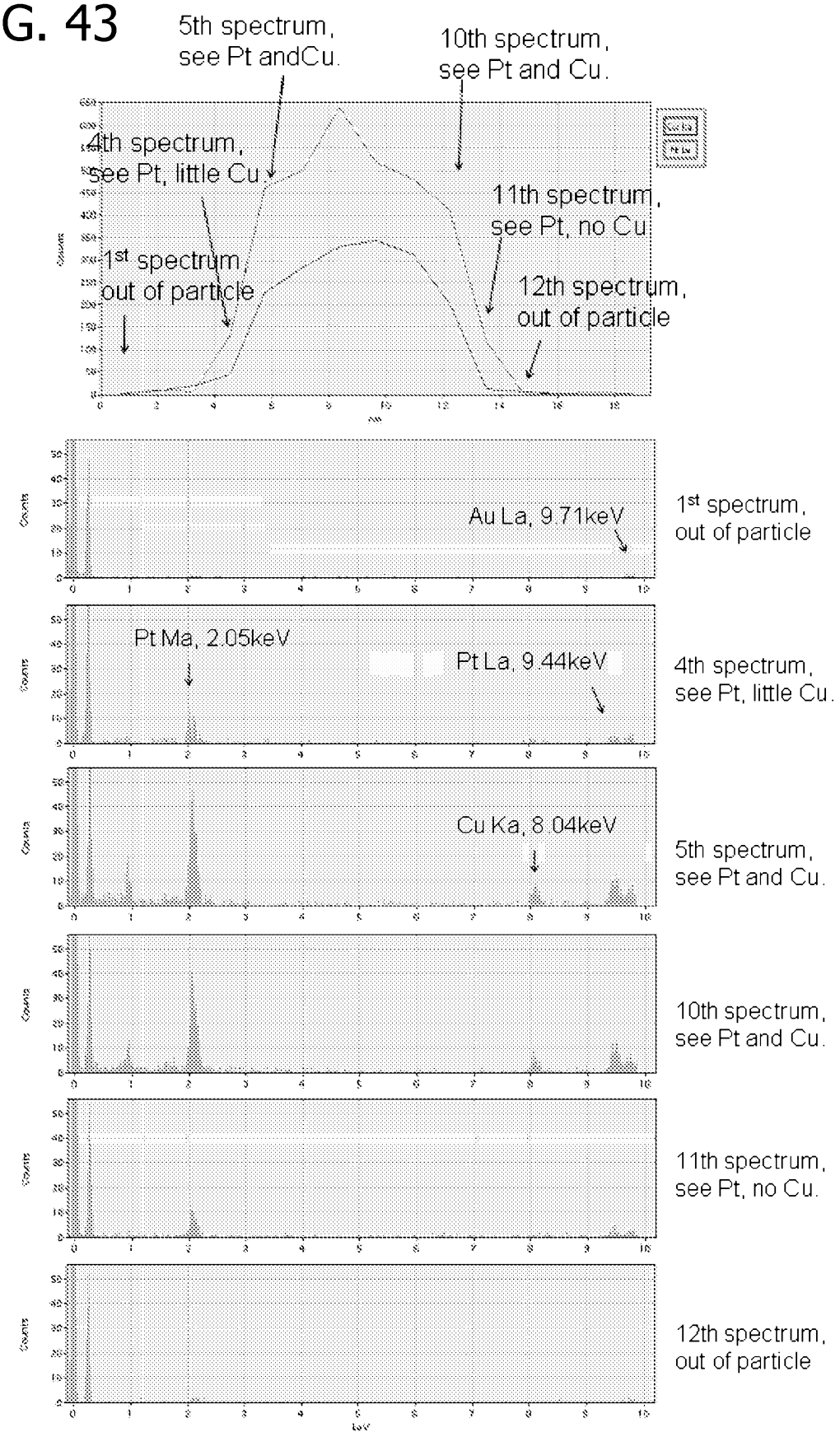

5th spectrum, see Pt andCu.
10th spectrum, see Pt and Cu.
4th spectrum, see Pt, little Cu
11th spectrum, see Pt, no Cu
1st spectrum, out of particle
12th spectrum, out of particle
Au La, 9.71keV
1st spectrum, out of particle
Pt Ma, 2.05keV
Pt La, 9.44keV
4th spectrum, see Pt, little Cu.
Cu Ka, 8.04keV
5th spectrum, see Pt and Cu.
10th spectrum, see Pt and Cu.
11th spectrum, see Pt, no Cu.
12th spectrum, out of particle

FIG. 44

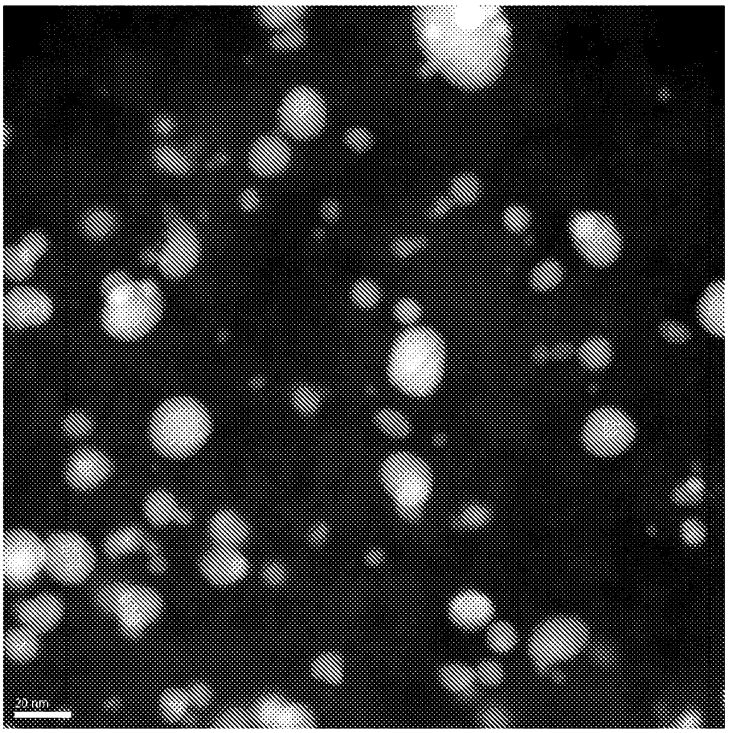


FIG. 45

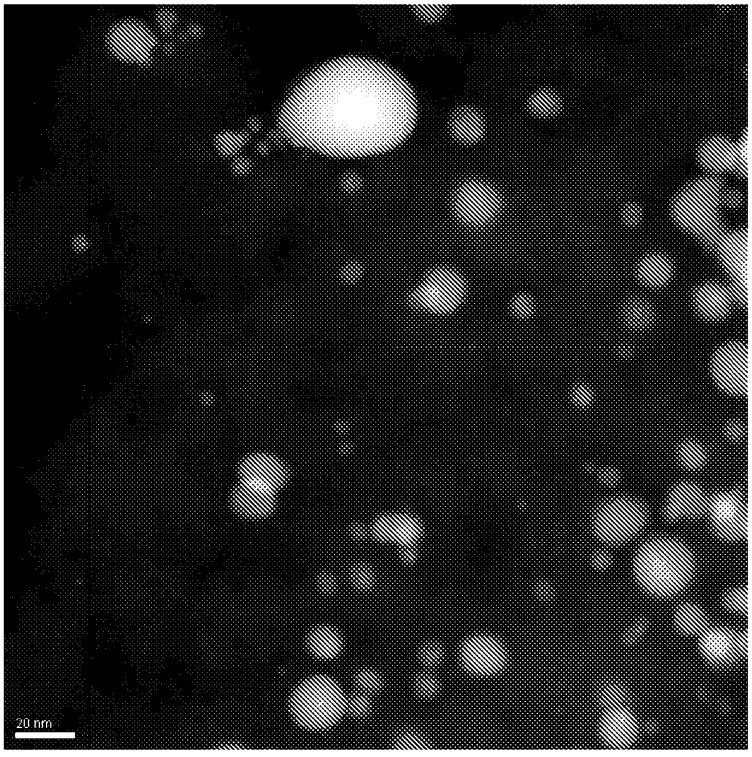


FIG. 46

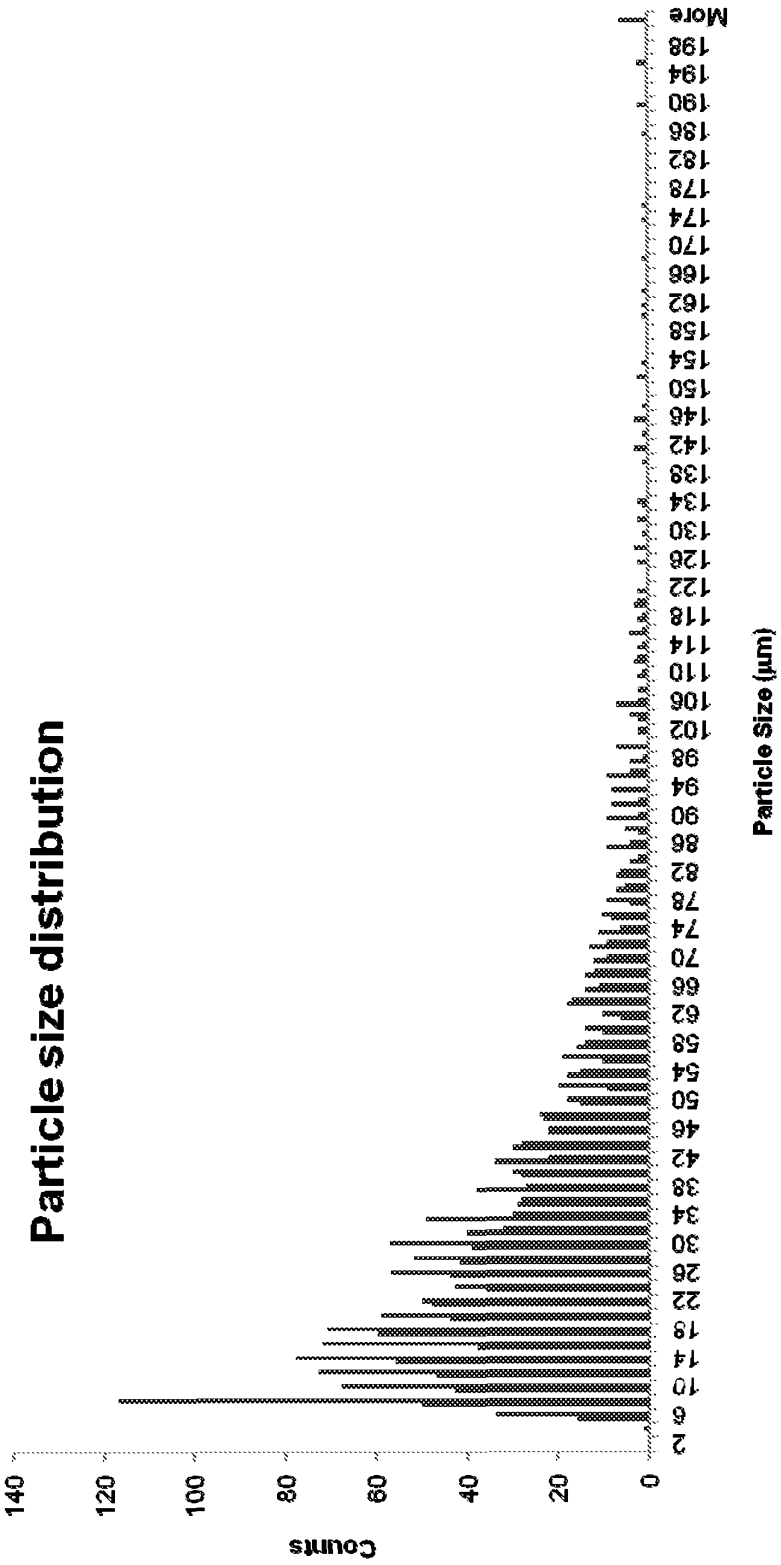

Particle size distribution
Counts
0
20
40
60
80
100
120
140
Particle Size (µm)
2
6
10
14
18
22
26
30
34
38
42
46
50
54
59
62
66
70
74
78
82
86
90
94
98
102
106
110
114
118
122
126
130
134
138
142
146
150
154
158
162
166
170
174
178
182
186
190
194
198
More

FIG. 47

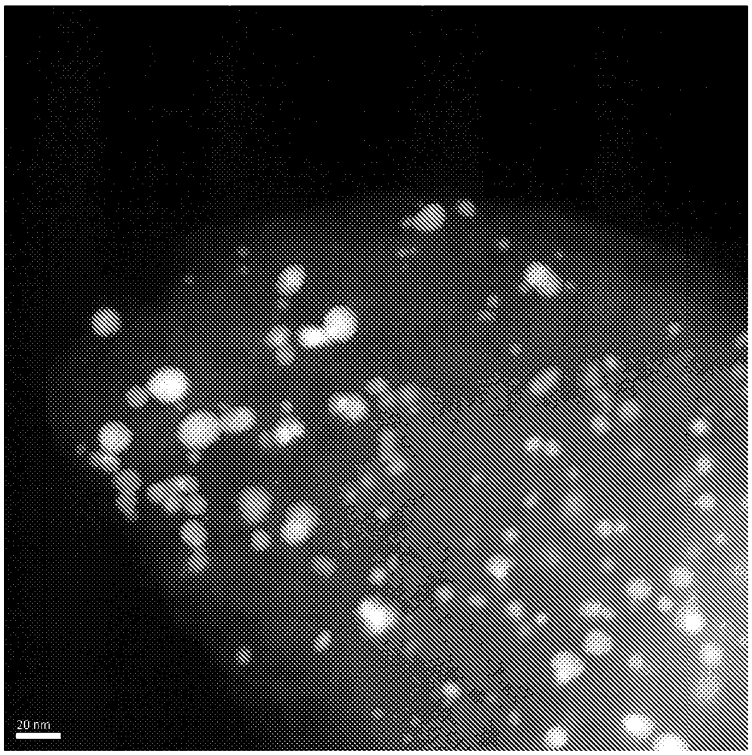


FIG. 48

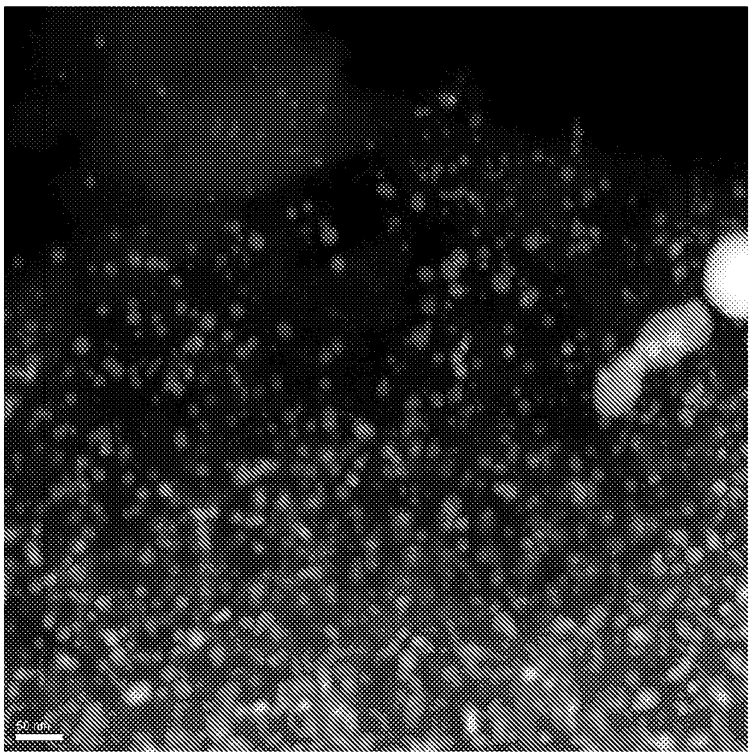


FIG. 49

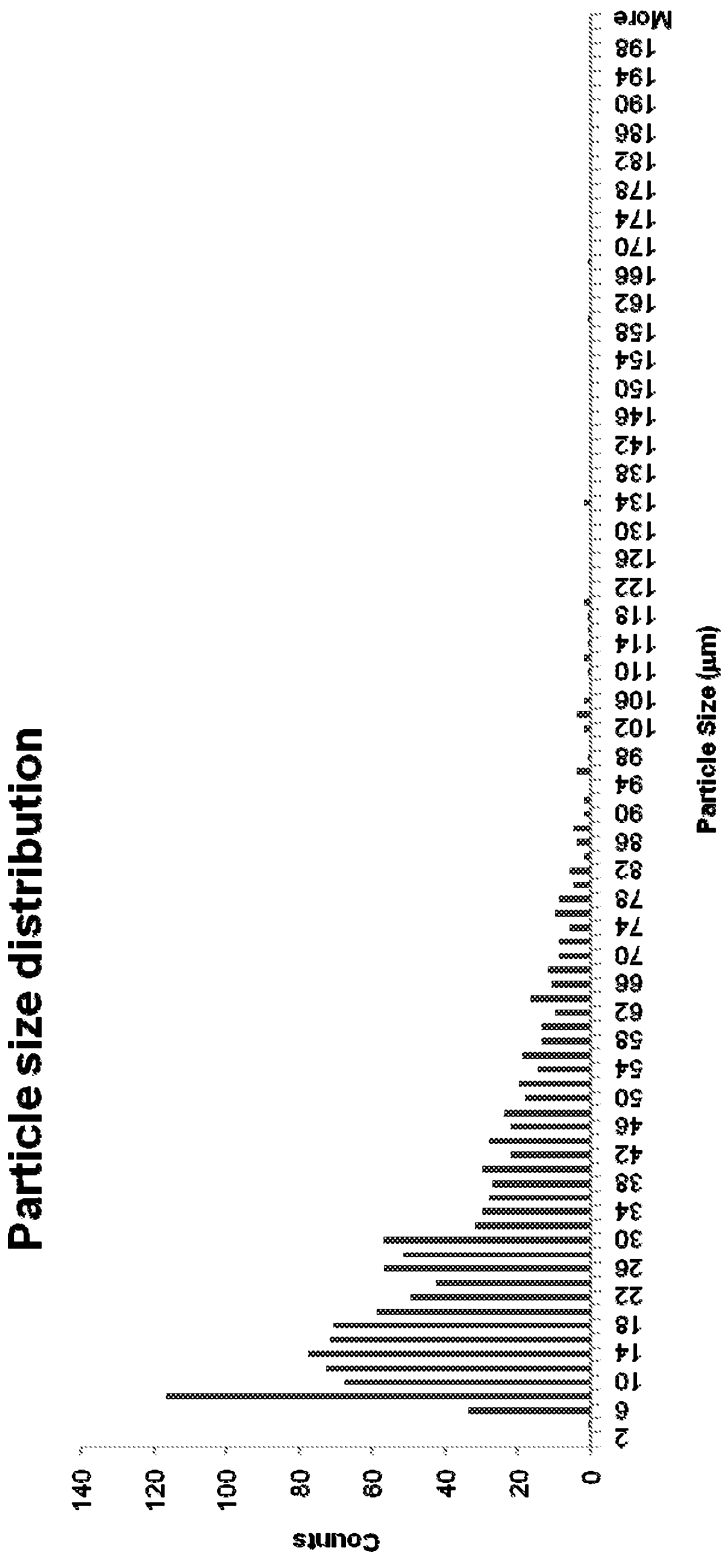

Particle size distribution
Counts
0
20
40
60
80
100
120
140
Particle Size (µm)
2
6
10
14
18
22
26
30
34
38
42
46
50
54
58
62
66
70
74
78
82
86
90
94
98
102
106
110
114
118
122
126
130
134
138
142
146
150
154
158
162
166
170
174
178
182
186
190
194
198
More

FIG. 50

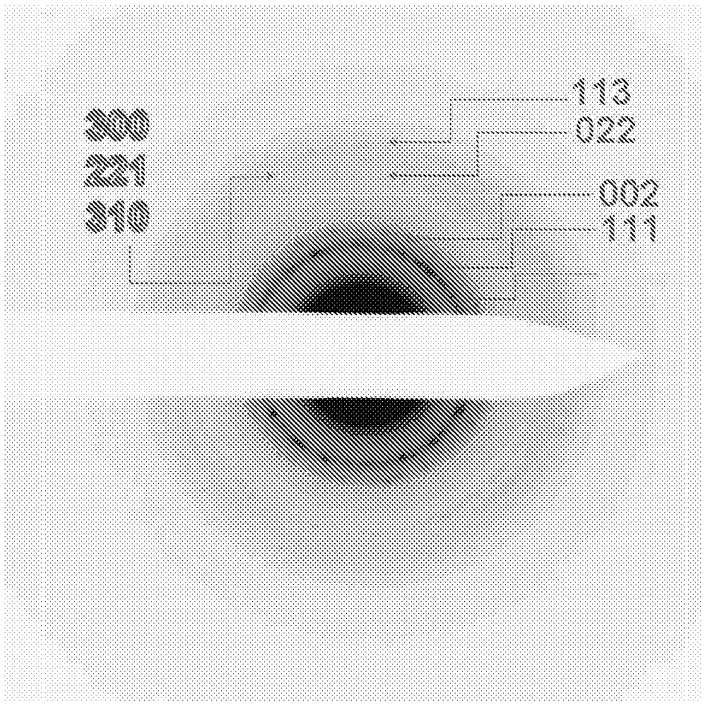


FIG. 51

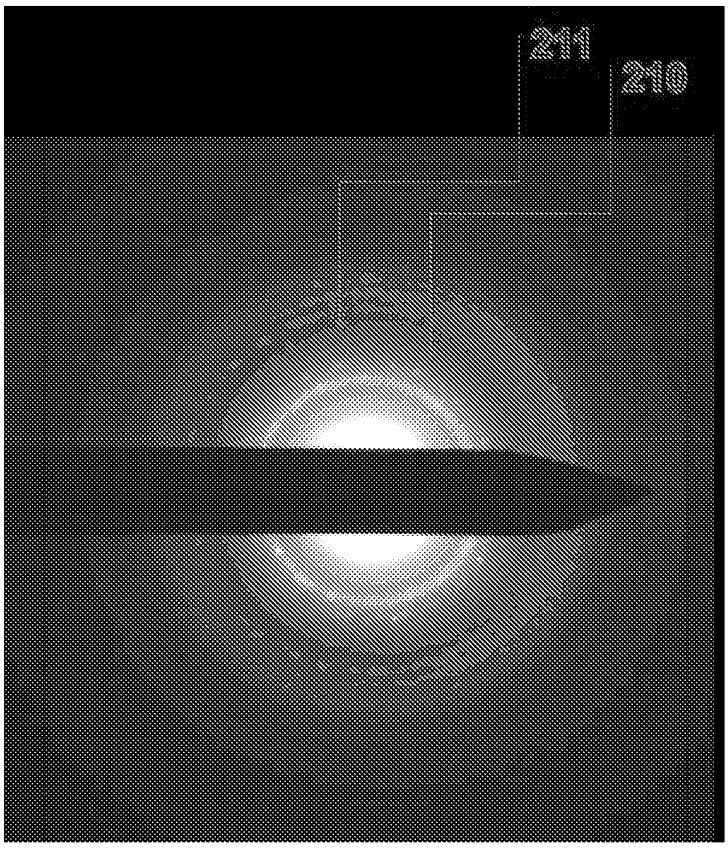


FIG. 52

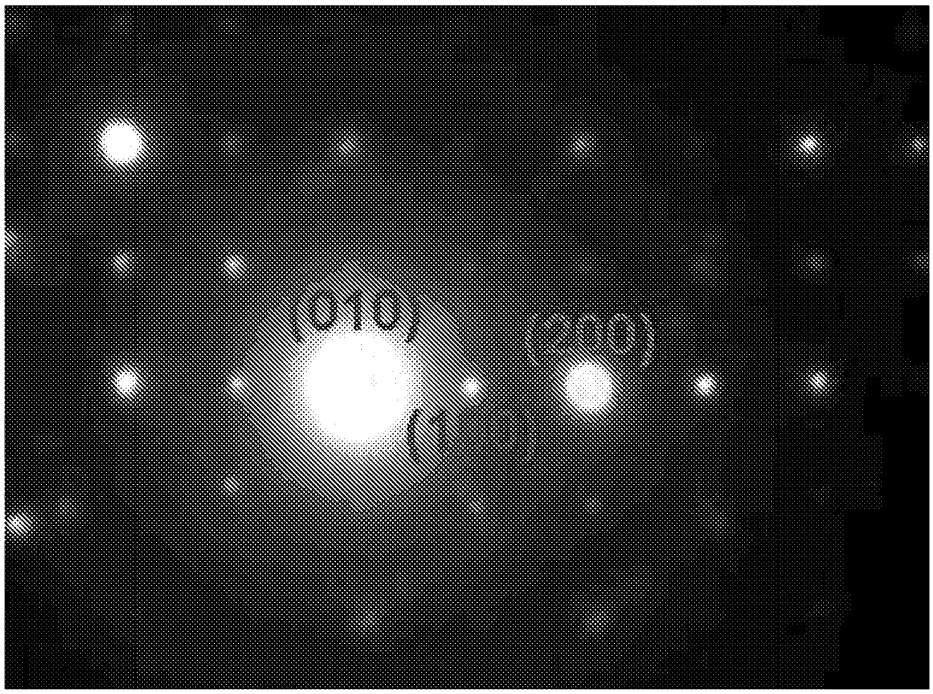


FIG. 53

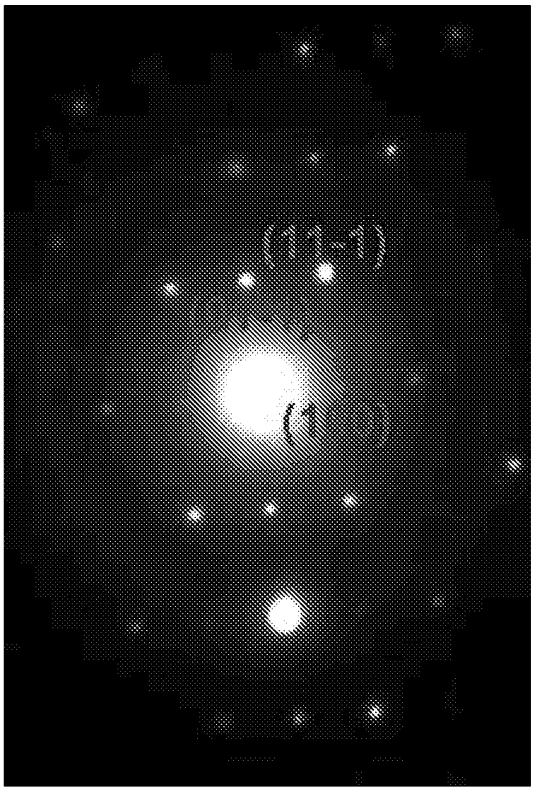


FIG. 54

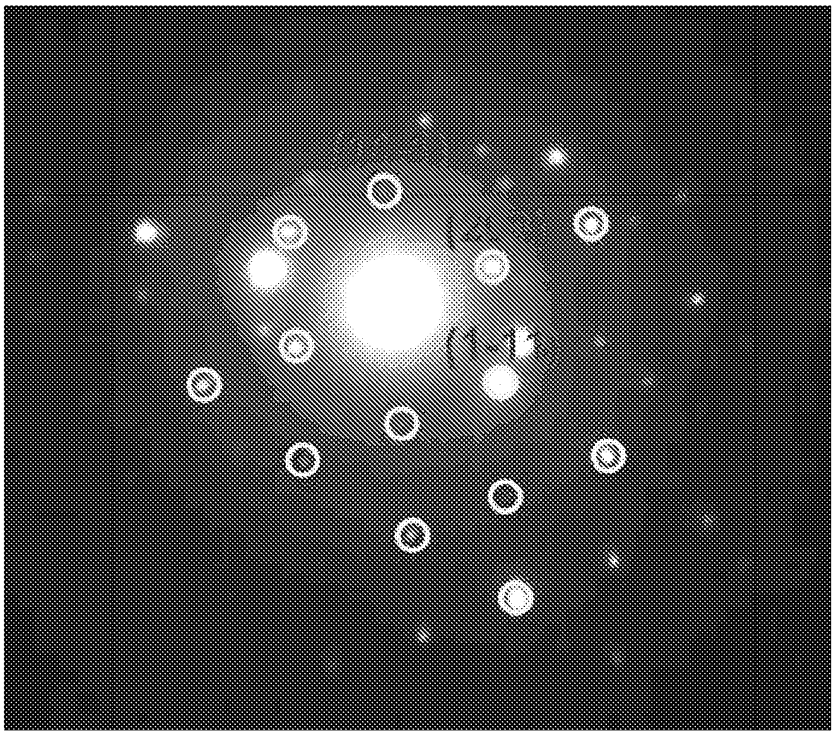


FIG. 55

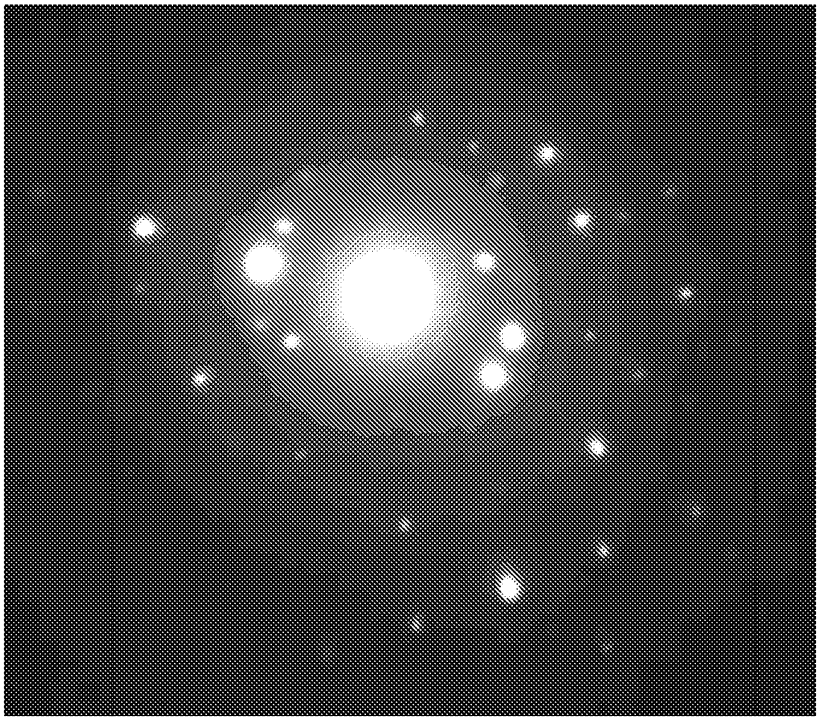


FIG. 56

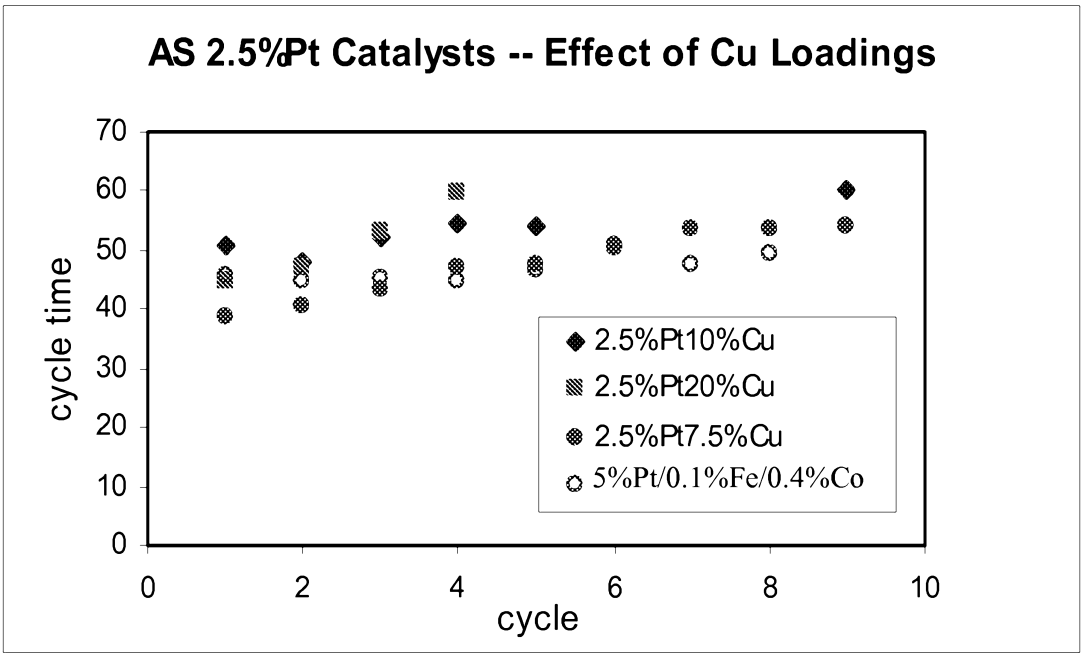

AS 2.5%Pt Catalysts -- Effect of Cu Loadings
cycle time
cycle
0
10
20
30
40
50
60
70
0
2
4
6
8
10
2.5%Pt10%Cu
2.5%Pt20%Cu
2.5%Pt7.5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 57

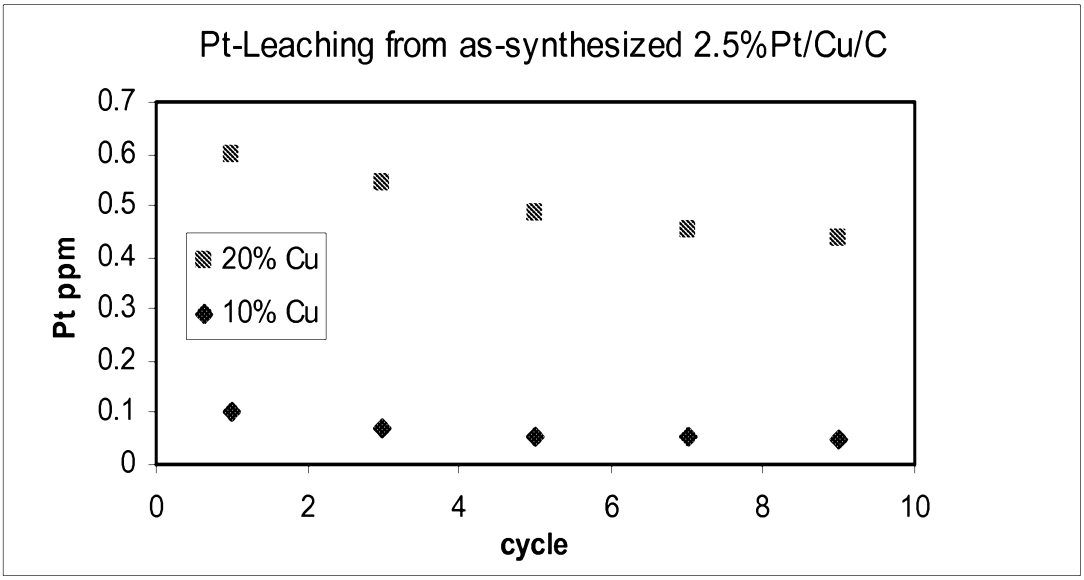

Pt-Leaching from as-synthesized 2.5%Pt/Cu/C
Pt ppm
cycle
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
2
4
6
8
10
20% Cu
10% Cu

FIG. 58

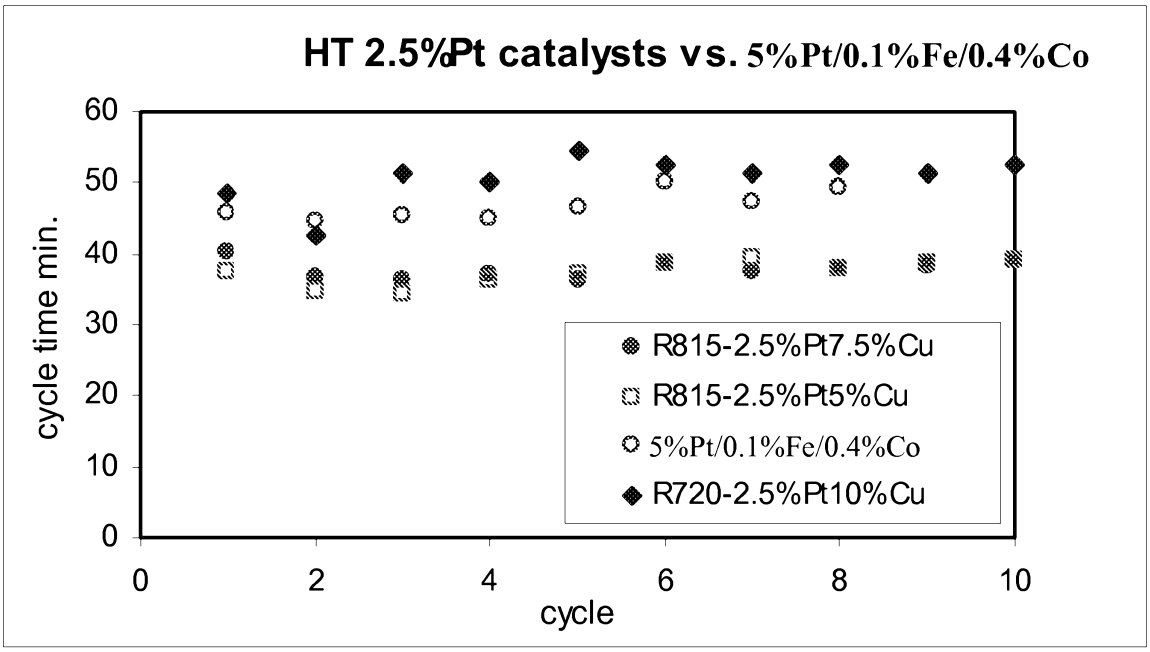

HT 2.5%Pt catalysts vs. 5%Pt/0.1%Fe/0.4%Co
cycle time min.
60
50
40
30
20
10
0
0
2
4
6
8
10
cycle
R815-2.5%Pt7.5%Cu
R815-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co
R720-2.5%Pt10%Cu

FIG. 59

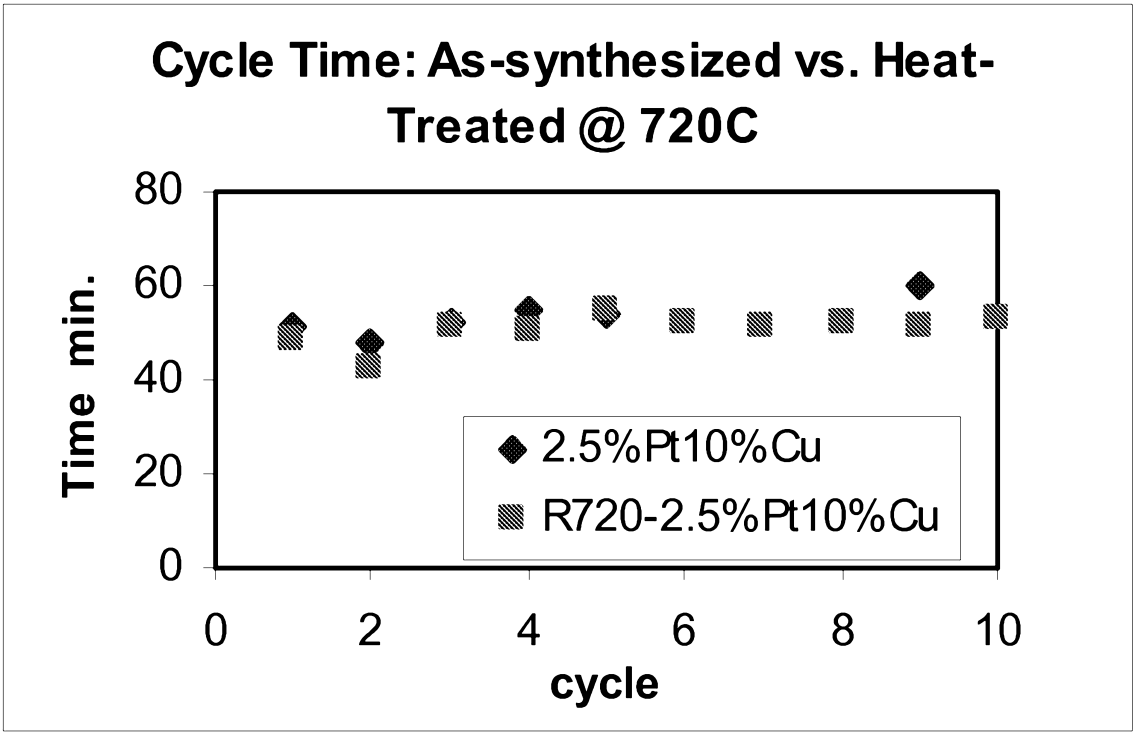

Cycle Time: As-synthesized vs. Heat-Treated @ 720C
Time min.
80
60
40
20
0
0
2
4
6
8
10
cycle
2.5%Pt10%Cu
R720-2.5%Pt10%Cu

FIG. 60

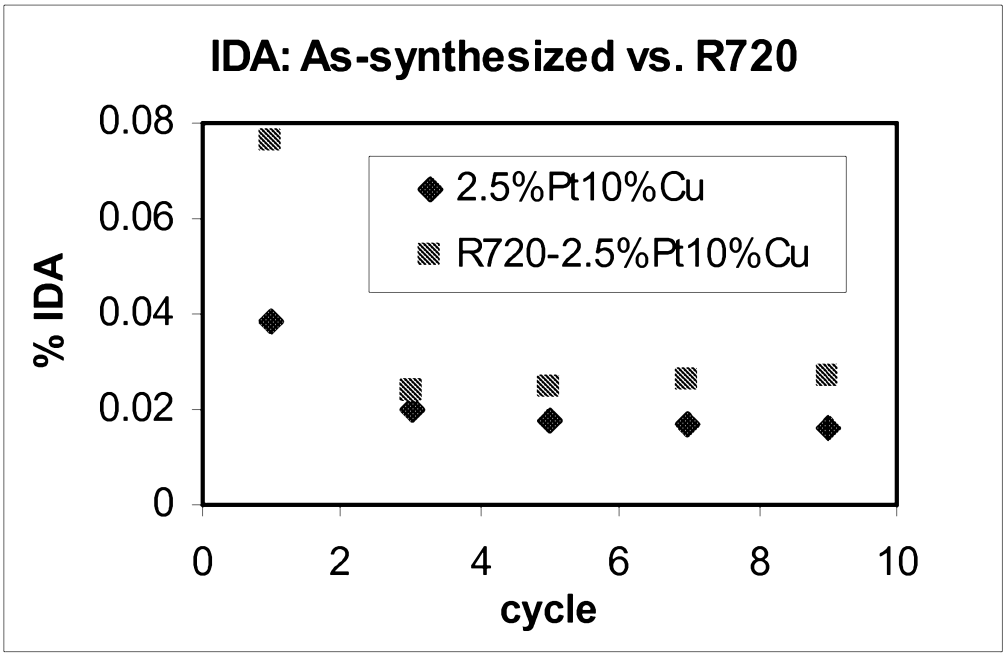

IDA: As-synthesized vs. R720
% IDA
0.08
0.06
0.04
0.02
0
0
2
4
6
8
10
cycle
2.5%Pt10%Cu
R720-2.5%Pt10%Cu

FIG. 61

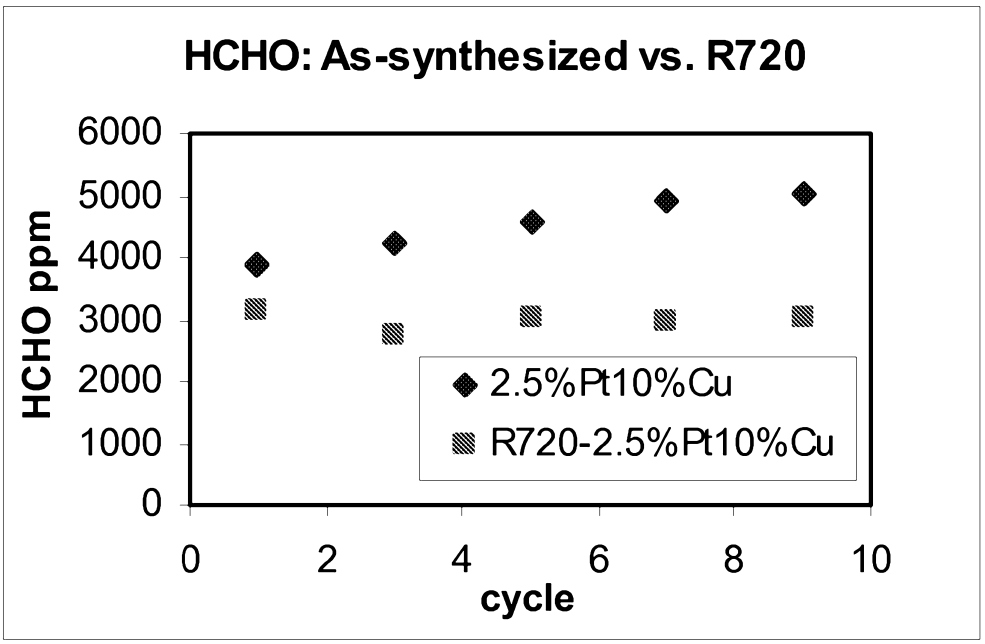

HCHO: As-synthesized vs. R720
HCHO ppm
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
2.5%Pt10%Cu
R720-2.5%Pt10%Cu

FIG. 62

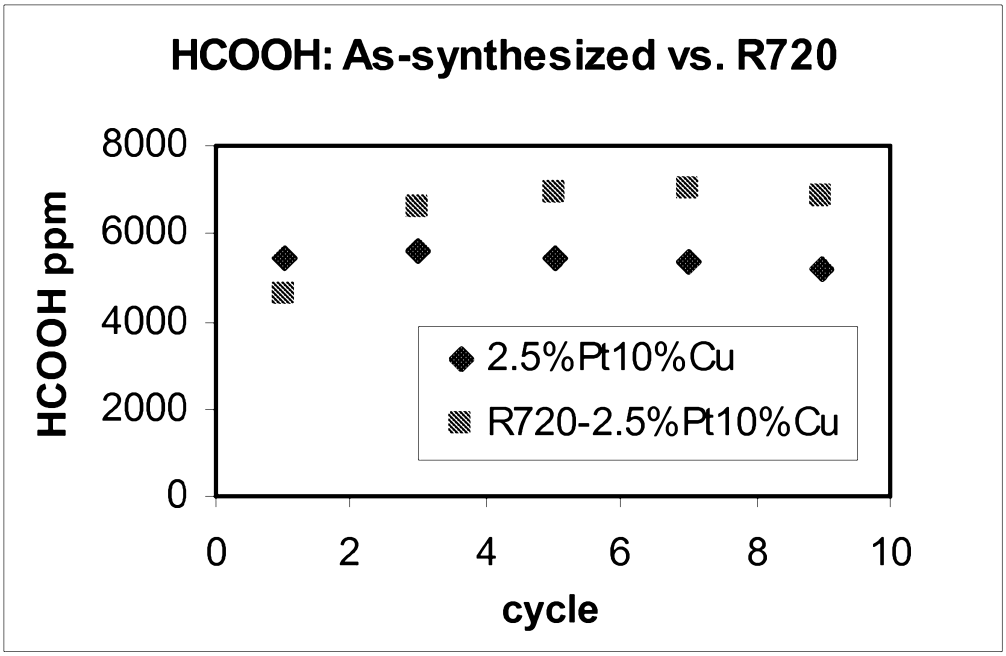

HCOOH: As-synthesized vs. R720
HCOOH ppm
8000
6000
4000
2000
0
0
2
4
6
8
10
cycle
2.5%Pt10%Cu
R720-2.5%Pt10%Cu

FIG. 63

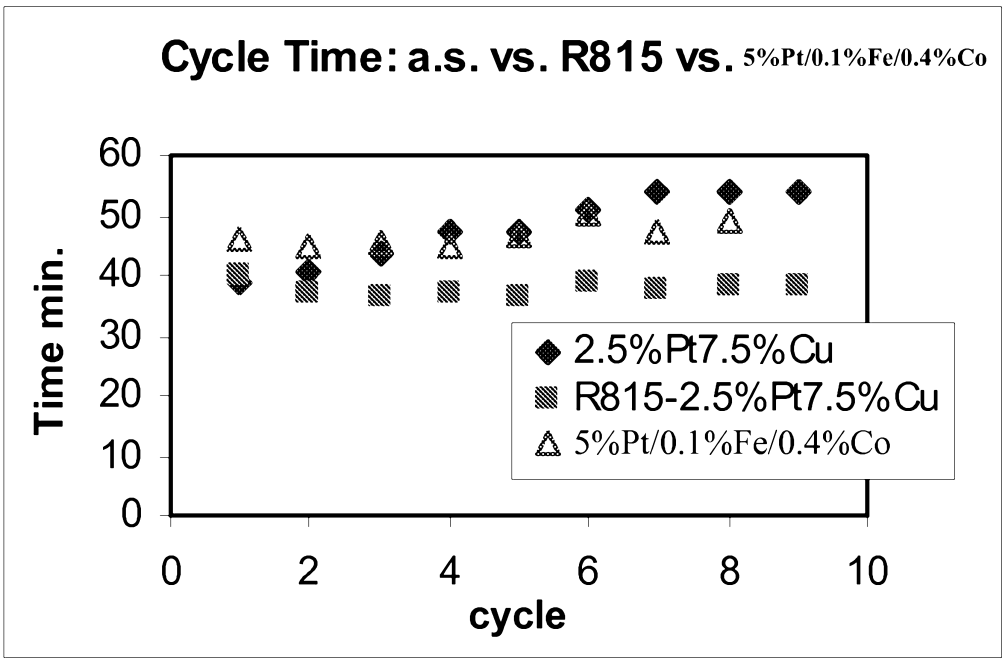

Cycle Time: a.s. vs. R815 vs. 5%Pt/0.1%Fe/0.4%Co
Time min.
60
50
40
30
20
10
0
0
2
4
6
8
10
cycle
2.5%Pt7.5%Cu
R815-2.5%Pt7.5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 64

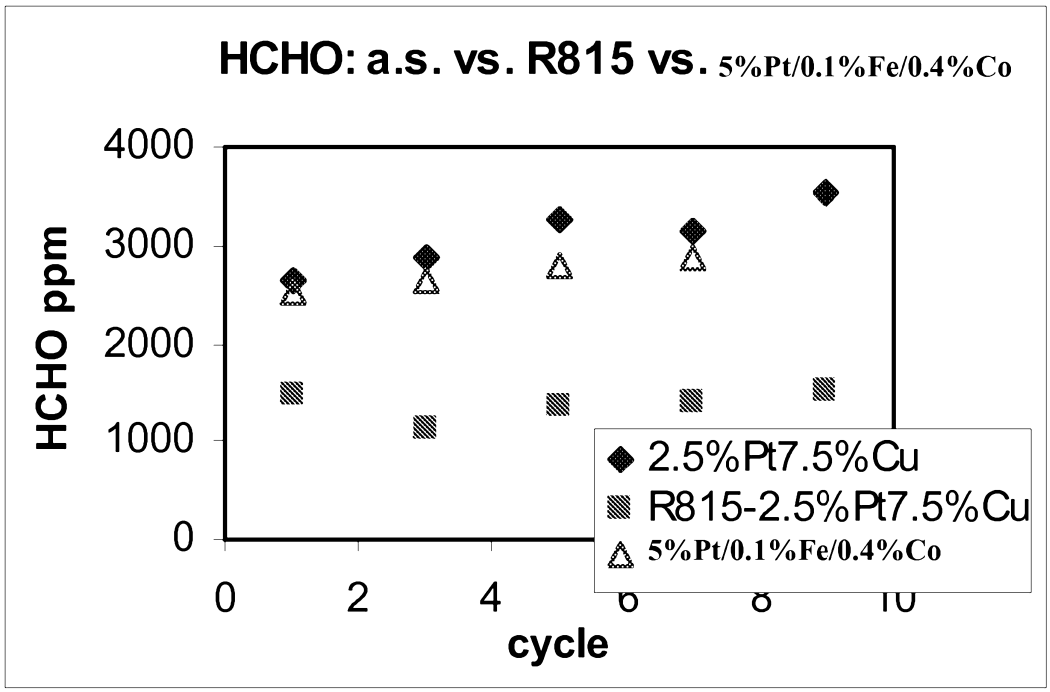

HCHO: a.s. vs. R815 vs. 5%Pt/0.1%Fe/0.4%Co
HCHO ppm
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
2.5%Pt7.5%Cu
R815-2.5%Pt7.5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 65

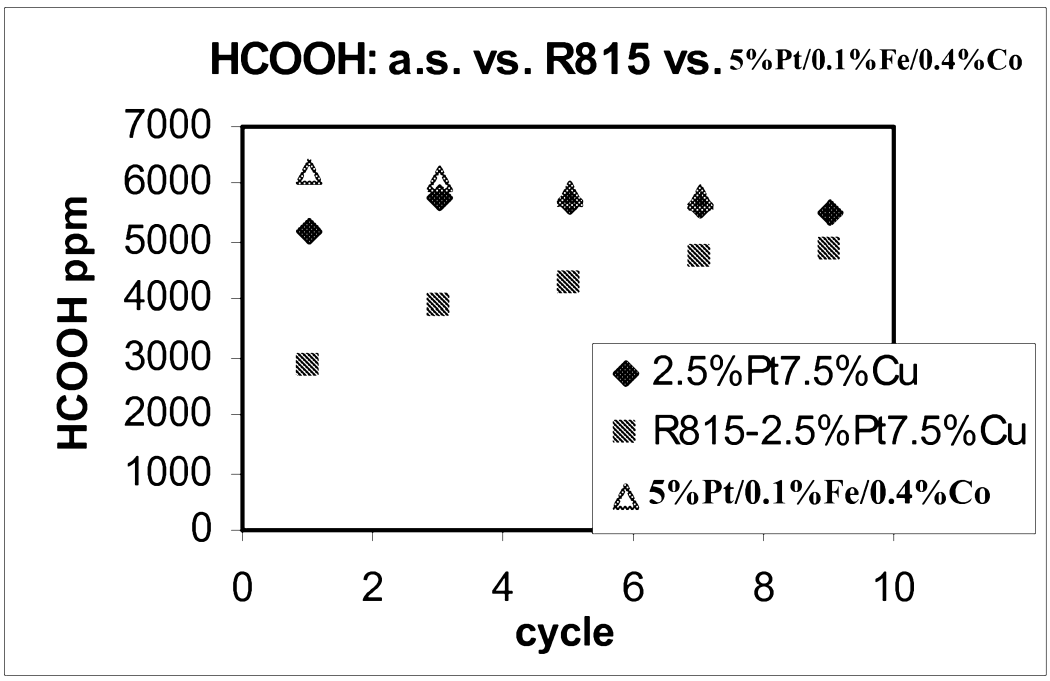

HCOOH: a.s. vs. R815 vs. 5%Pt/0.1%Fe/0.4%Co
HCOOH ppm
7000
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
2.5%Pt7.5%Cu
R815-2.5%Pt7.5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 66

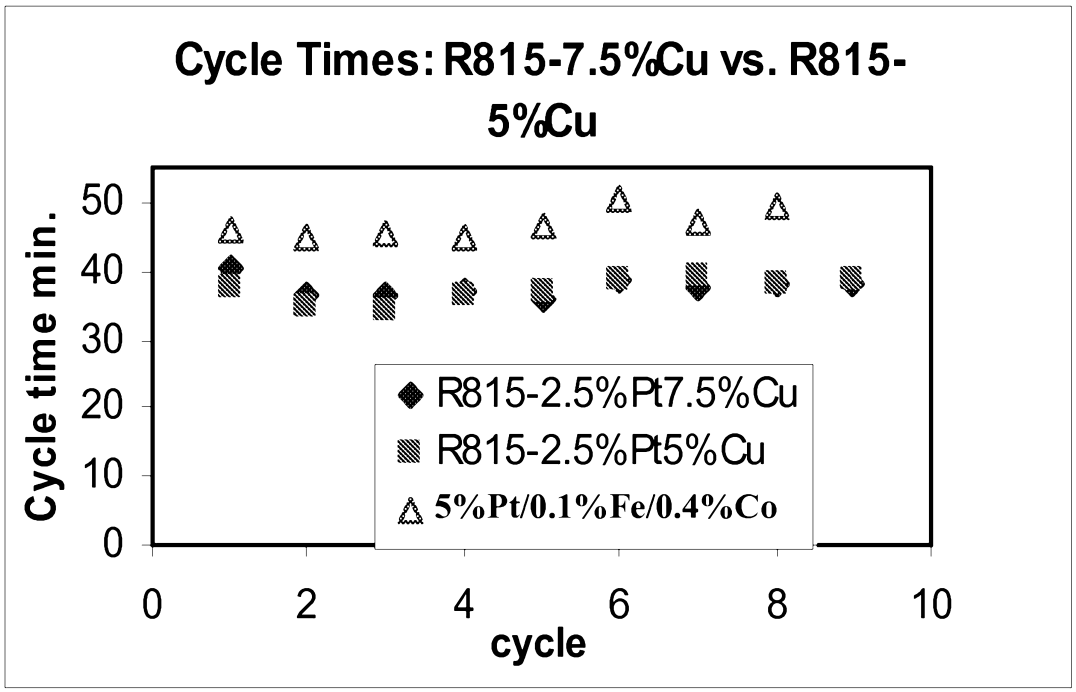

Cycle Times: R815-7.5%Cu vs. R815-5%Cu
Cycle time min.
50
40
30
20
10
0
0
2
4
6
8
10
cycle
R815-2.5%Pt7.5%Cu
R815-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 67

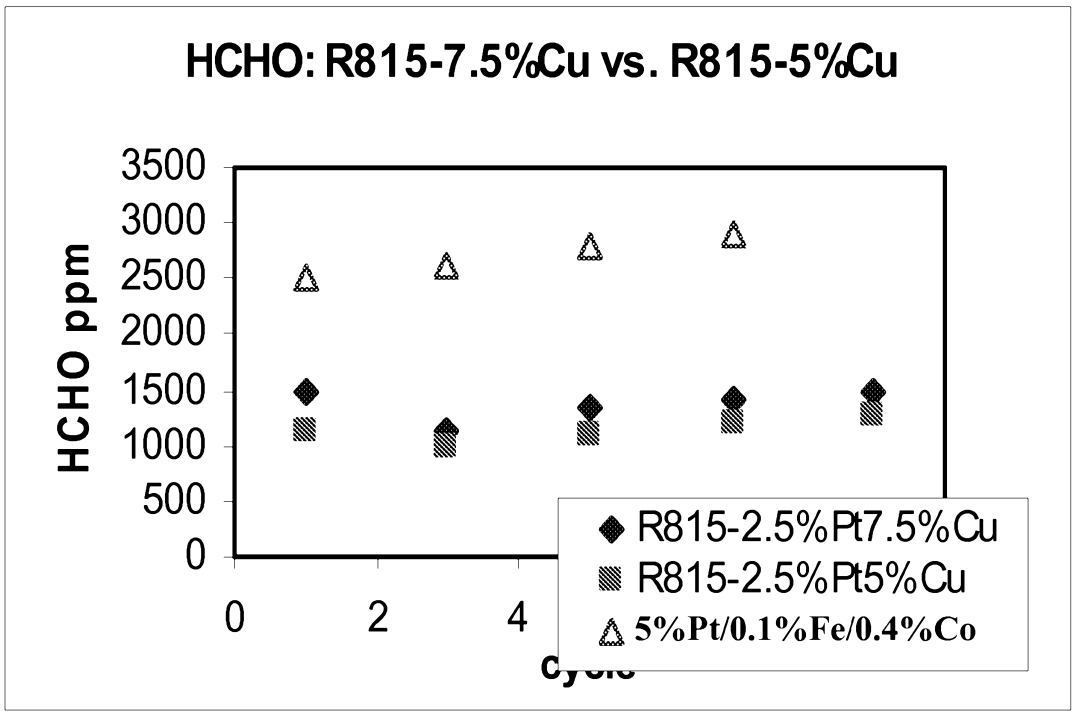

HCHO: R815-7.5%Cu vs. R815-5%Cu
HCHO ppm
3500
3000
2500
2000
1500
1000
500
0
0
2
4
R815-2.5%Pt7.5%Cu
R815-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 68

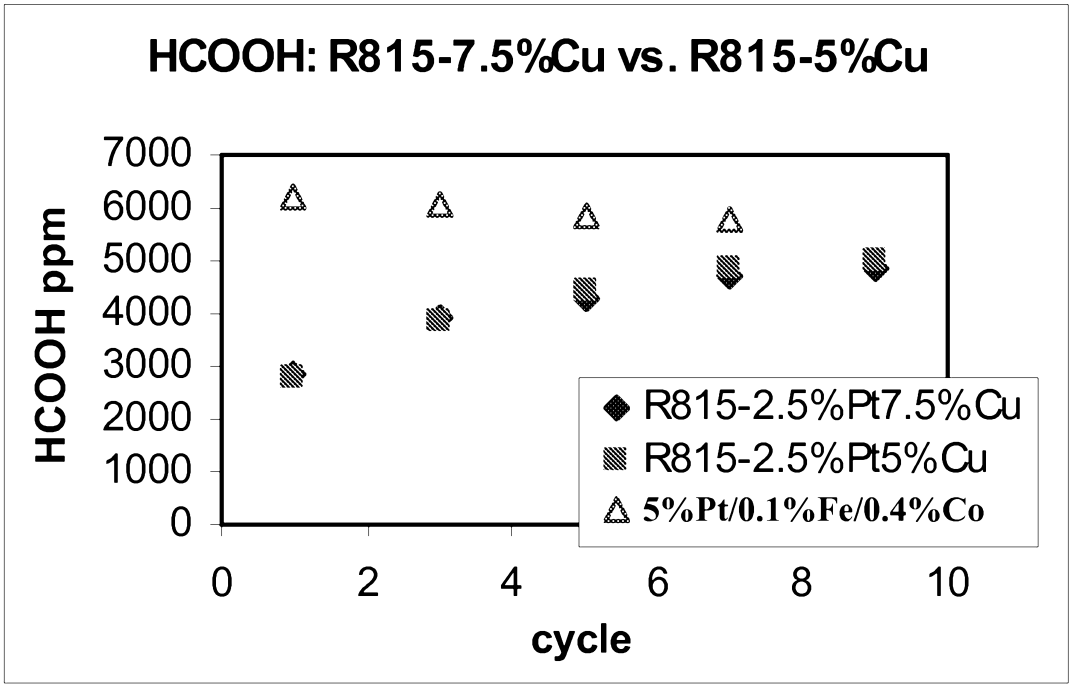

HCOOH: R815-7.5%Cu vs. R815-5%Cu
HCOOH ppm
7000
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
R815-2.5%Pt7.5%Cu
R815-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 69

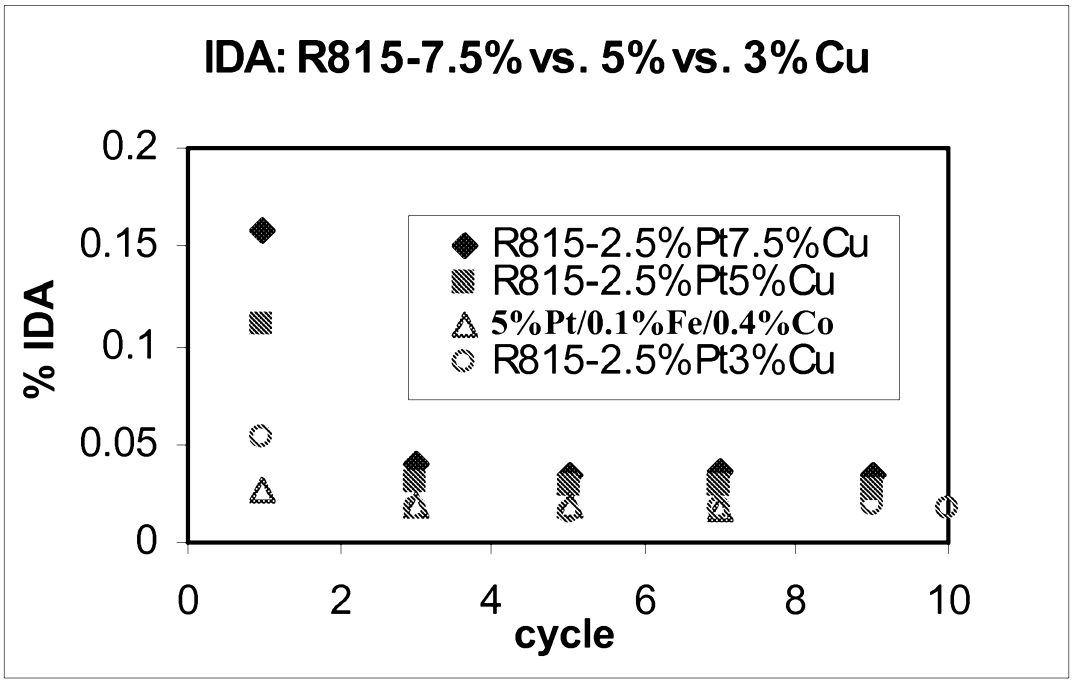

IDA: R815-7.5% vs. 5% vs. 3% Cu
% IDA
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
cycle
R815-2.5%Pt7.5%Cu
R815-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co
R815-2.5%Pt3%Cu

FIG. 70

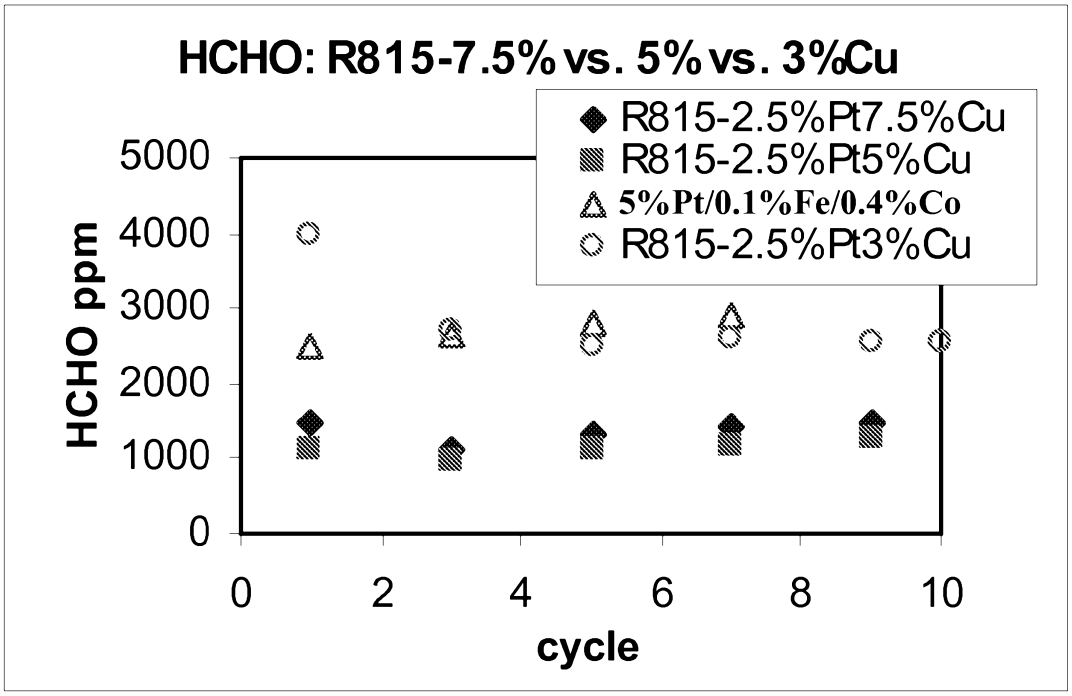

HCHO: R815-7.5% vs. 5% vs. 3%Cu
R815-2.5%Pt7.5%Cu
R815-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co
R815-2.5%Pt3%Cu
HCHO ppm
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle

FIG. 71

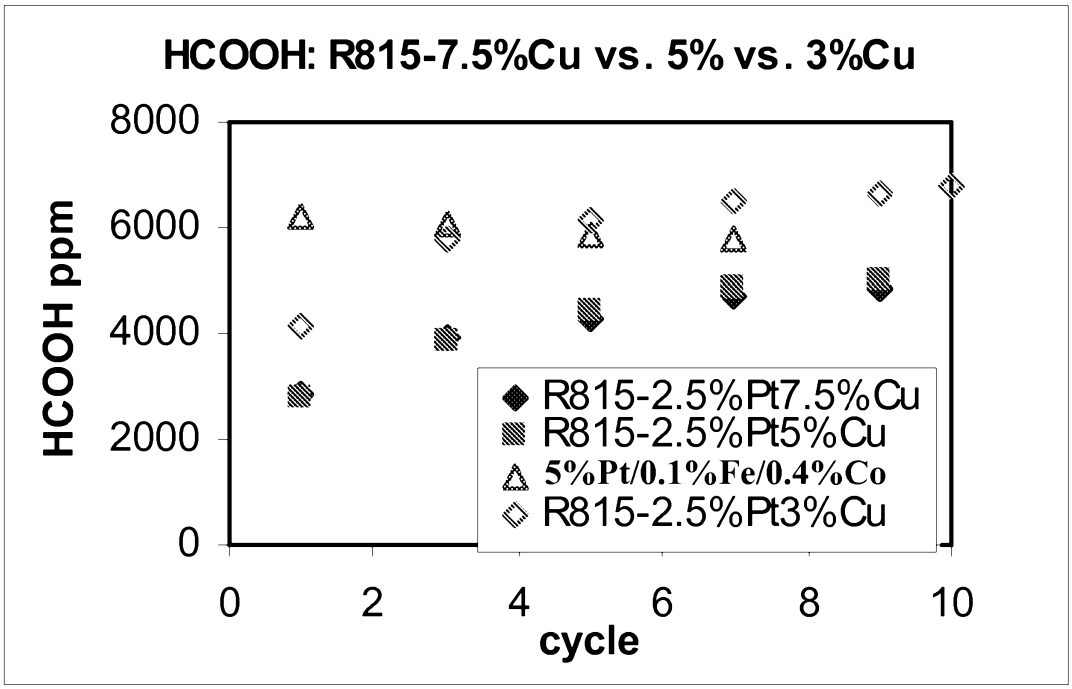

HCOOH: R815-7.5%Cu vs. 5% vs. 3%Cu
R815-2.5%Pt7.5%Cu
R815-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co
R815-2.5%Pt3%Cu
HCOOH ppm
8000
6000
4000
2000
0
0
2
4
6
8
10
cycle

FIG. 72

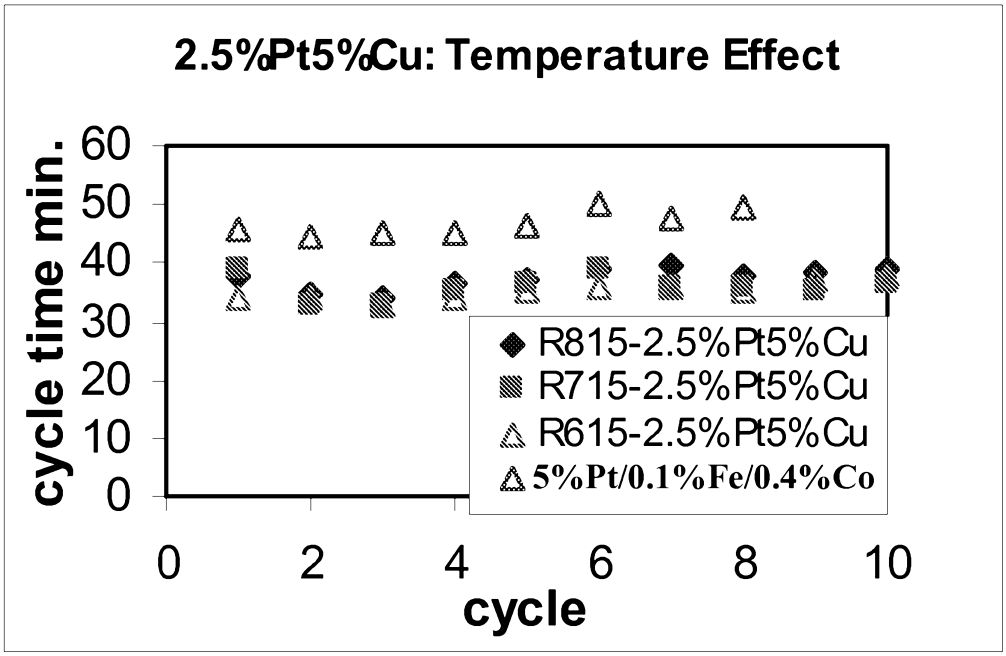

2.5%Pt5%Cu: Temperature Effect
cycle time min.
60
50
40
30
20
10
0
0
2
4
6
8
10
cycle
R815-2.5%Pt5%Cu
R715-2.5%Pt5%Cu
R615-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 73

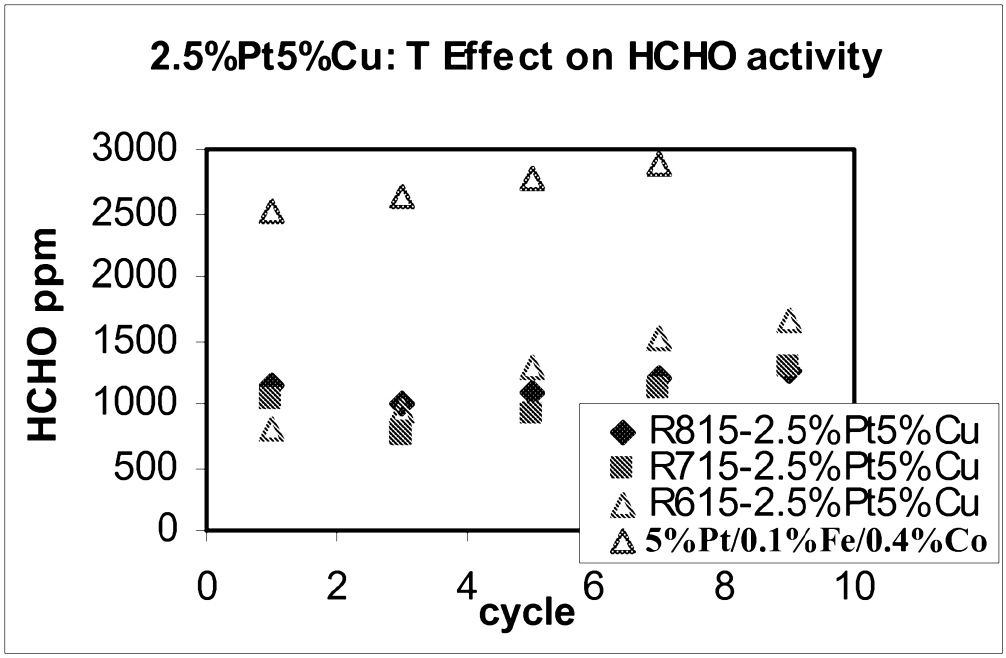

2.5%Pt5%Cu: T Effect on HCHO activity
HCHO ppm
3000
2500
2000
1500
1000
500
0
0
2
4
6
8
10
cycle
R815-2.5%Pt5%Cu
R715-2.5%Pt5%Cu
R615-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 74

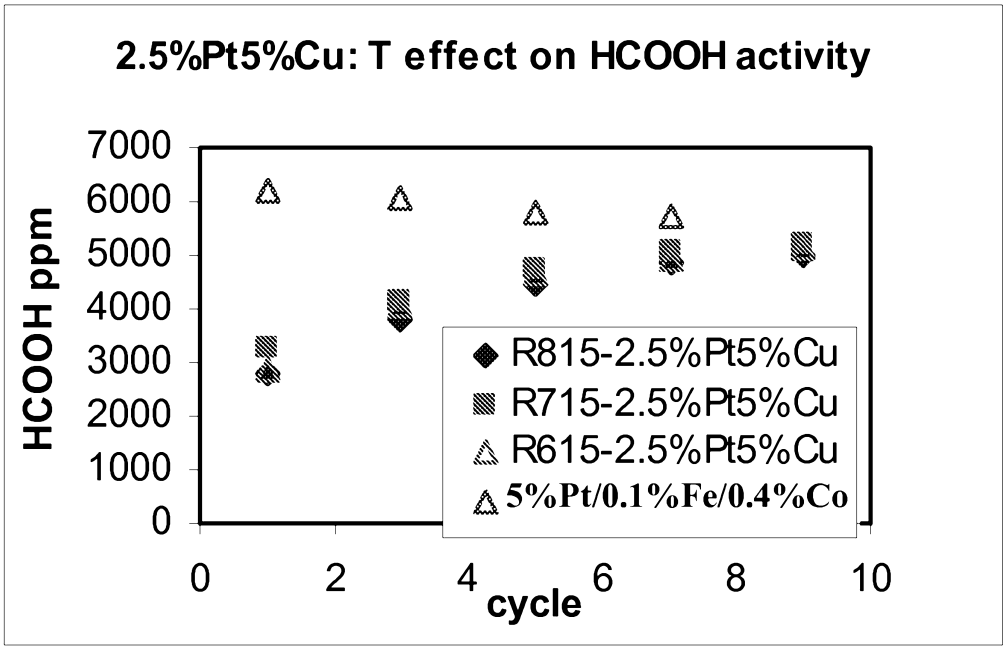

2.5%Pt5%Cu: T effect on HCOOH activity
HCOOH ppm
7000
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
R815-2.5%Pt5%Cu
R715-2.5%Pt5%Cu
R615-2.5%Pt5%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 75

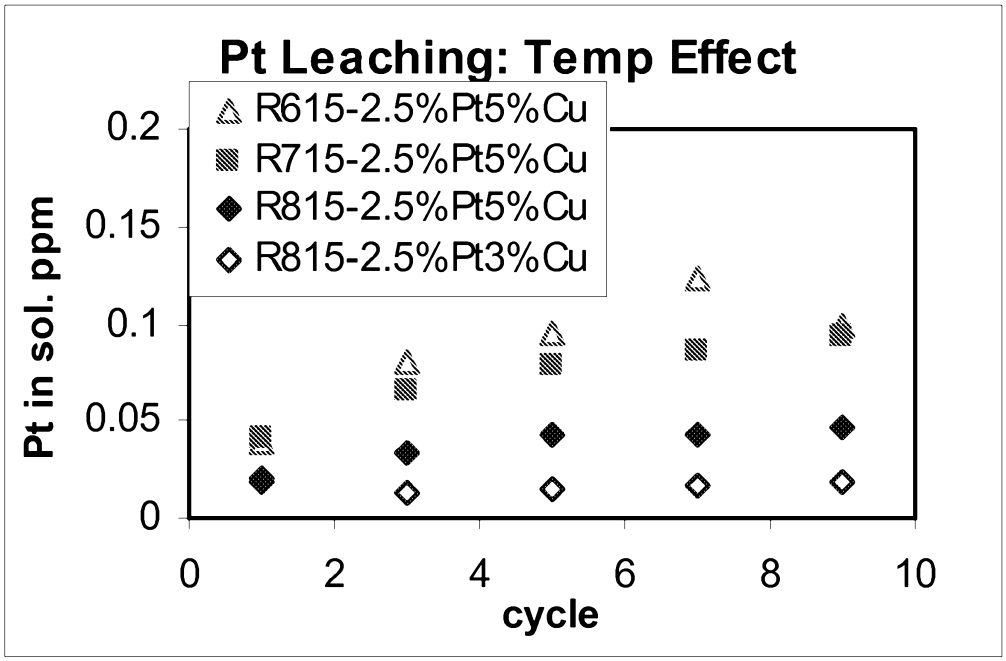

Pt Leaching: Temp Effect
Pt in sol. ppm
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
cycle
R615-2.5%Pt5%Cu
R715-2.5%Pt5%Cu
R815-2.5%Pt5%Cu
R815-2.5%Pt3%Cu

FIG. 76

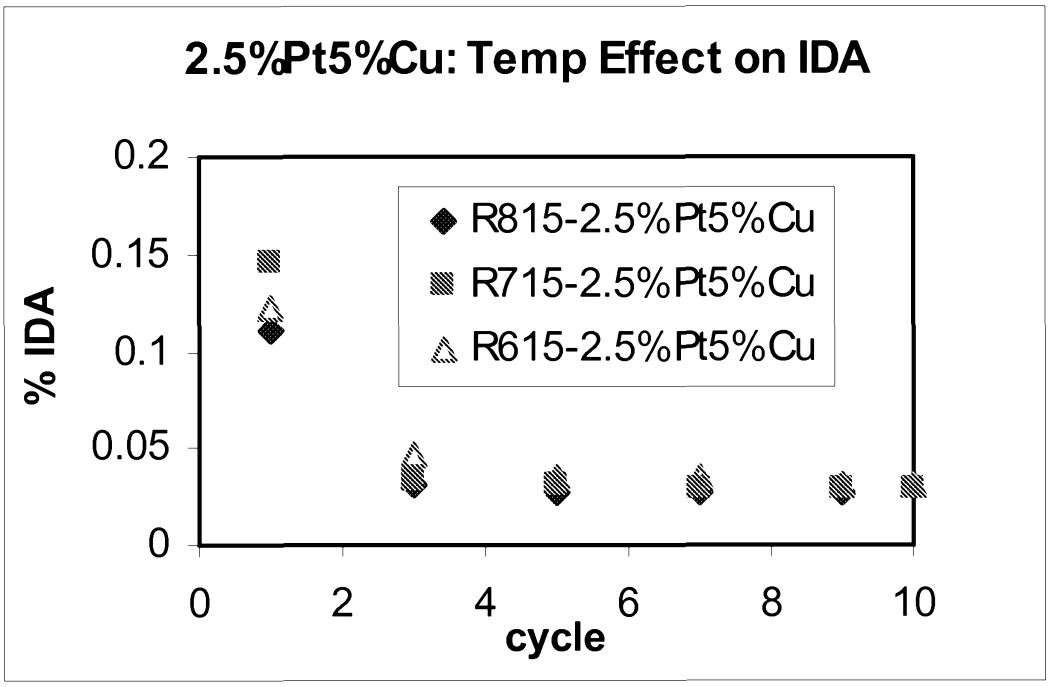

2.5%Pt5%Cu: Temp Effect on IDA
% IDA
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
cycle
R815-2.5%Pt5%Cu
R715-2.5%Pt5%Cu
R615-2.5%Pt5%Cu

FIG. 77

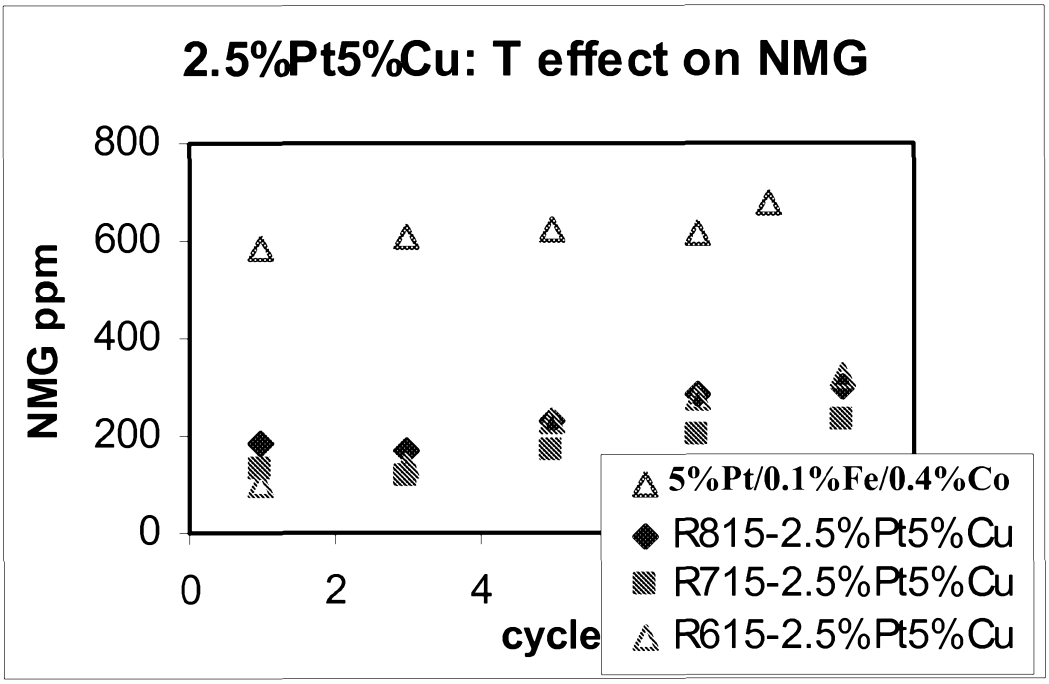

2.5%Pt5%Cu: T effect on NMG
NMG ppm
800
600
400
200
0
0
2
4
cycle
5%Pt/0.1%Fe/0.4%Co
R815-2.5%Pt5%Cu
R715-2.5%Pt5%Cu
R615-2.5%Pt5%Cu

FIG. 78

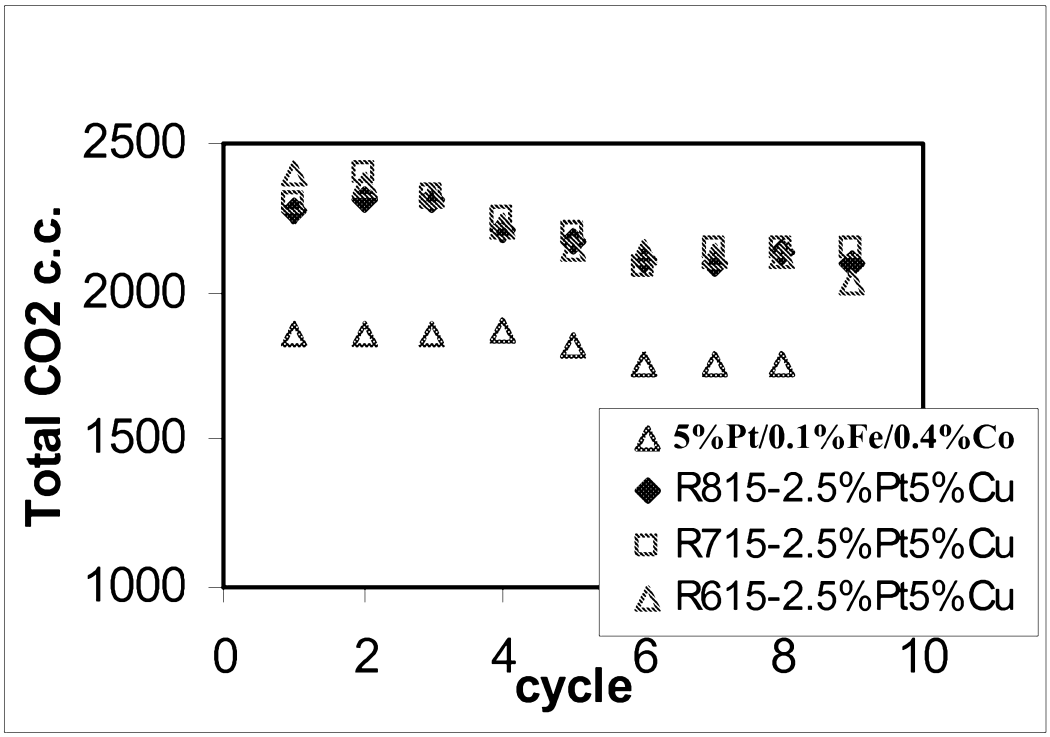

Total CO2 c.c.
2500
2000
1500
1000
0
2
4
6
8
10
cycle
5%Pt/0.1%Fe/0.4%Co
R815-2.5%Pt5%Cu
R715-2.5%Pt5%Cu
R615-2.5%Pt5%Cu

FIG. 79

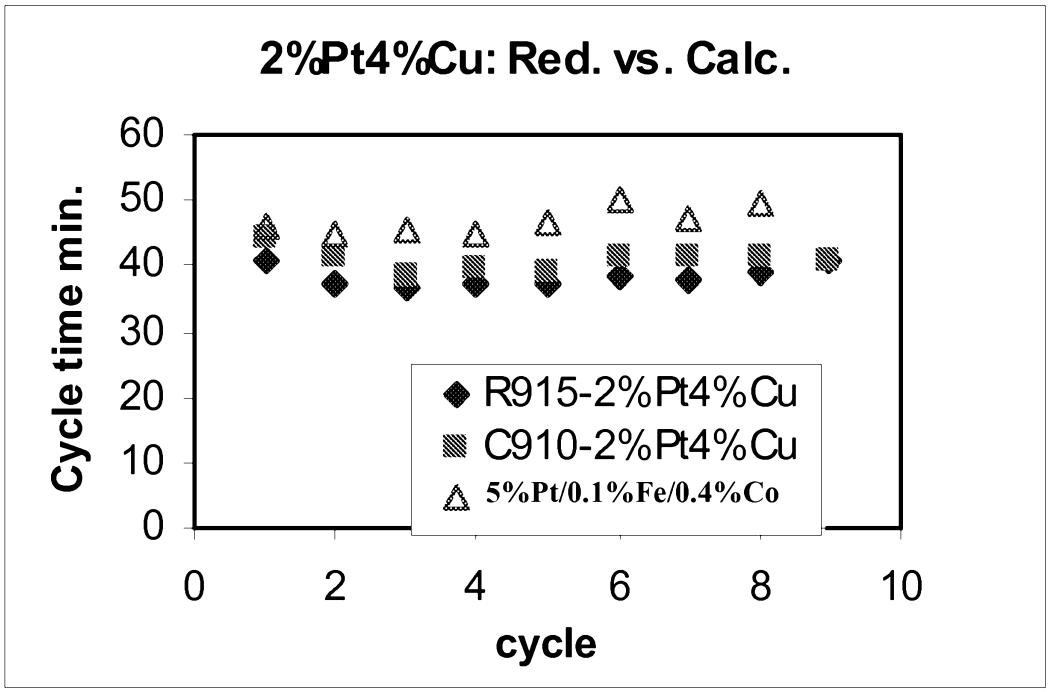

2%Pt4%Cu: Red. vs. Calc.
Cycle time min.
60
50
40
30
20
10
0
0
2
4
6
8
10
cycle
R915-2%Pt4%Cu
C910-2%Pt4%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 80

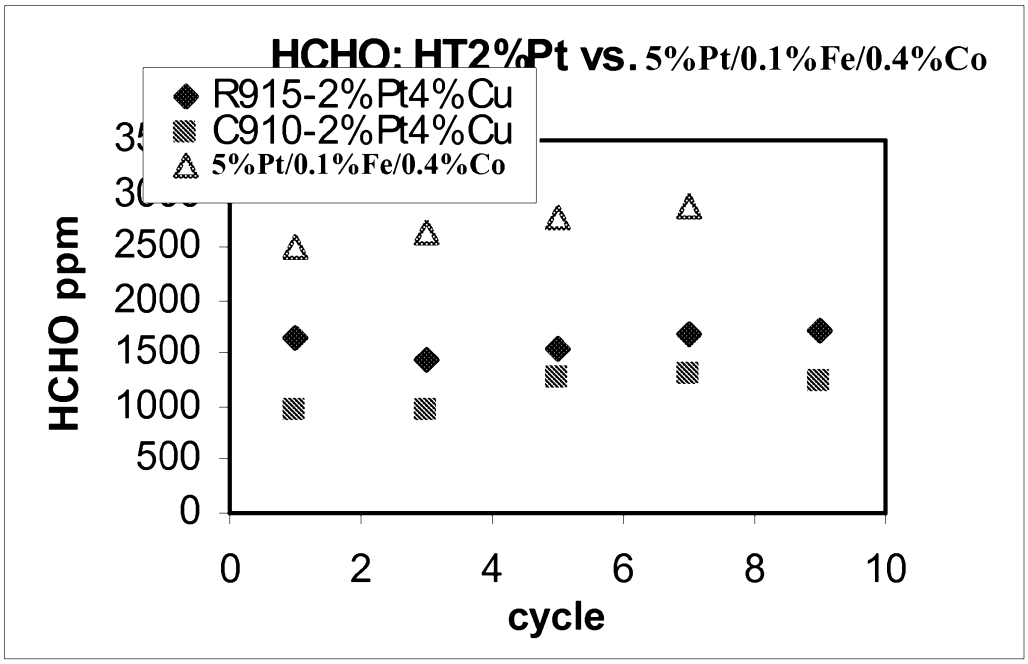

HCHO: HT2%Pt vs. 5%Pt/0.1%Fe/0.4%Co
R915-2%Pt4%Cu
C910-2%Pt4%Cu
5%Pt/0.1%Fe/0.4%Co
HCHO ppm
2500
2000
1500
1000
500
0
0
2
4
6
8
10
cycle

FIG. 81

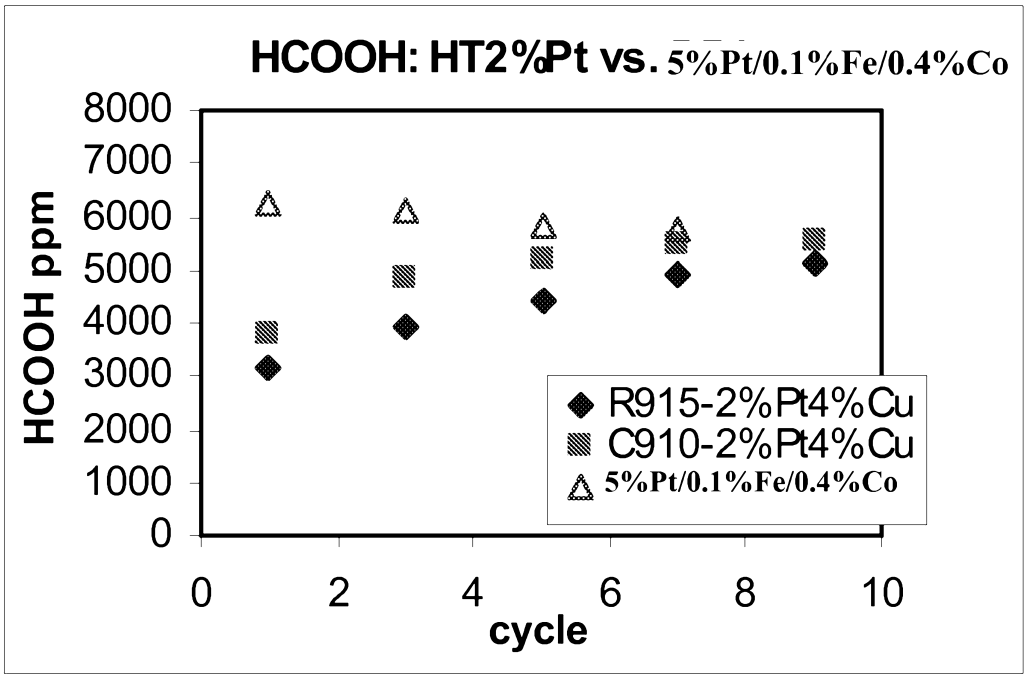

HCOOH: HT2%Pt vs. 5%Pt/0.1%Fe/0.4%Co
HCOOH ppm
8000
7000
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
R915-2%Pt4%Cu
C910-2%Pt4%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 82

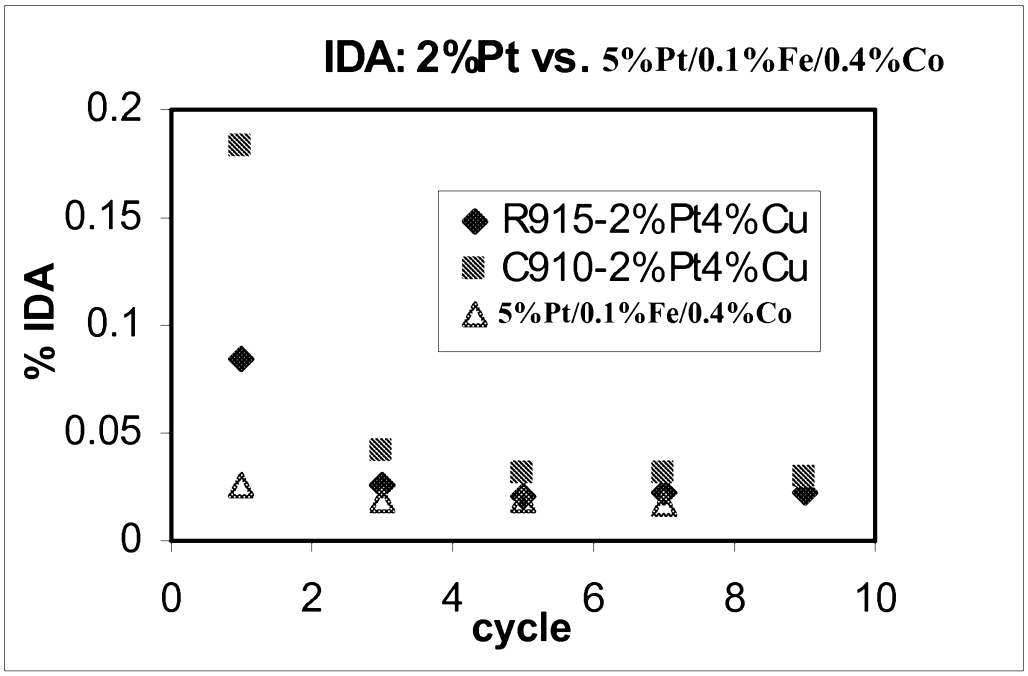

IDA: 2%Pt vs. 5%Pt/0.1%Fe/0.4%Co
% IDA
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
cycle
R915-2%Pt4%Cu
C910-2%Pt4%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 83

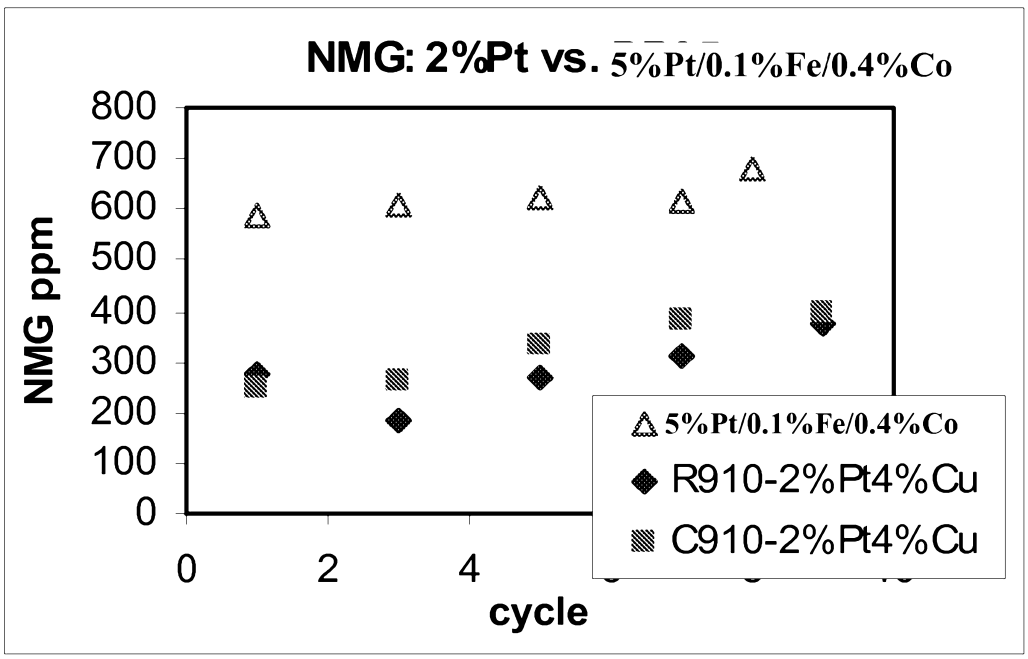

NMG: 2%Pt vs. 5%Pt/0.1%Fe/0.4%Co
NMG ppm
800
700
600
500
400
300
200
100
0
0
2
4
cycle
5%Pt/0.1%Fe/0.4%Co
R910-2%Pt4%Cu
C910-2%Pt4%Cu

FIG. 84

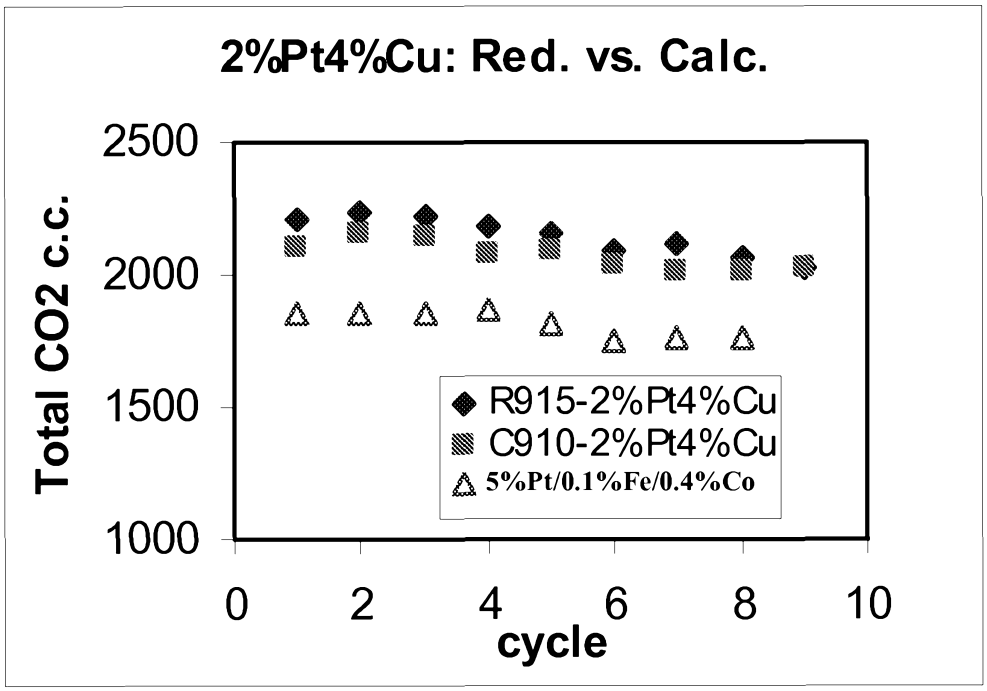

2%Pt4%Cu: Red. vs. Calc.
Total CO2 c.c.
2500
2000
1500
1000
0
2
4
6
8
10
cycle
R915-2%Pt4%Cu
C910-2%Pt4%Cu
5%Pt/0.1%Fe/0.4%Co

FIG. 85

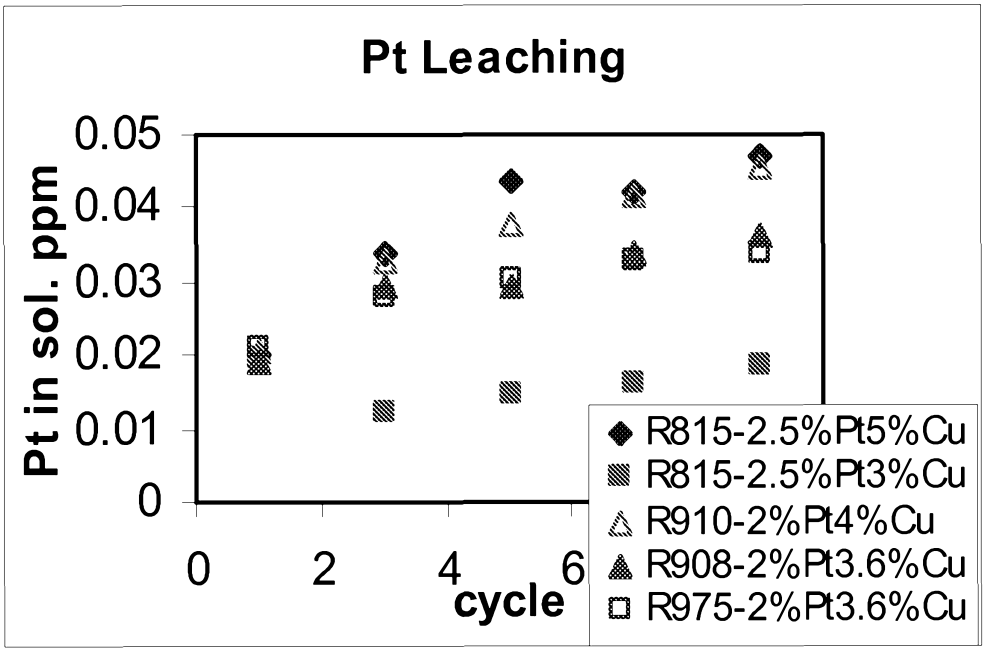

Pt Leaching
Pt in sol. ppm
0.05
0.04
0.03
0.02
0.01
0
0
2
4
6
cycle
R815-2.5%Pt5%Cu
R815-2.5%Pt3%Cu
R910-2%Pt4%Cu
R908-2%Pt3.6%Cu
R975-2%Pt3.6%Cu

FIG. 86

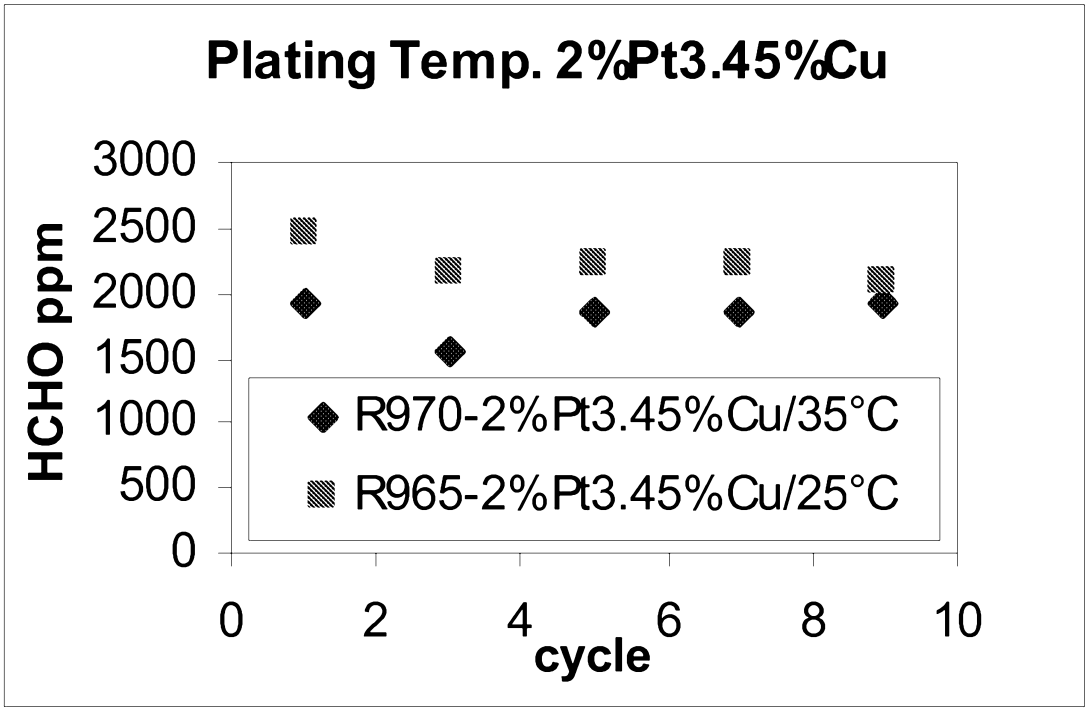

Plating Temp. 2%Pt3.45%Cu
HCHO ppm
3000
2500
2000
1500
1000
500
0
0
2
4
6
8
10
cycle
R970-2%Pt3.45%Cu/35°C
R965-2%Pt3.45%Cu/25°C

FIG. 87

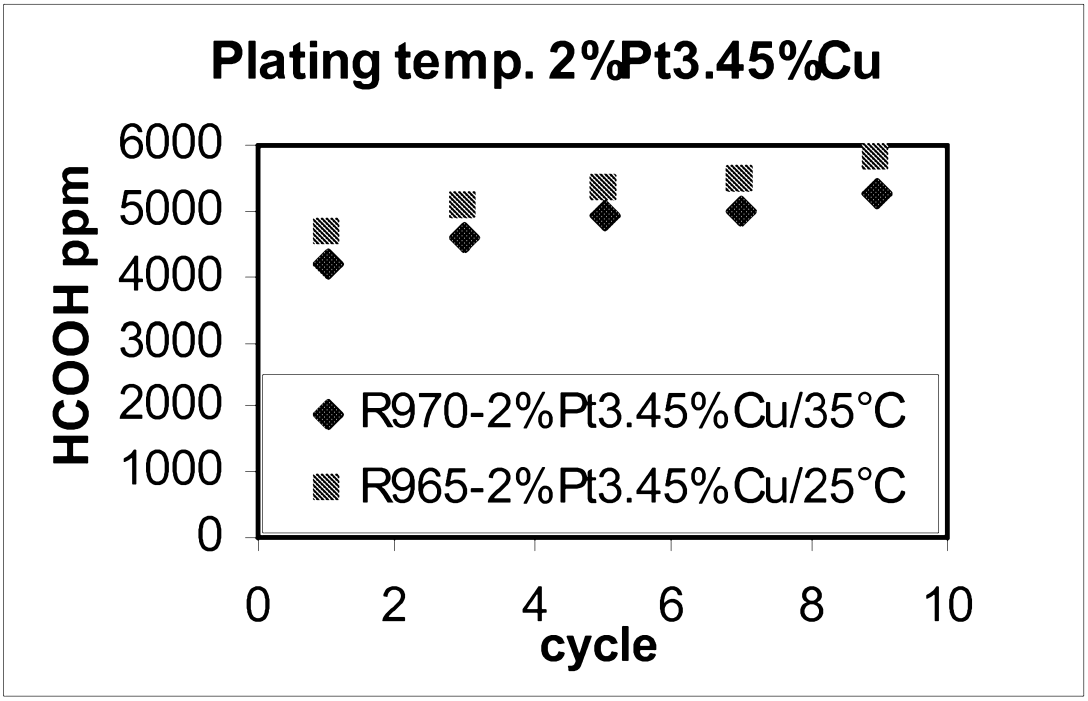

Plating temp. 2%Pt3.45%Cu
HCOOH ppm
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
R970-2%Pt3.45%Cu/35°C
R965-2%Pt3.45%Cu/25°C

FIG. 88

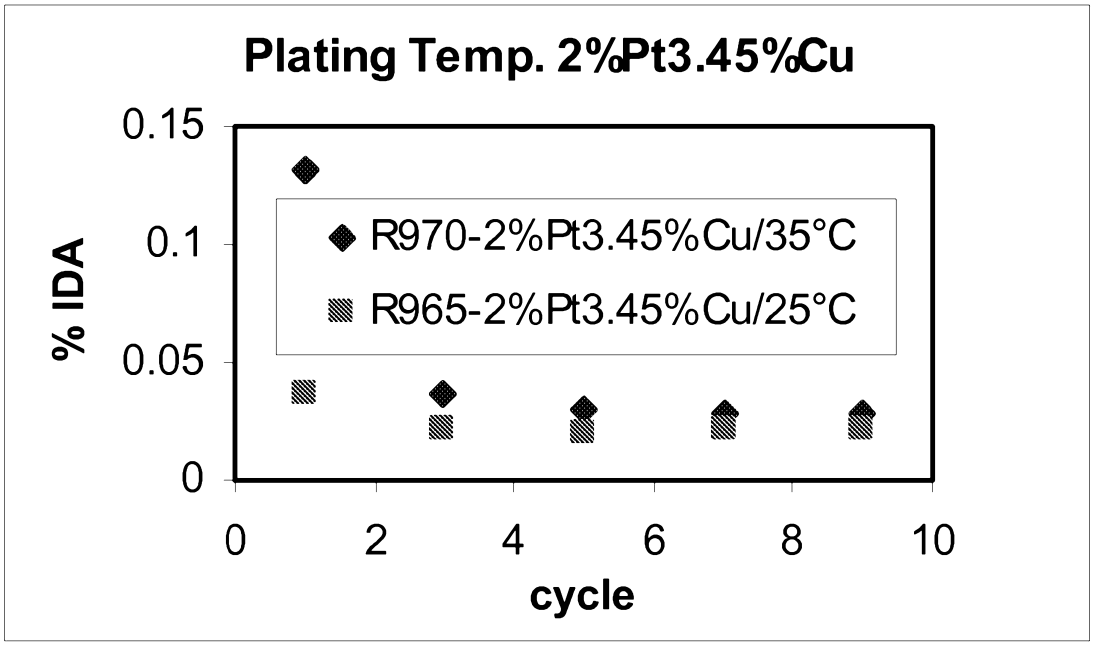

Plating Temp. 2%Pt3.45%Cu
% IDA
0.15
0.1
0.05
0
0
2
4
6
8
10
cycle
R970-2%Pt3.45%Cu/35°C
R965-2%Pt3.45%Cu/25°C

FIG. 89

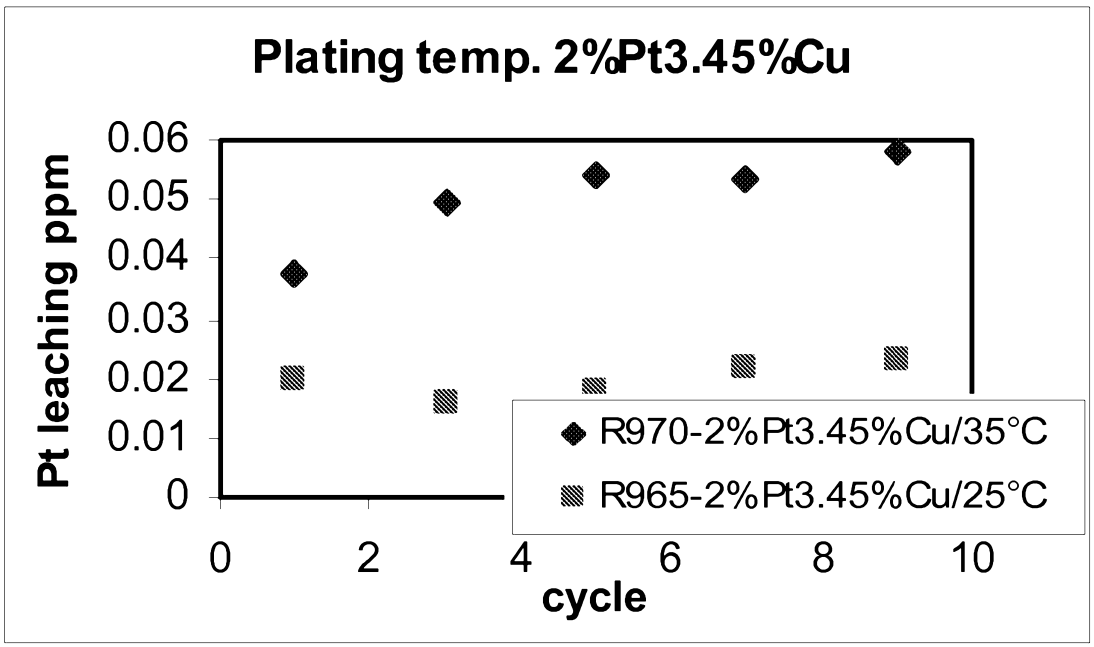

Plating temp. 2%Pt3.45%Cu
Pt leaching ppm
0.06
0.05
0.04
0.03
0.02
0.01
0
0
2
4
6
8
10
cycle
R970-2%Pt3.45%Cu/35°C
R965-2%Pt3.45%Cu/25°C

FIG. 90

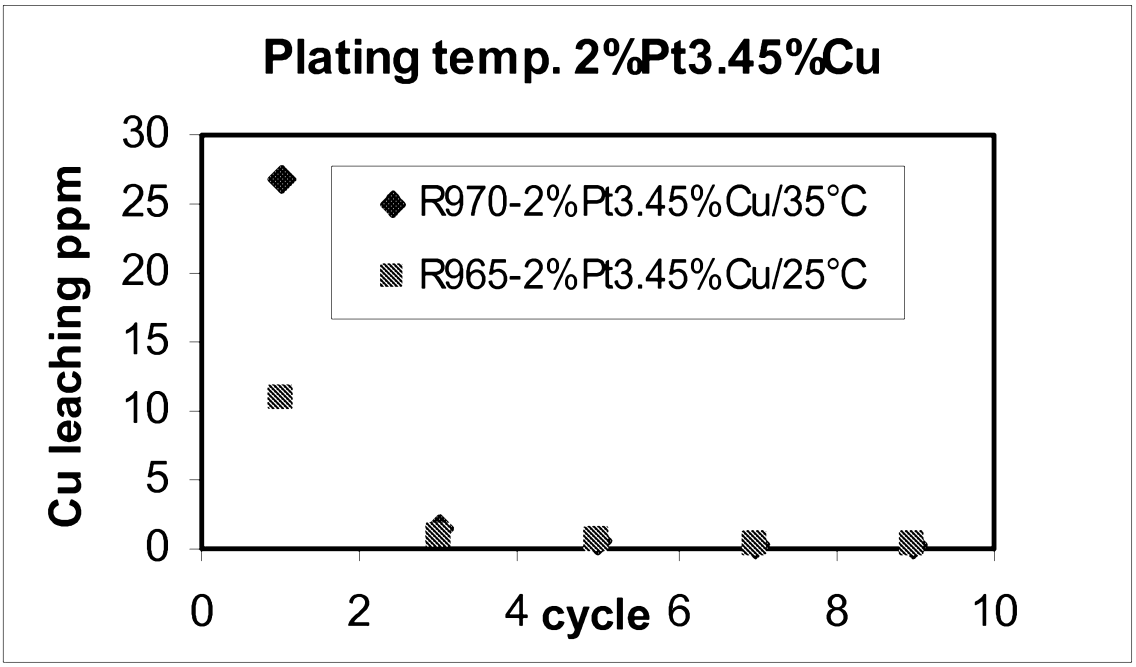

Plating temp. 2%Pt3.45%Cu
Cu leaching ppm
30
25
20
15
10
5
0
0
2
4
6
8
10
cycle
R970-2%Pt3.45%Cu/35°C
R965-2%Pt3.45%Cu/25°C

FIG. 91

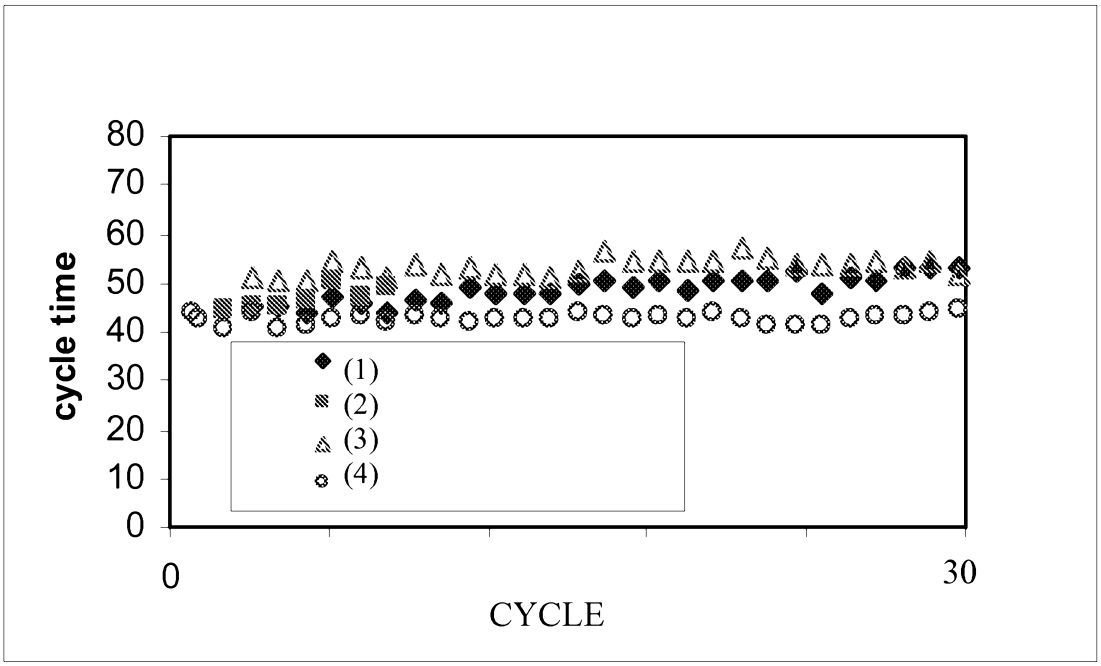

cycle time
80
70
60
50
40
30
20
10
0
0
30
CYCLE
(1)
(2)
(3)
(4)

FIG. 92

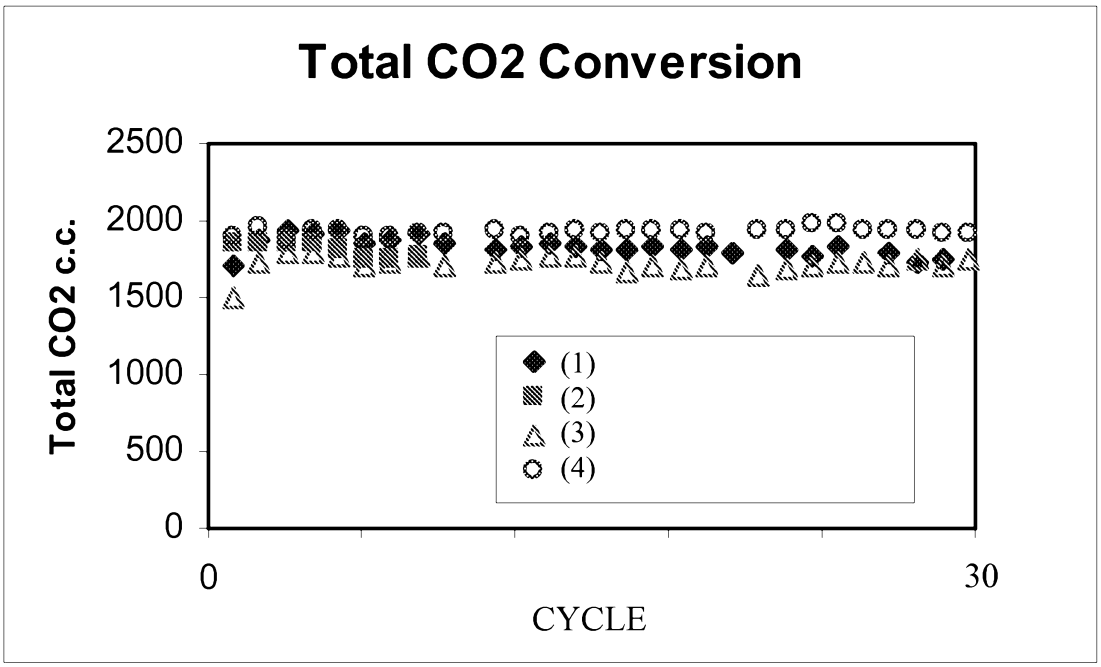

Total CO2 Conversion
Total CO2 c.c.
2500
2000
1500
1000
500
0
0
30
CYCLE
(1)
(2)
(3)
(4)

FIG. 93

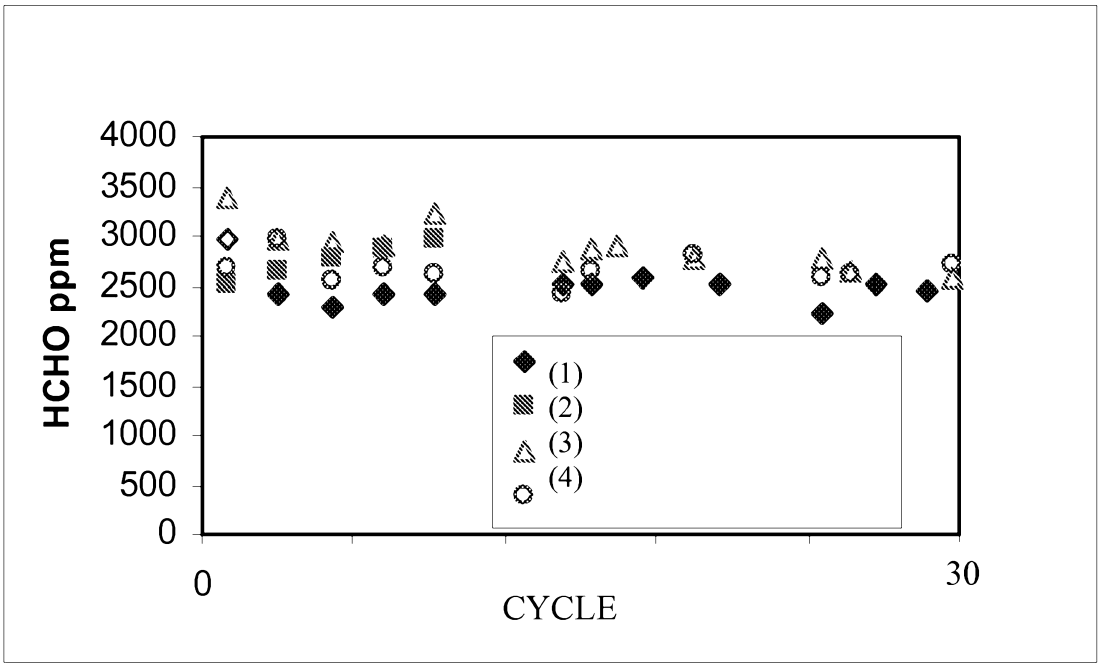

HCHO ppm
4000
3500
3000
2500
2000
1500
1000
500
0
0
30
CYCLE
(1)
(2)
(3)
(4)

FIG. 94

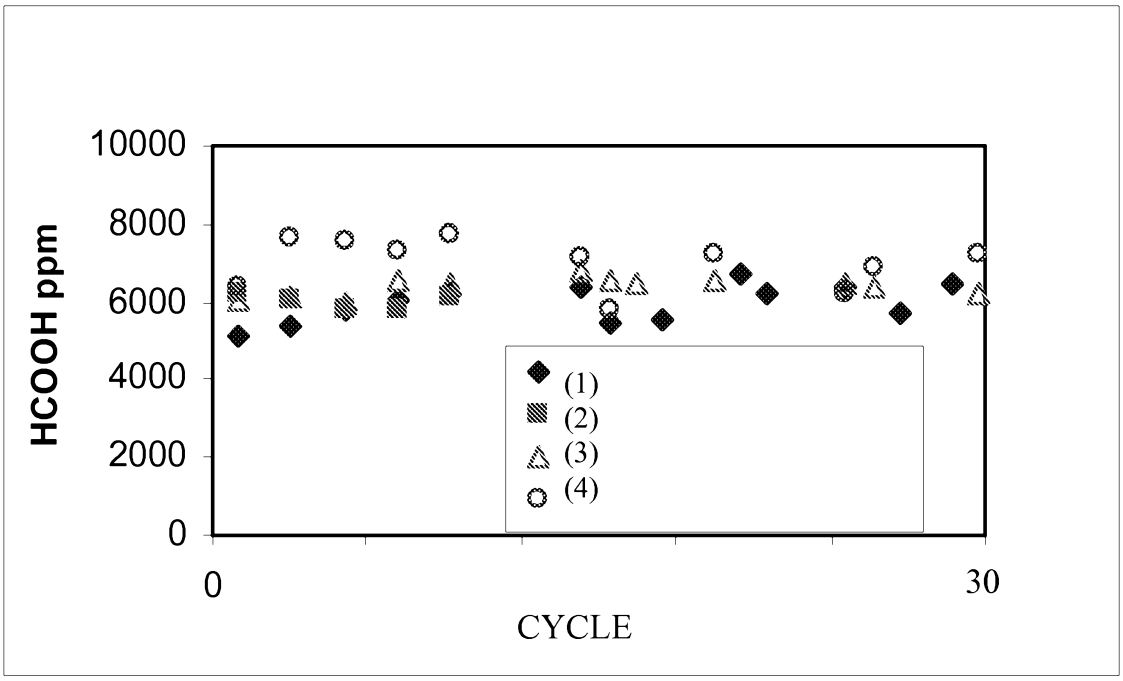

10000
8000
6000
4000
2000
0
HCOOH ppm
0
30
CYCLE
(1)
(2)
(3)
(4)

FIG. 95

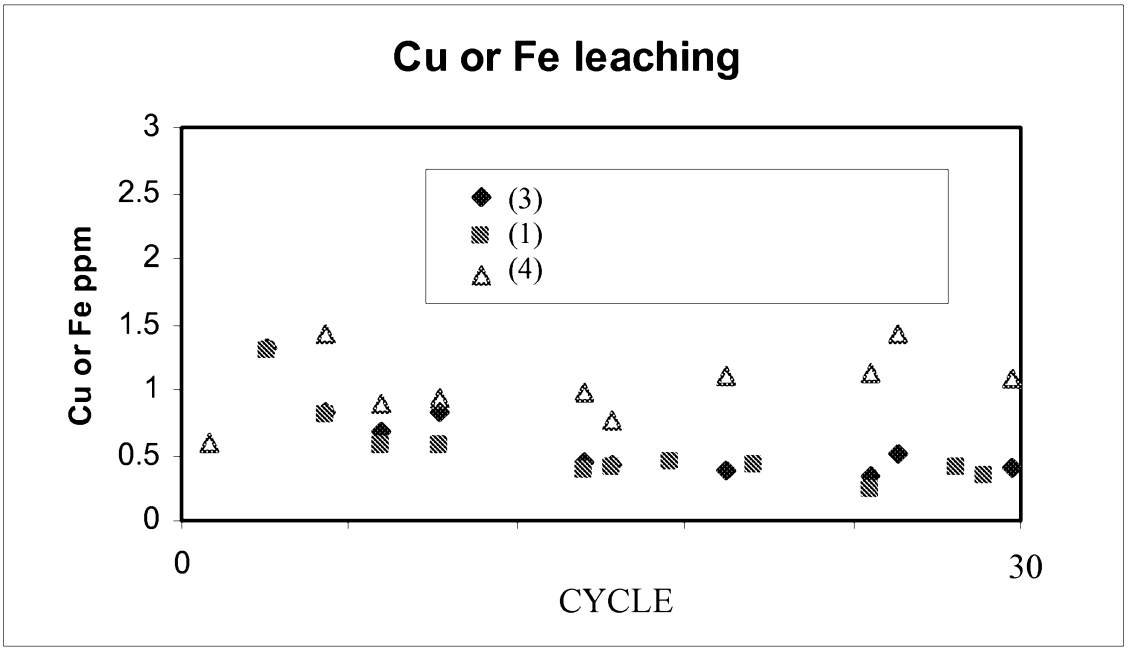

Cu or Fe leaching
3
2.5
2
1.5
1
0.5
0
Cu or Fe ppm
0
30
CYCLE
(3)
(1)
(4)

FIG. 96

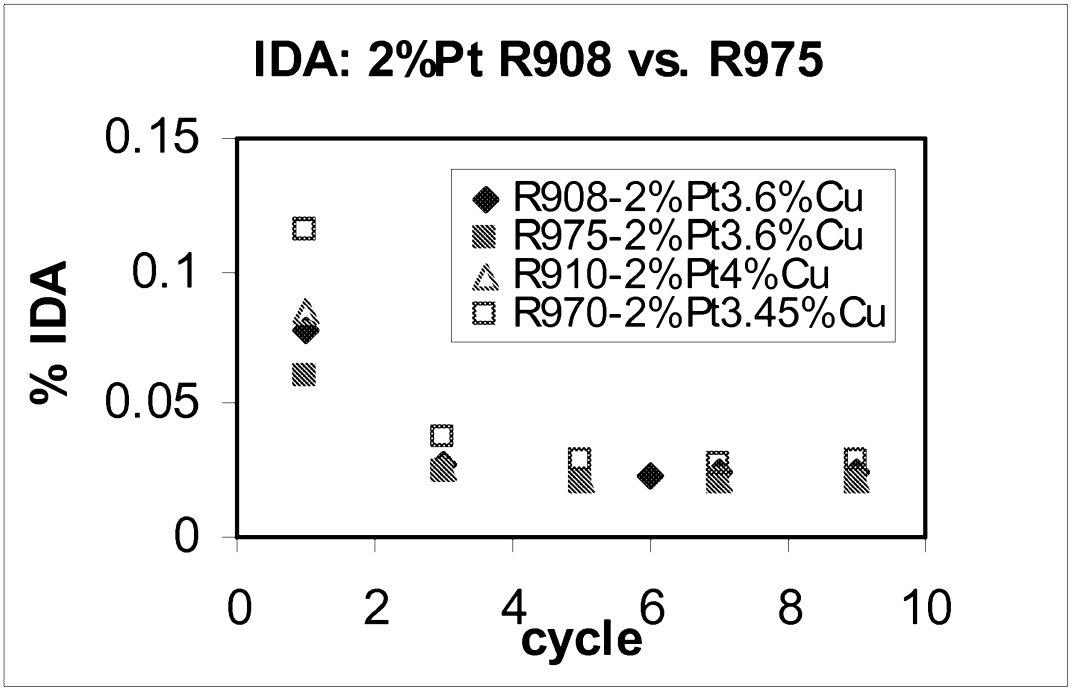

IDA: 2%Pt R908 vs. R975
% IDA
0.15
0.1
0.05
0
0
2
4
6
8
10
cycle
R908-2%Pt3.6%Cu
R975-2%Pt3.6%Cu
R910-2%Pt4%Cu
R970-2%Pt3.45%Cu

FIG. 97

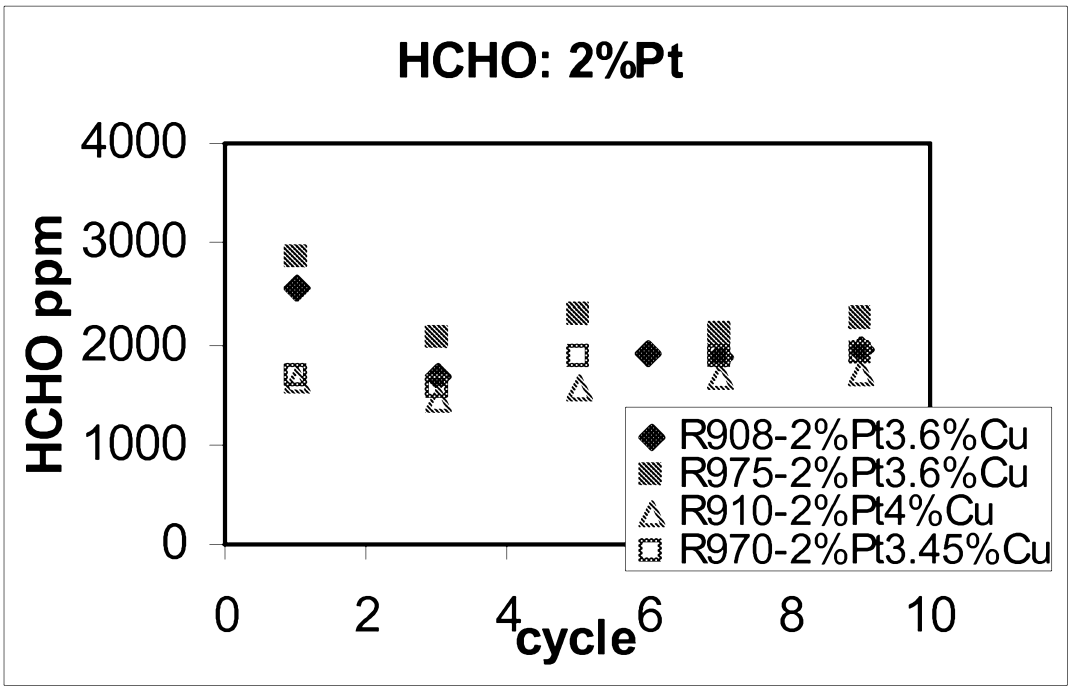

HCHO: 2%Pt
HCHO ppm
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
R908-2%Pt3.6%Cu
R975-2%Pt3.6%Cu
R910-2%Pt4%Cu
R970-2%Pt3.45%Cu

FIG. 98

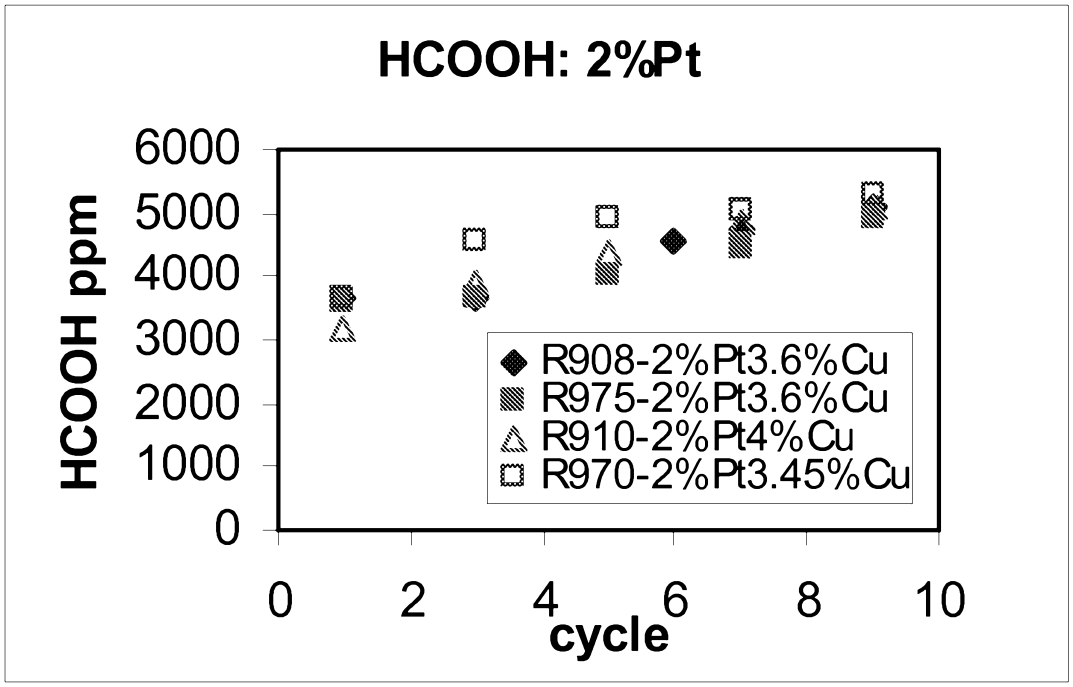

HCOOH: 2%Pt
HCOOH ppm
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
cycle
R908-2%Pt3.6%Cu
R975-2%Pt3.6%Cu
R910-2%Pt4%Cu
R970-2%Pt3.45%Cu

FIG. 99

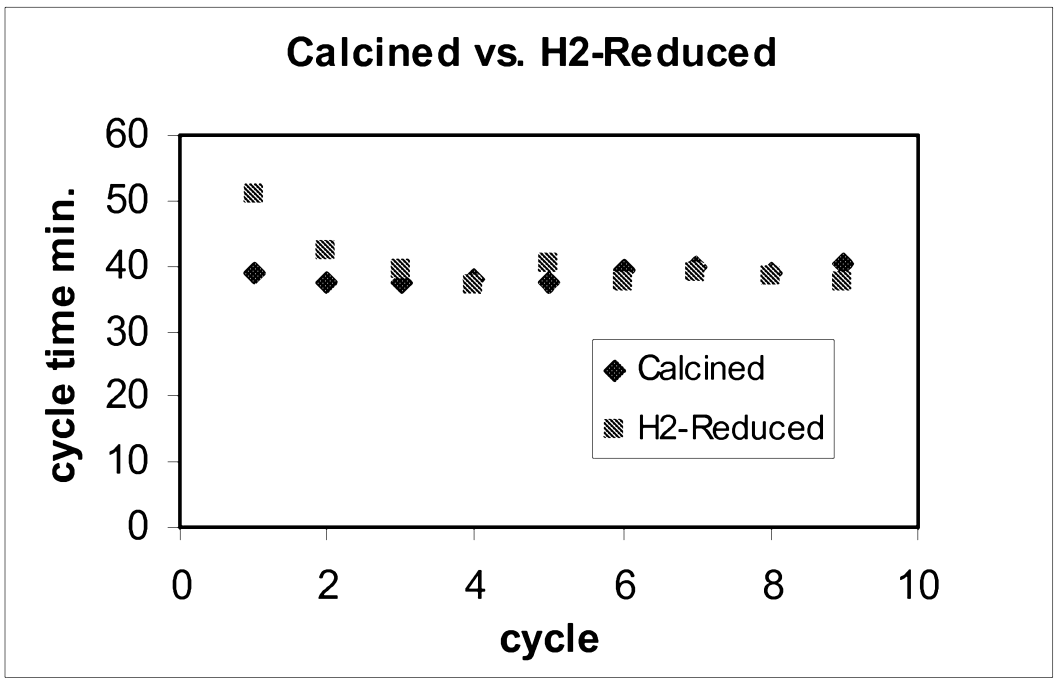

Calcined vs. H2-Reduced
cycle time min.
60
50
40
30
20
10
0
0
2
4
6
8
10
cycle
Calcined
H2-Reduced

FIG. 100

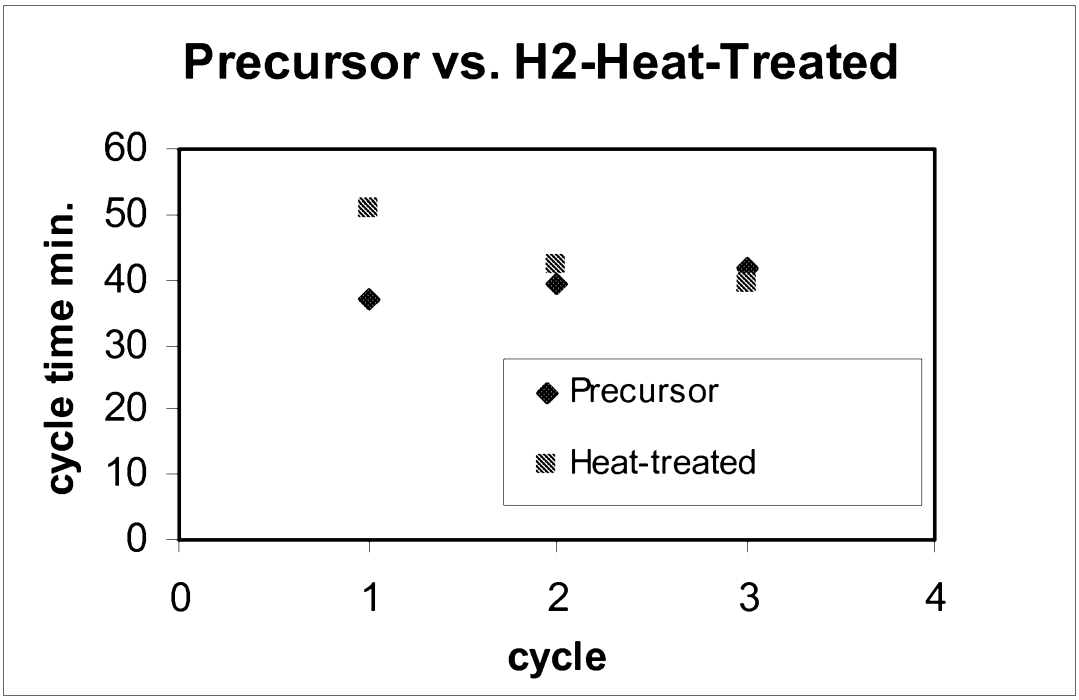


FIG. 101

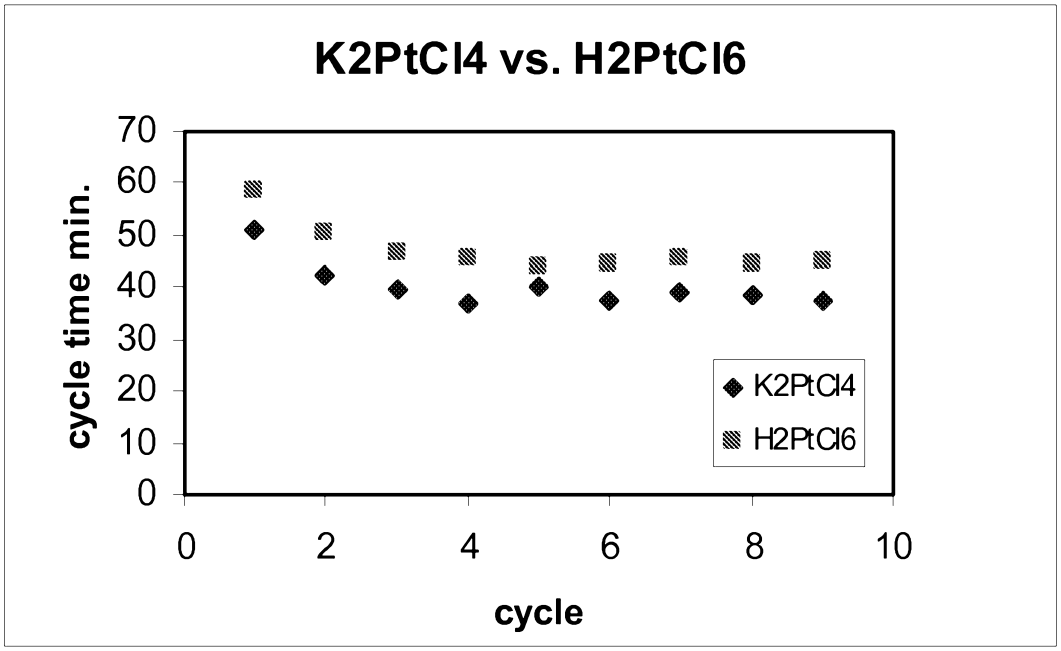


FIG. 102

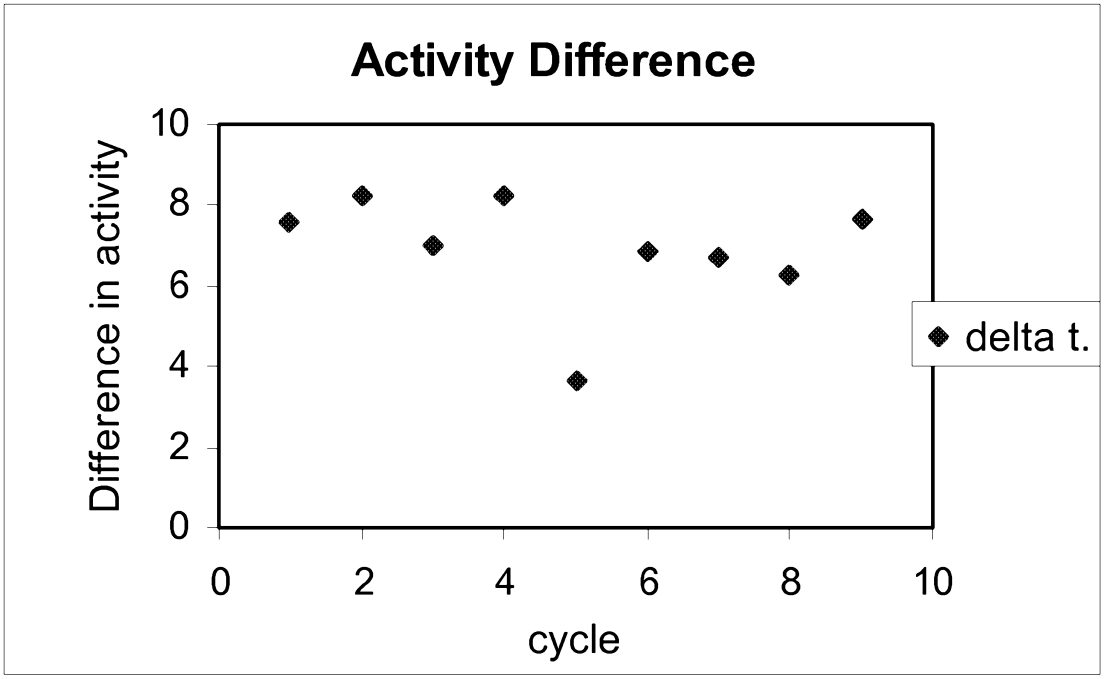


FIG. 103

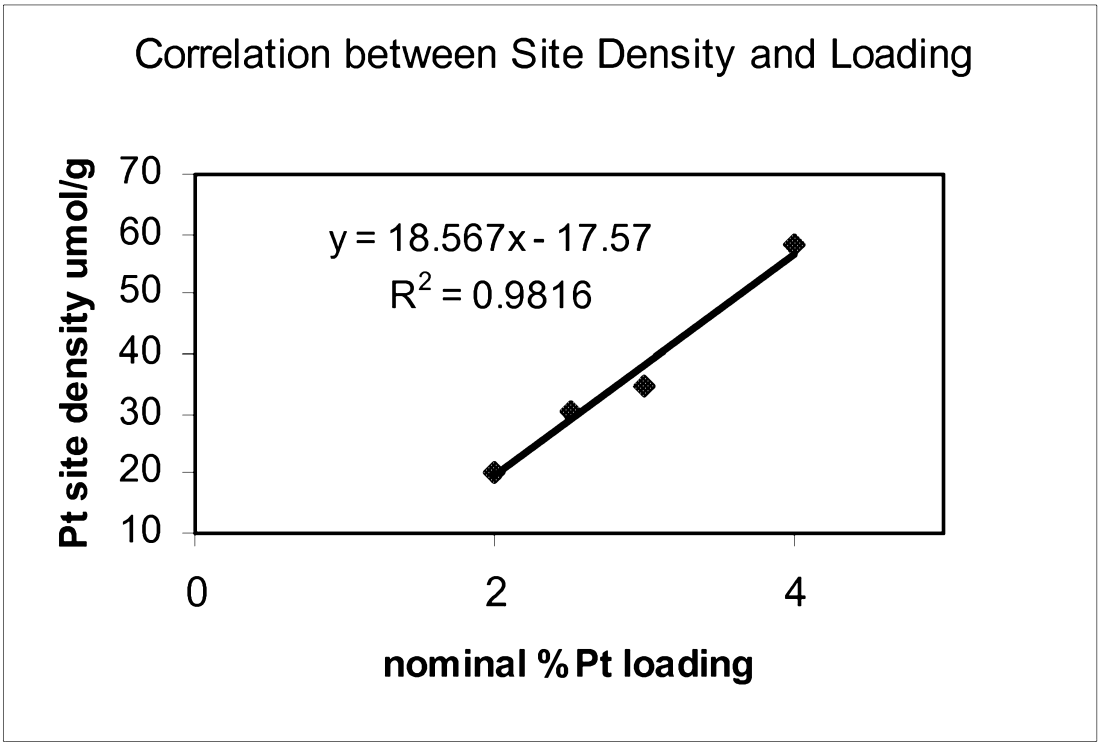


FIG. 104

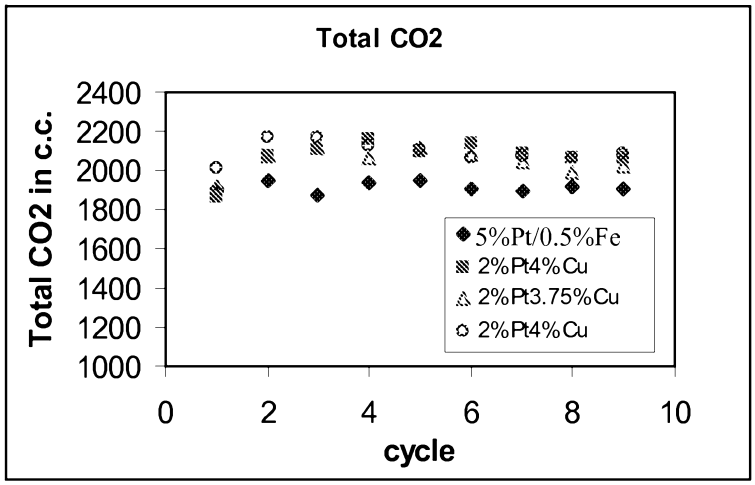


FIG. 105

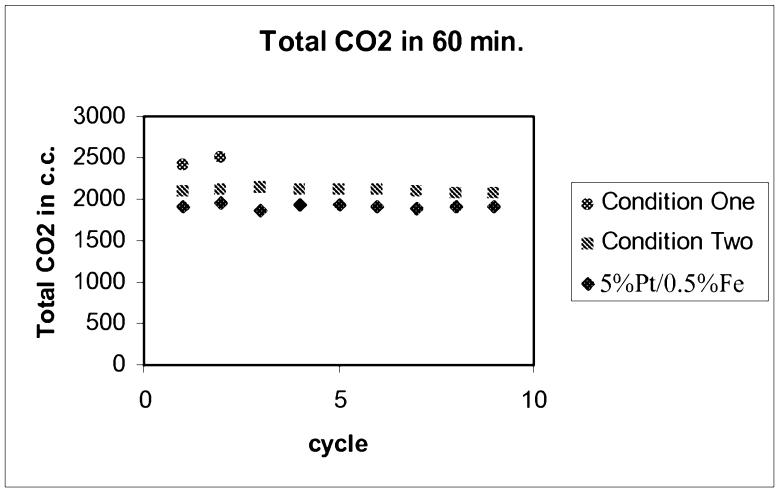


FIG. 106

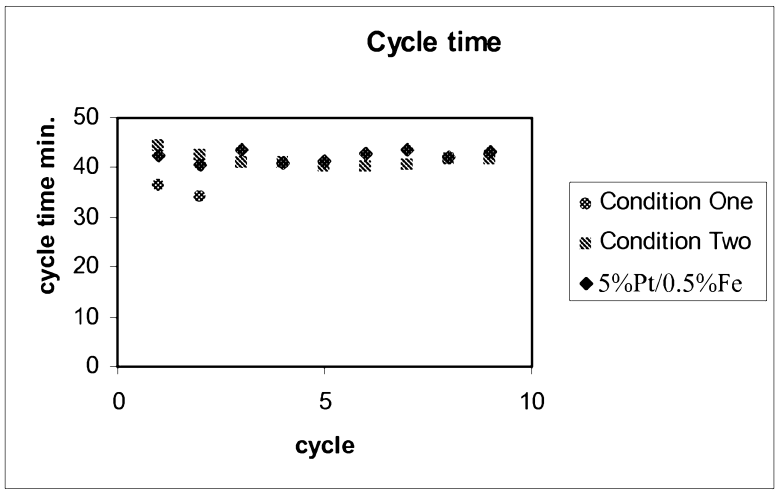


FIG. 107

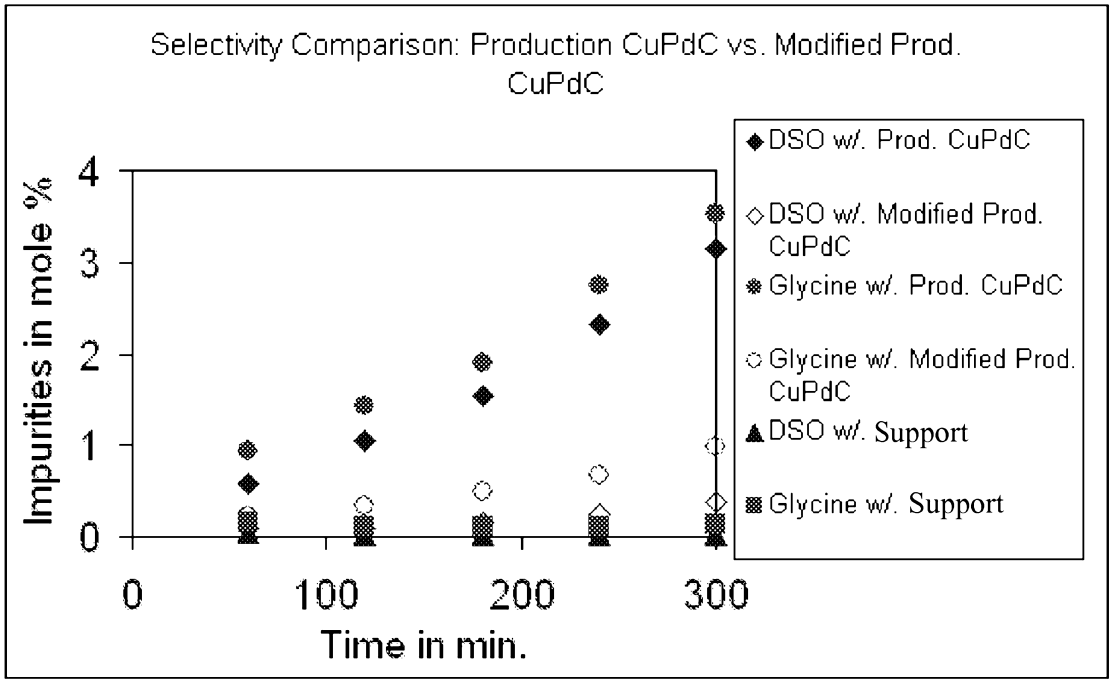


FIG. 108

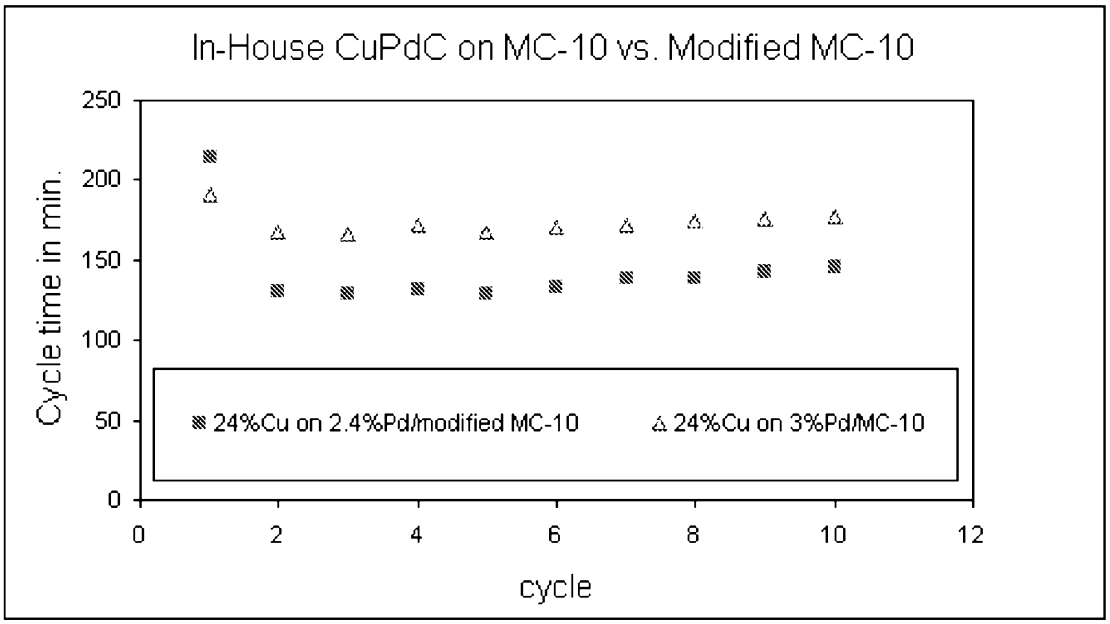


FIG. 109

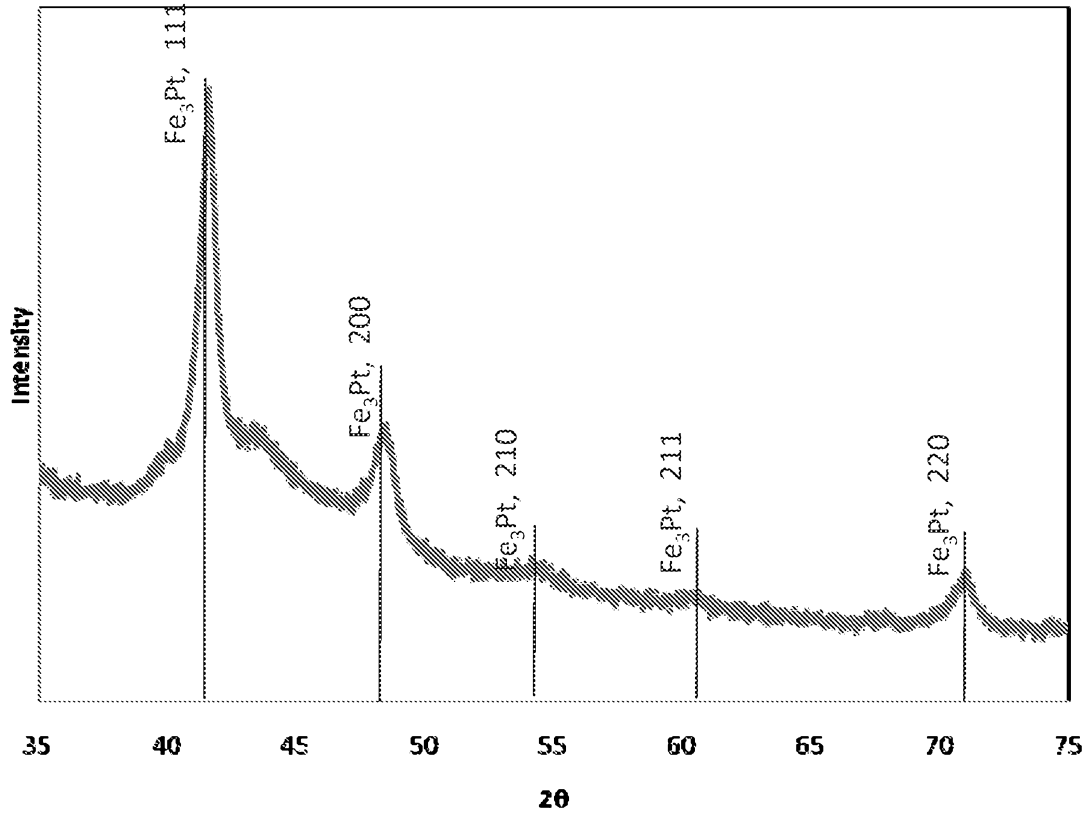

Intensity
Fe3Pt, 111
Fe3Pt, 200
Fe3Pt, 210
Fe3Pt, 211
Fe3Pt, 220
35
40
45
50
55
60
65
70
75
2θ

FIG. 110

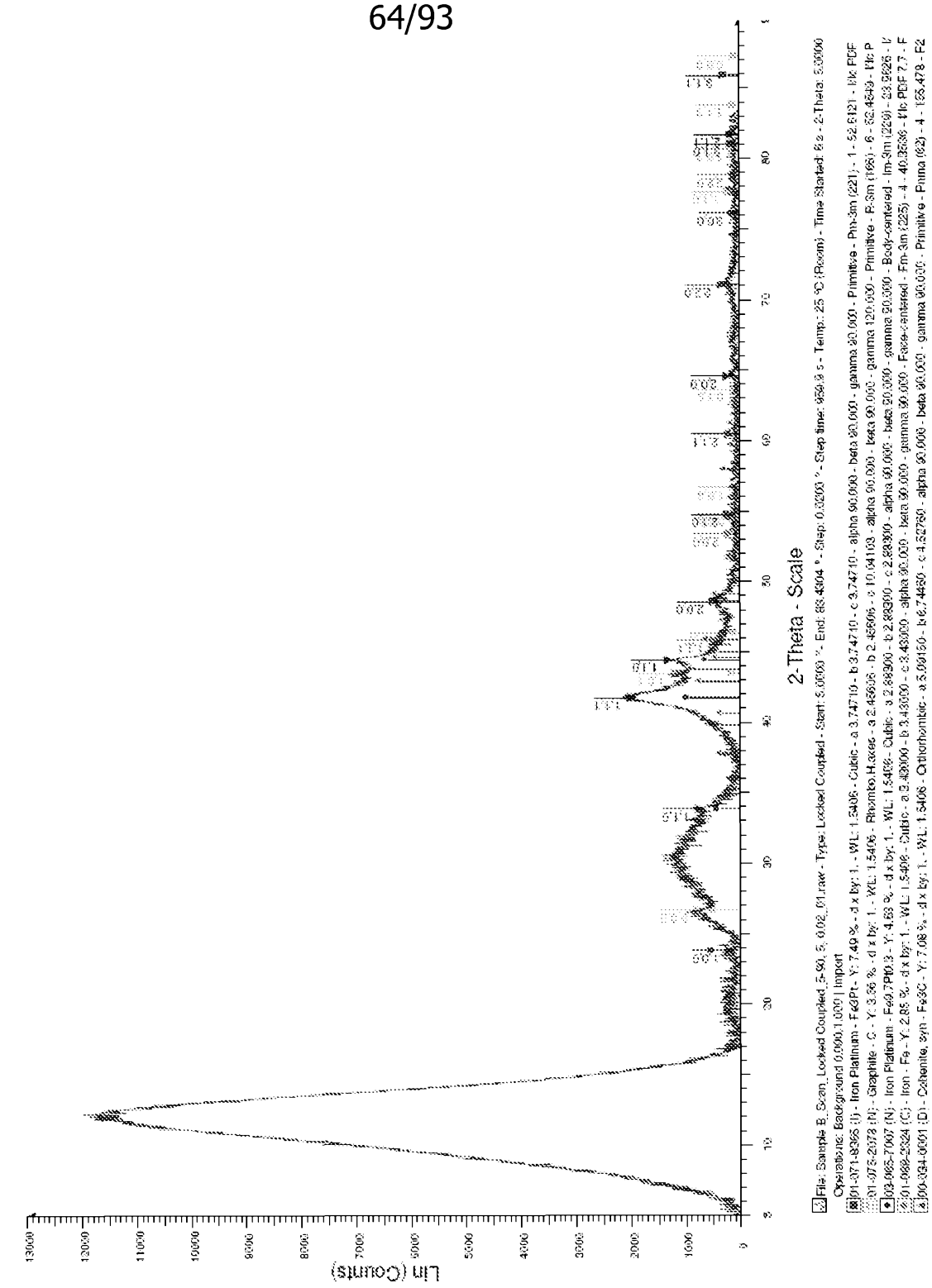


FIG. 111

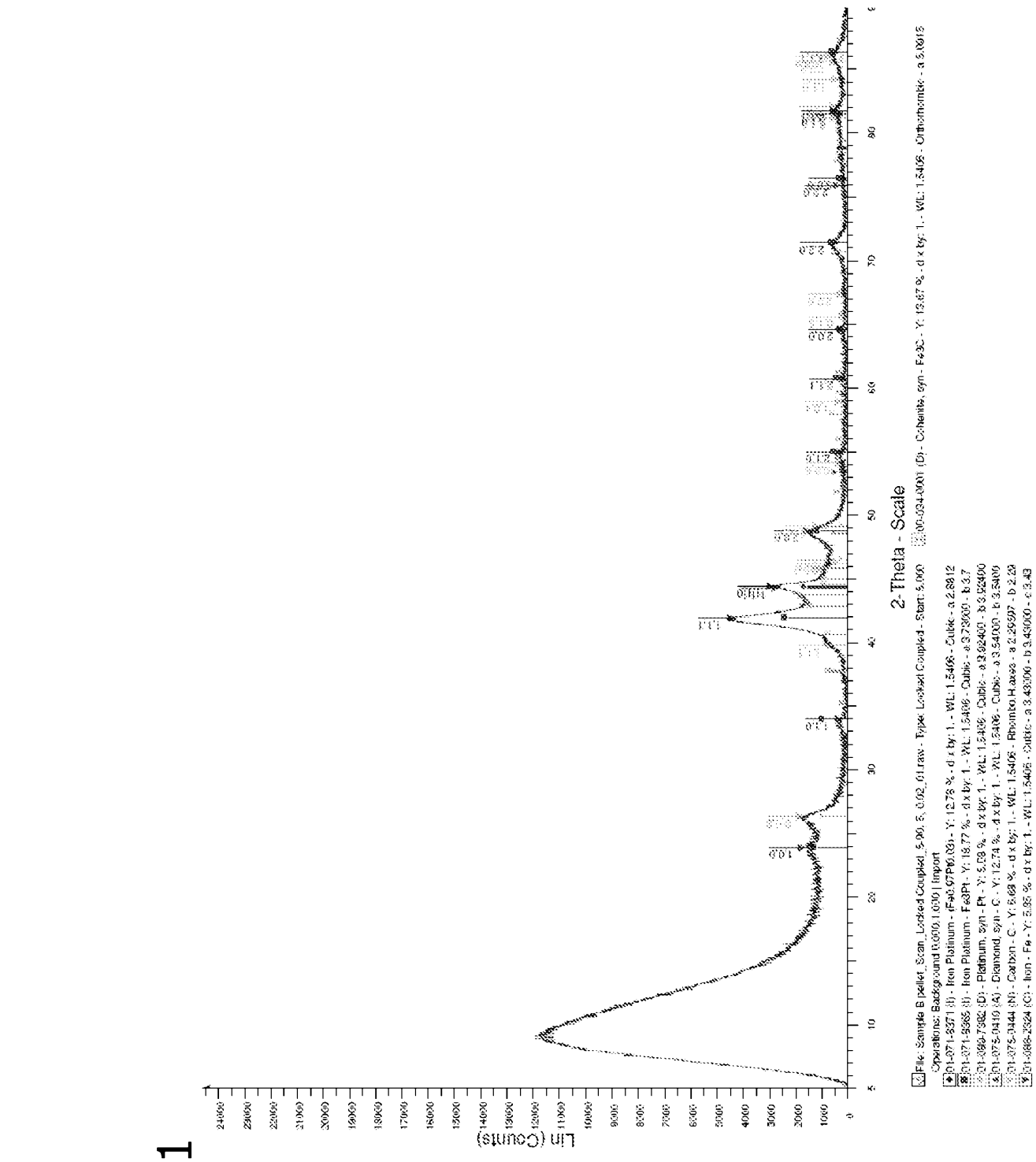

Lin (Counts)
2-Theta - Scale
File: Sample B pellet_Scan_Locked Coupled_5.00_5_002_01.raw - Type: Locked Coupled - Start: 5.000
Operations: Background 0.000,1.000 | Import
01-071-8371 (B) - Iron Platinum - rFe0.97Pt0.03 - Y: 12.78 % - d x by: 1. - WL: 1.5406 - Cubic - a 2.8812
01-071-8365 (B) - Iron Platinum - Fe3Pt - Y: 18.77 % - d x by: 1. - WL: 1.5406 - Cubic - a 3.73600 - b 3.7
01-089-7382 (D) - Platinum, syn - Pt - Y: 5.08 % - d x by: 1. - WL: 1.5406 - Cubic - a 3.92400 - b 3.92400
01-075-0419 (A) - Diamond, syn - C - Y: 12.74 % - d x by: 1. - WL: 1.5406 - Cubic - a 3.54000 - b 3.5400
01-075-0444 (N) - Carbon - C - Y: 6.68 % - d x by: 1. - WL: 1.5406 - Rhombo Hexag - a 2.25597 - b 2.25
01-089-2324 (C) - Iron - Fe - Y: 5.85 % - d x by: 1. - WL: 1.5406 - Cubic - a 3.43500 - b 3.43500 - c 3.43

FIG. 111A

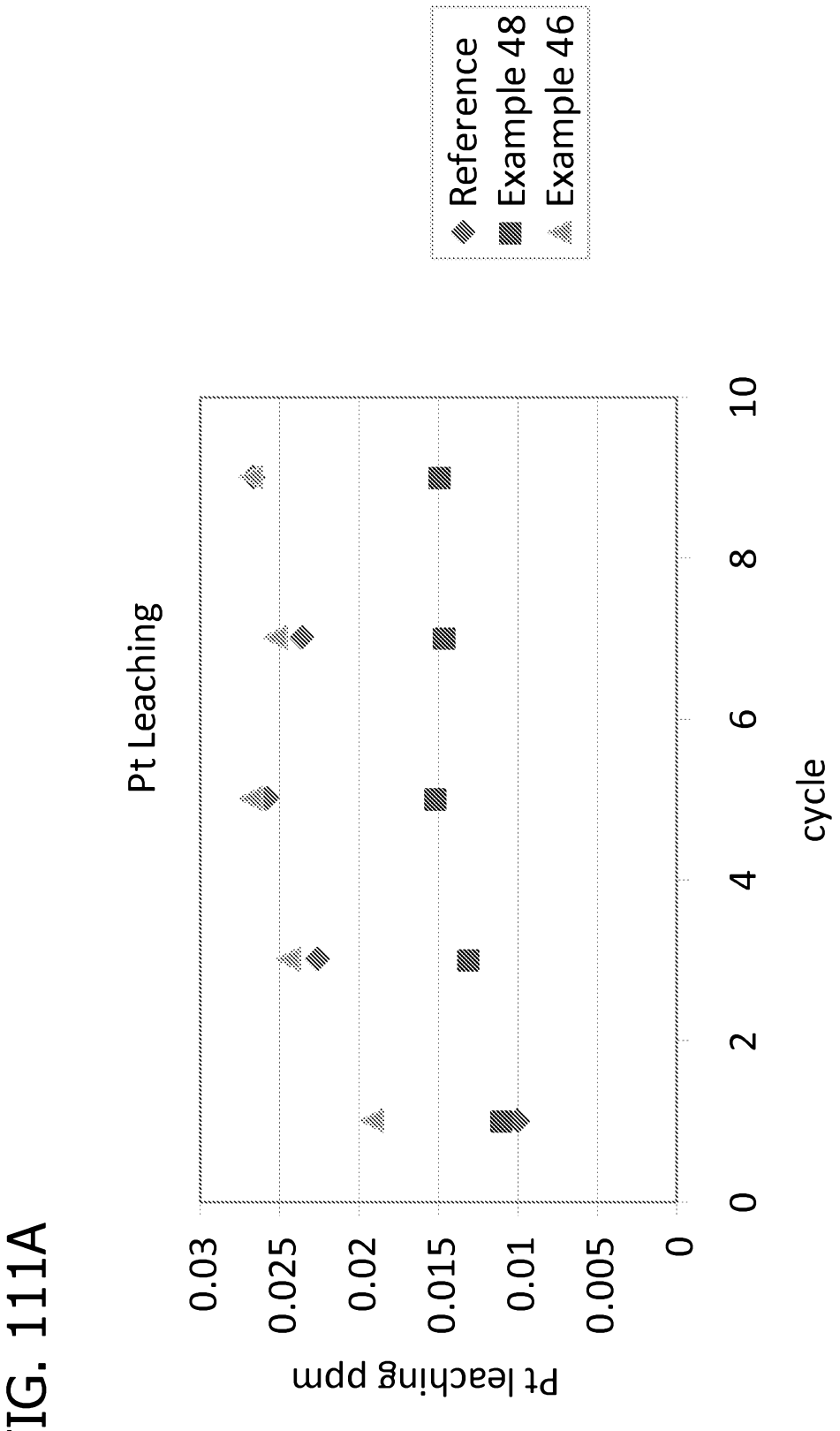

Pt Leaching
Reference
Example 48
Example 46
Pt leaching ppm
0.03
0.025
0.02
0.015
0.01
0.005
0
0
2
4
6
8
10
cycle

FIG. 112

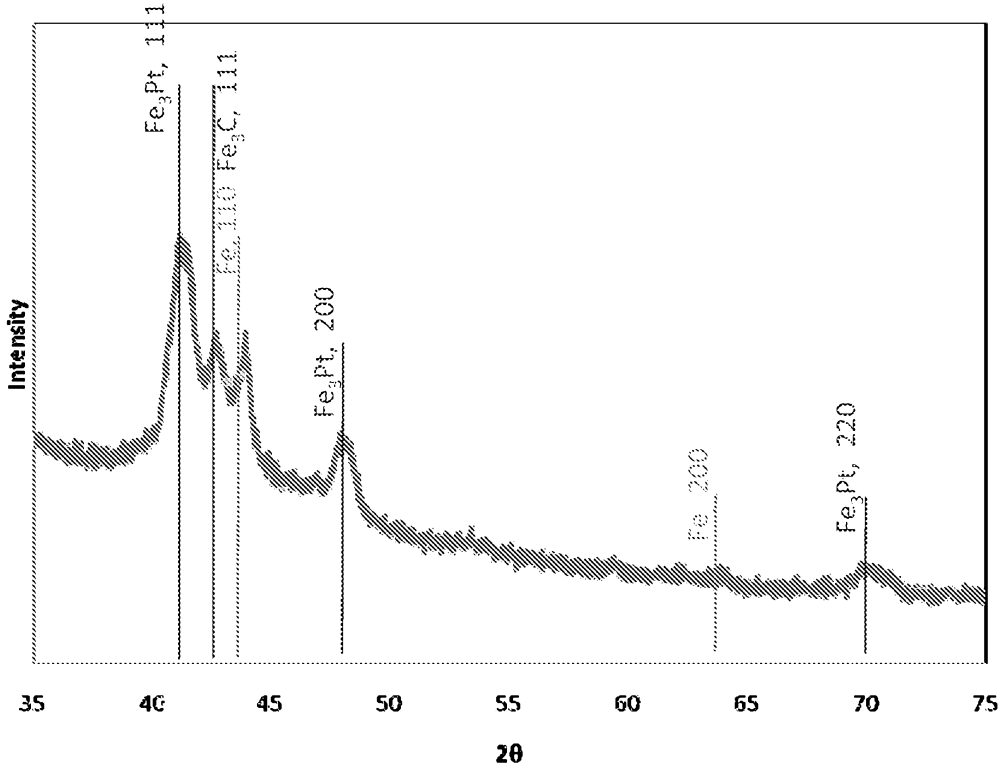


FIG. 113

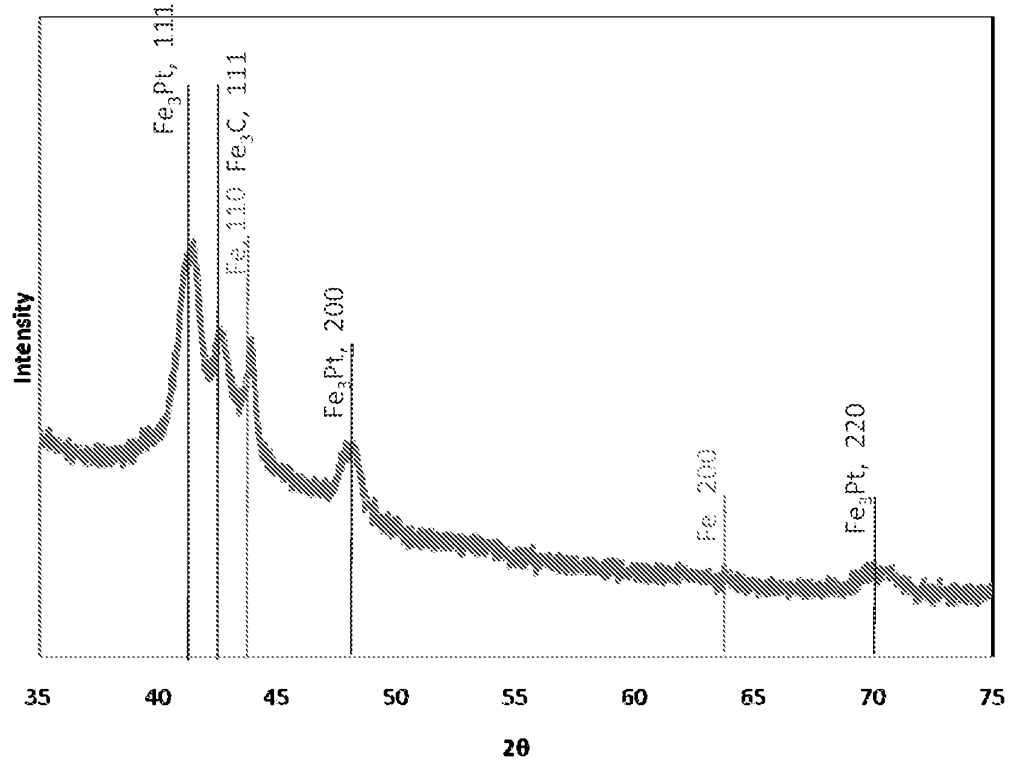


FIG. 114

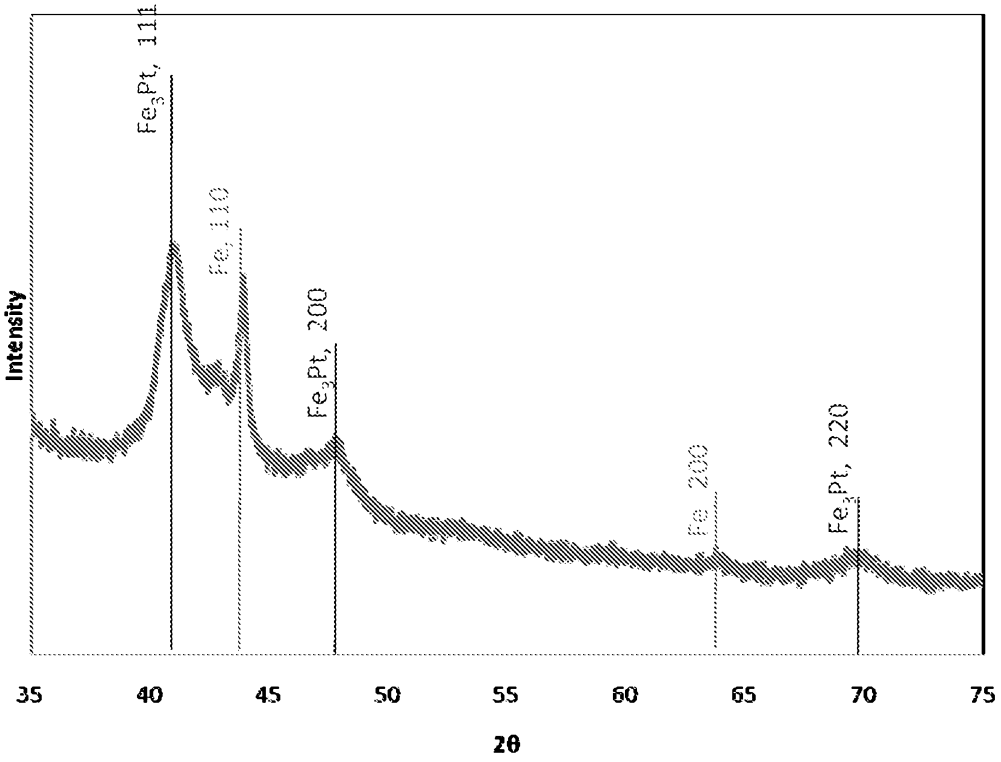


FIG. 115

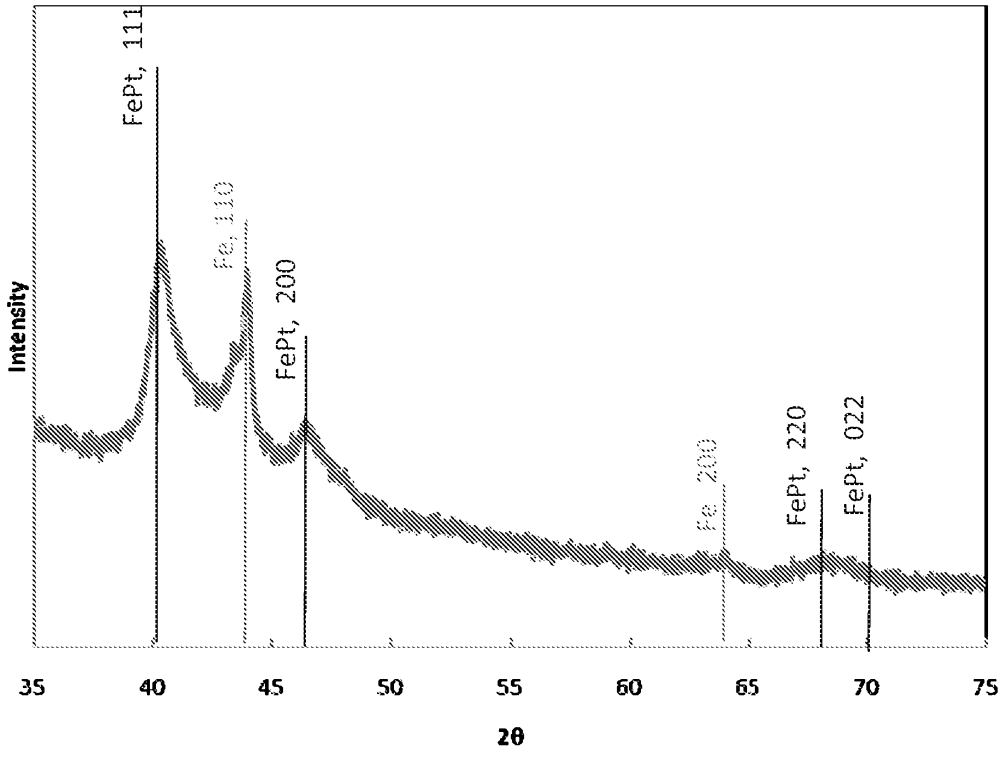


FIG. 116

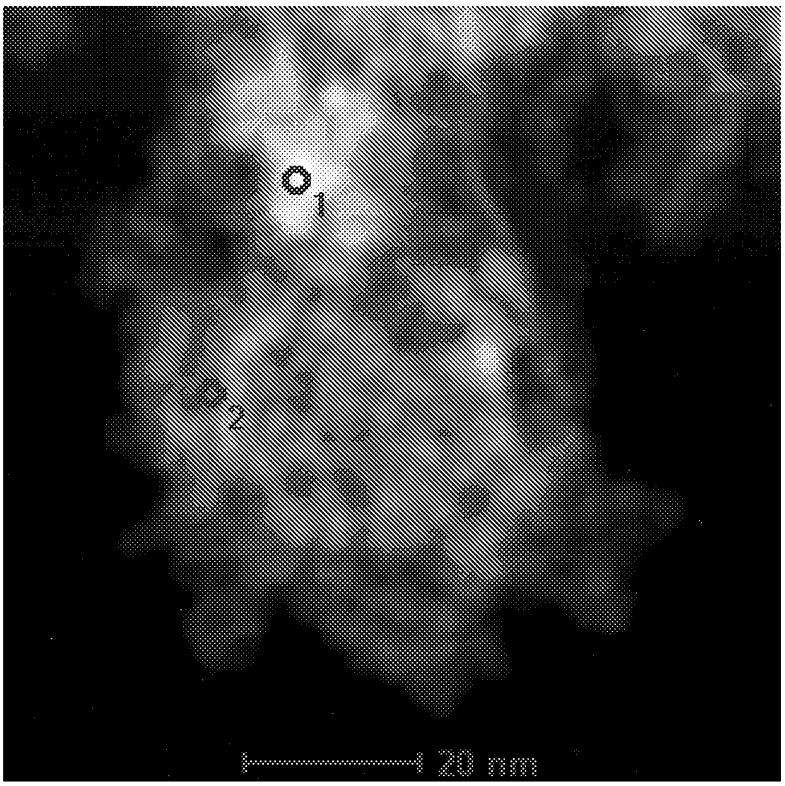


FIG. 117

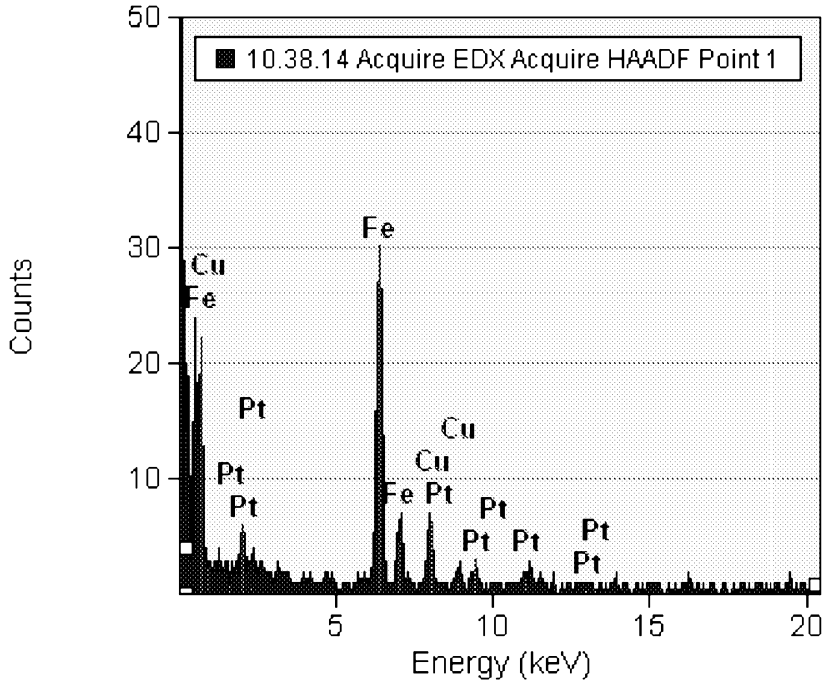


FIG. 118

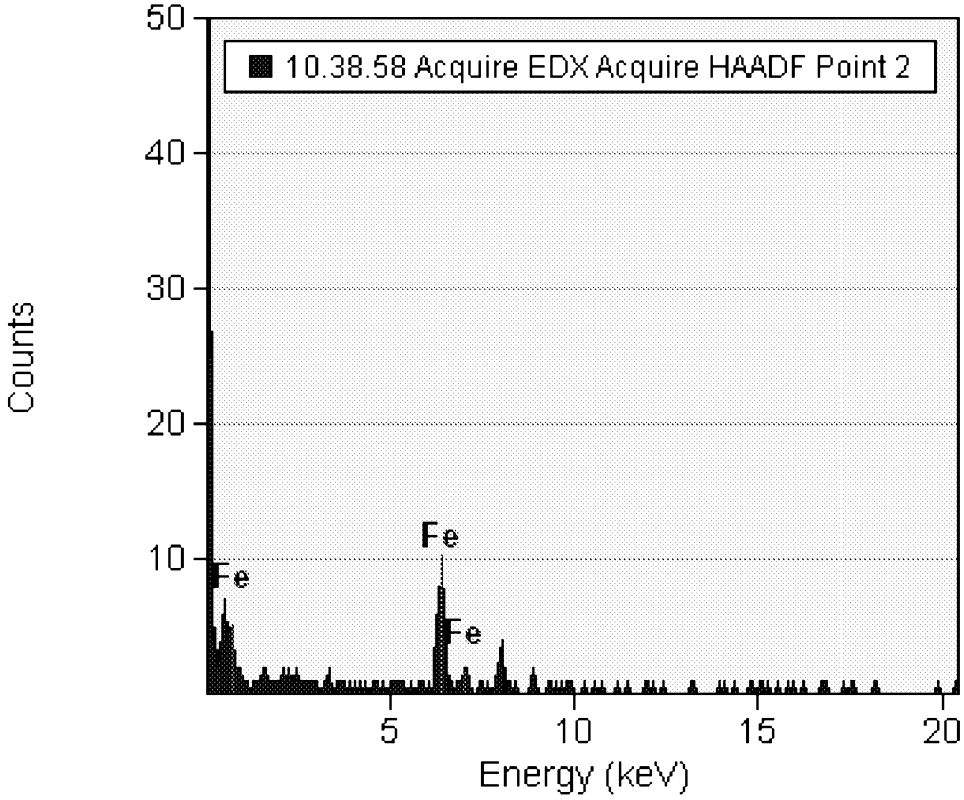


FIG. 119

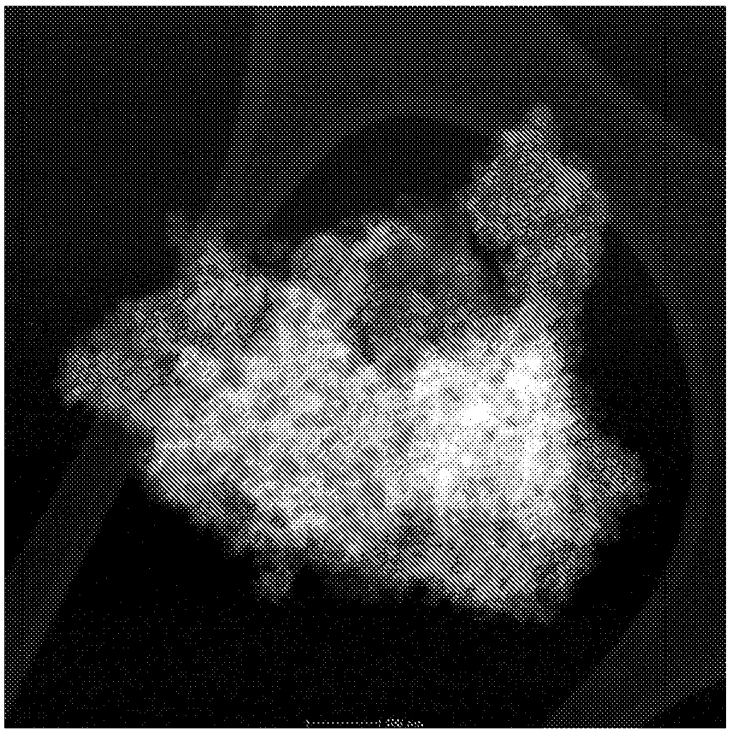


FIG. 120

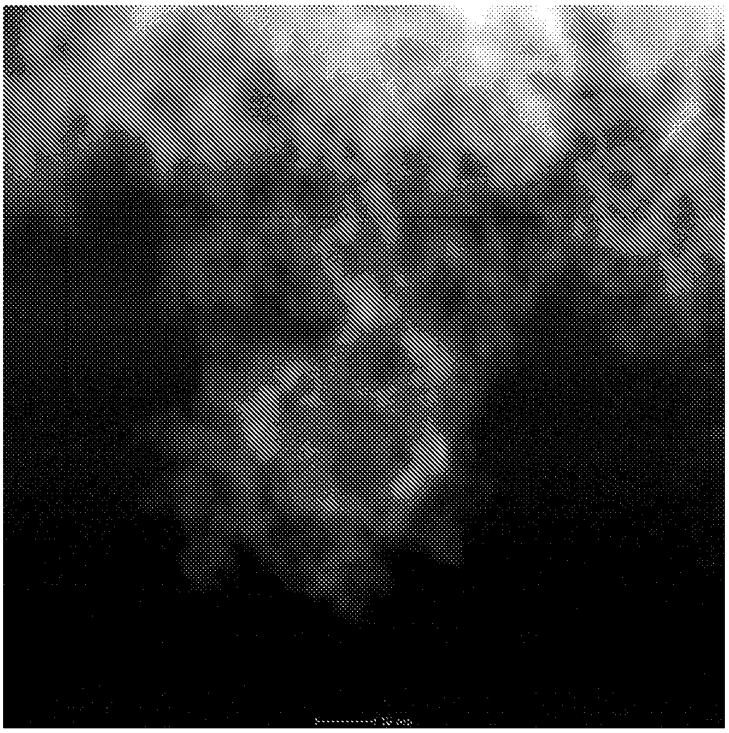


FIG. 121

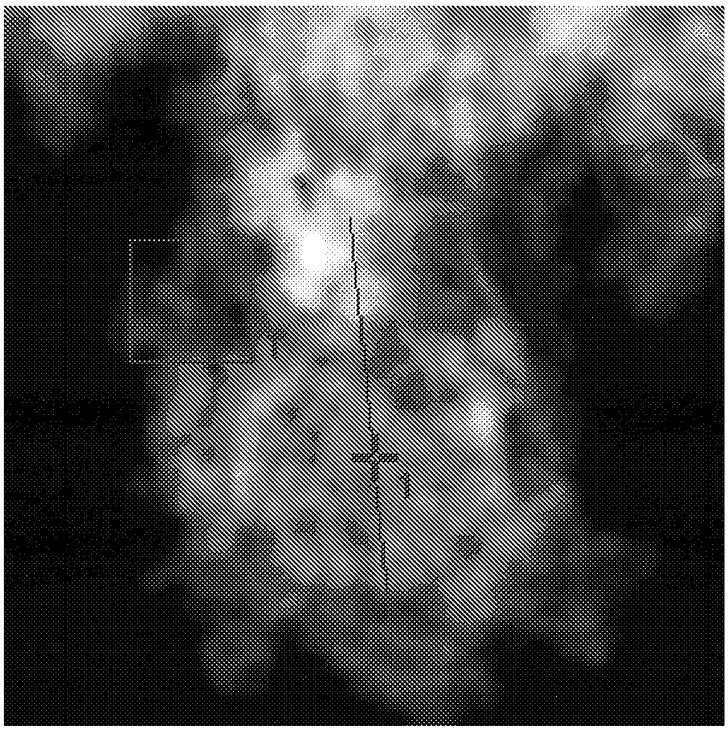


FIG. 122

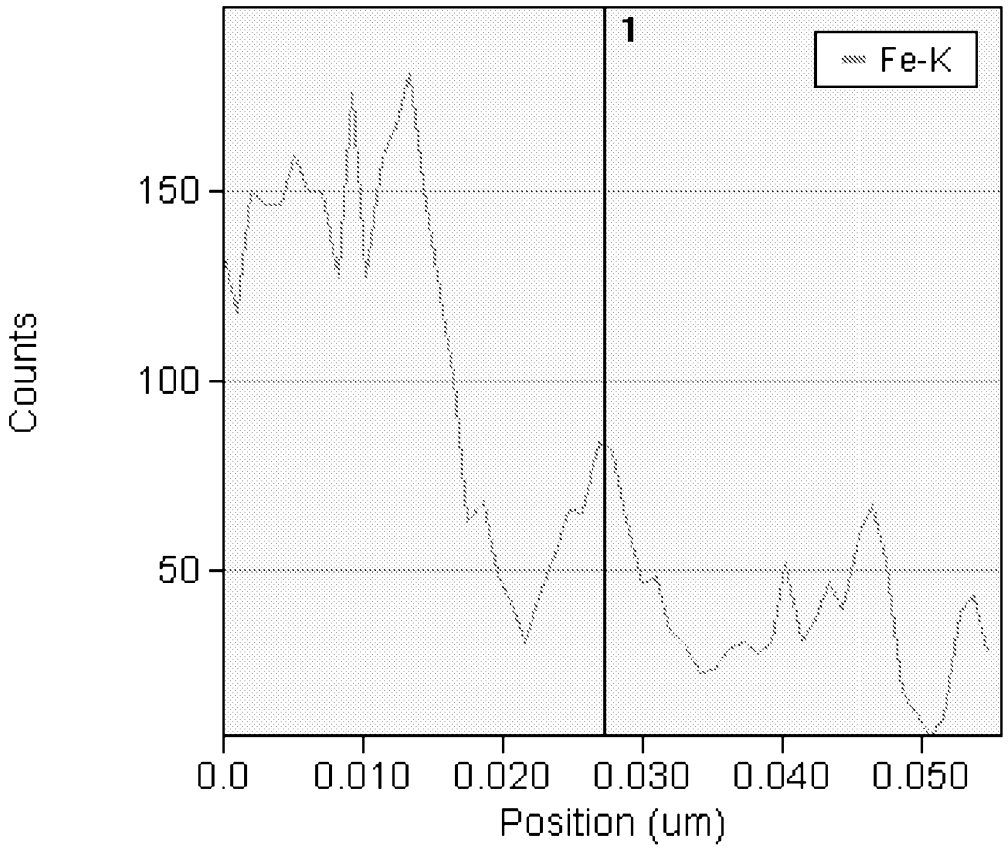


FIG. 123

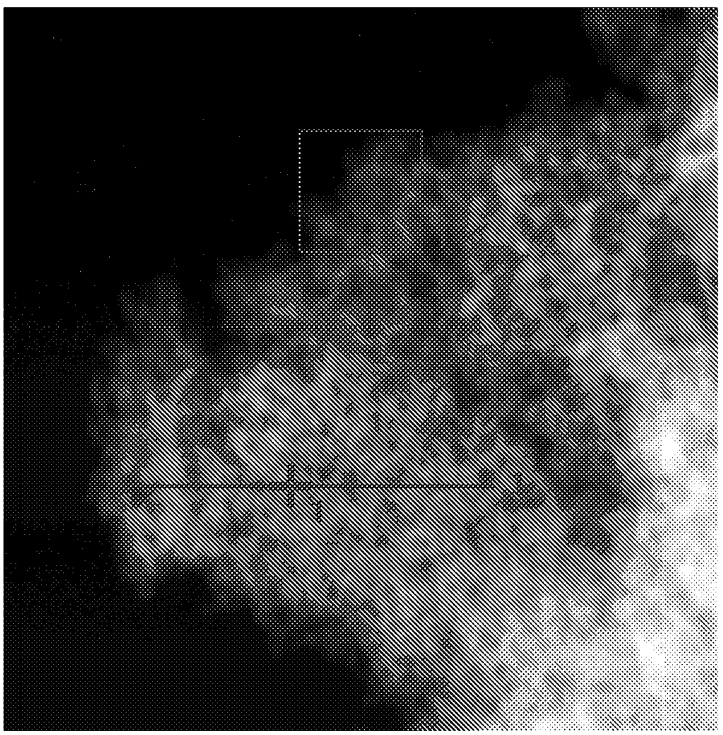


FIG. 124

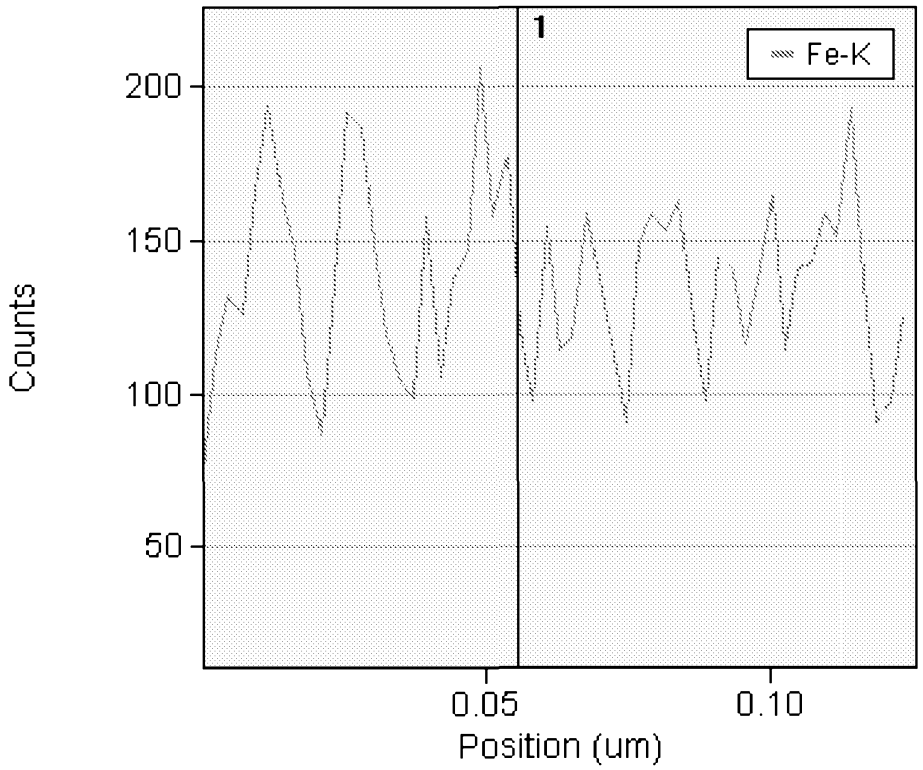


FIG. 125

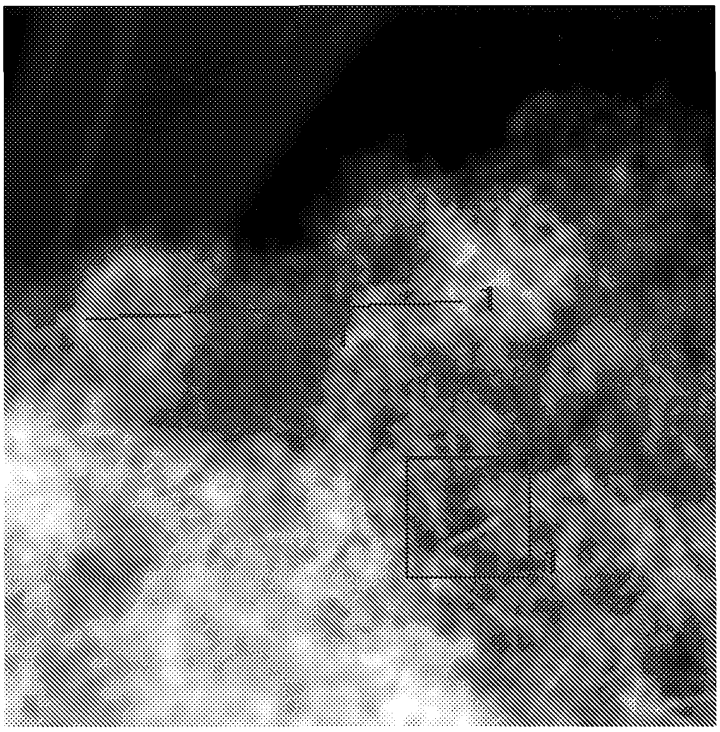


FIG. 126

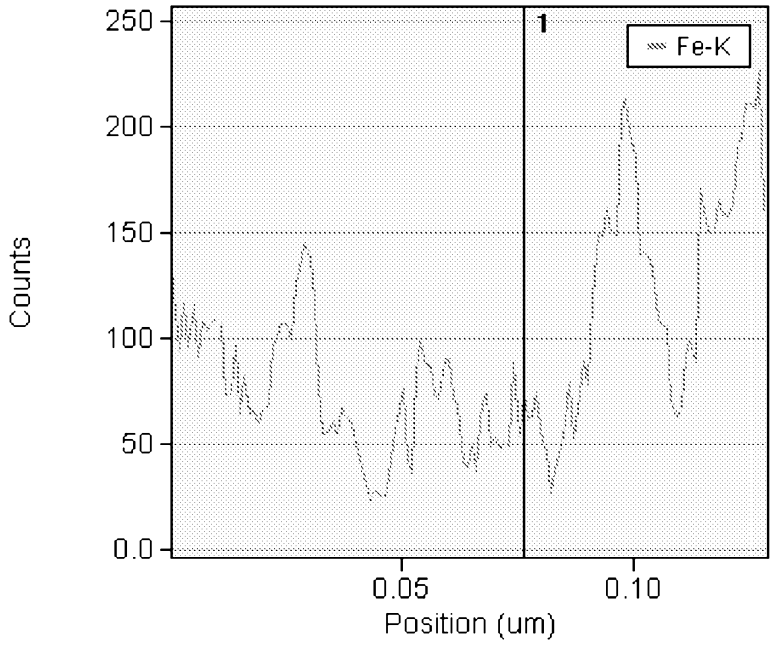


FIG. 127

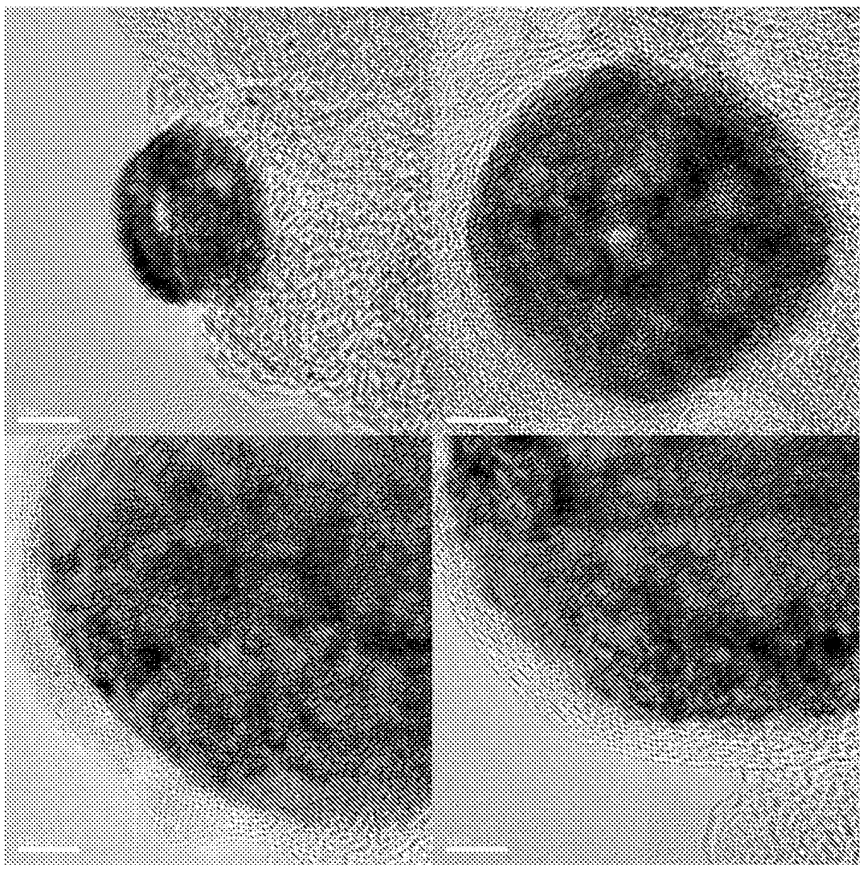


FIG. 128

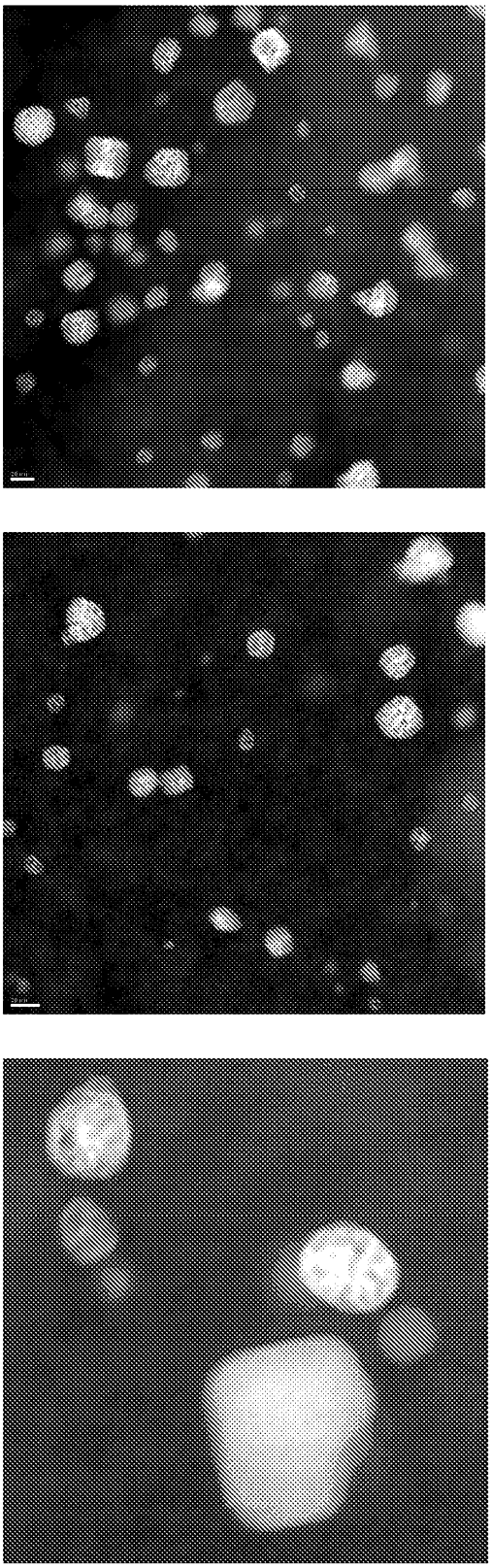


FIG. 129

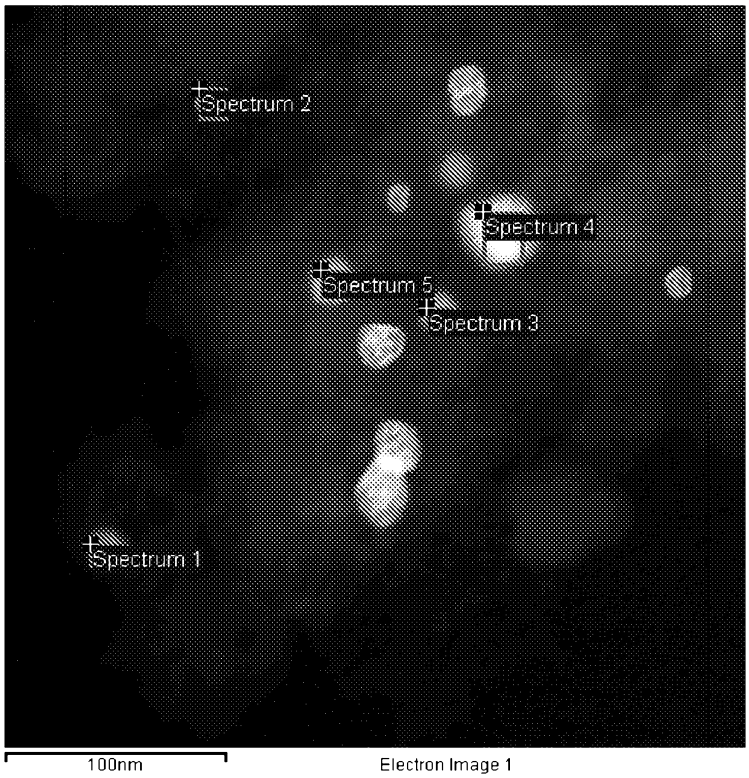


FIG. 130

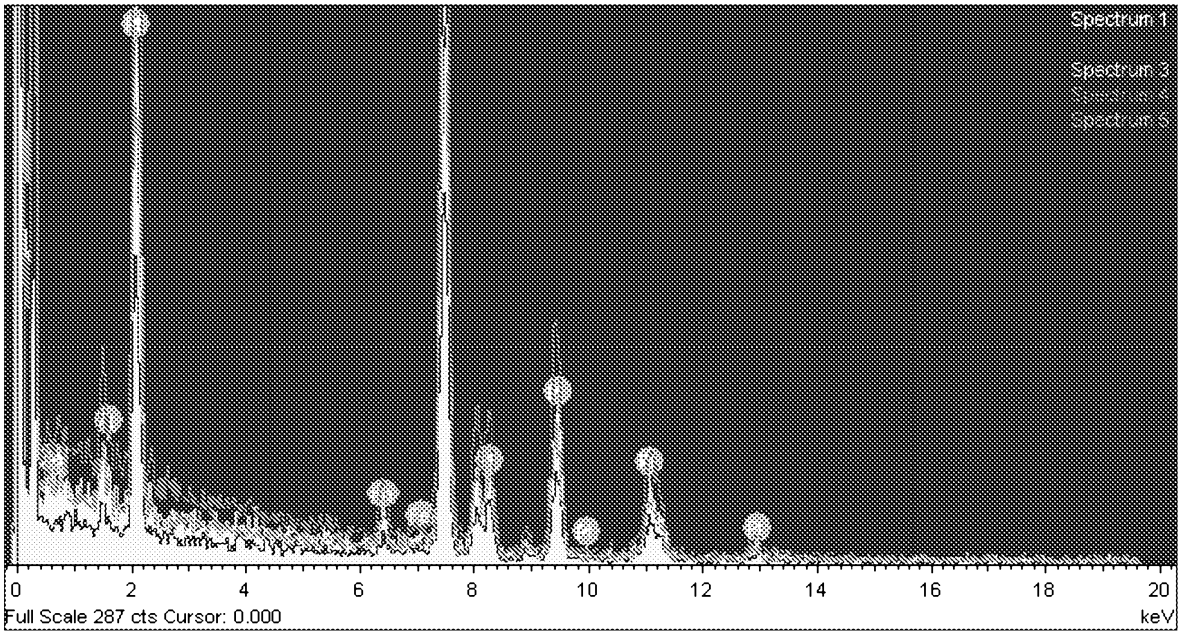


FIG. 131

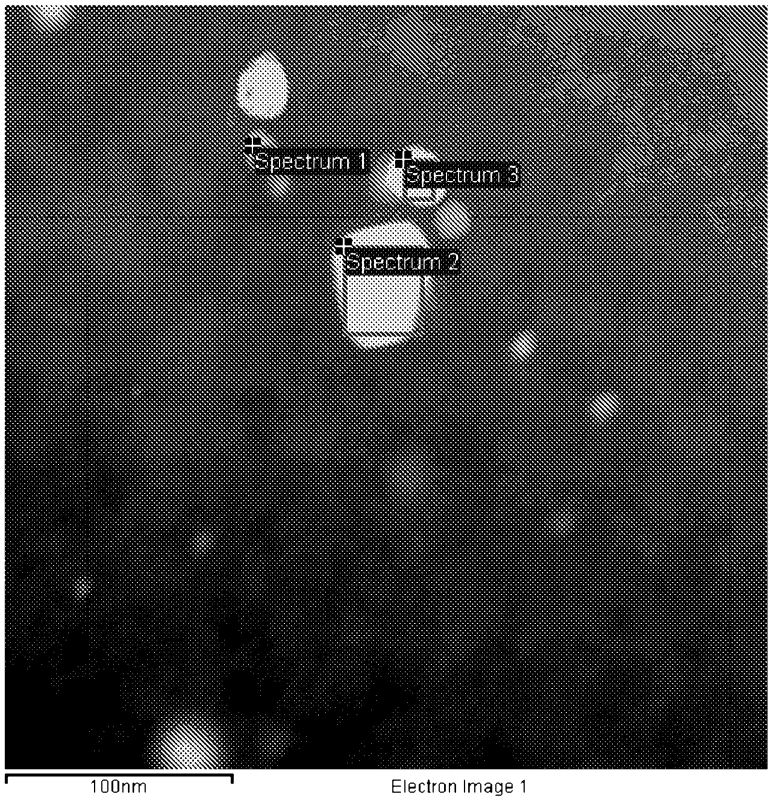


FIG. 132

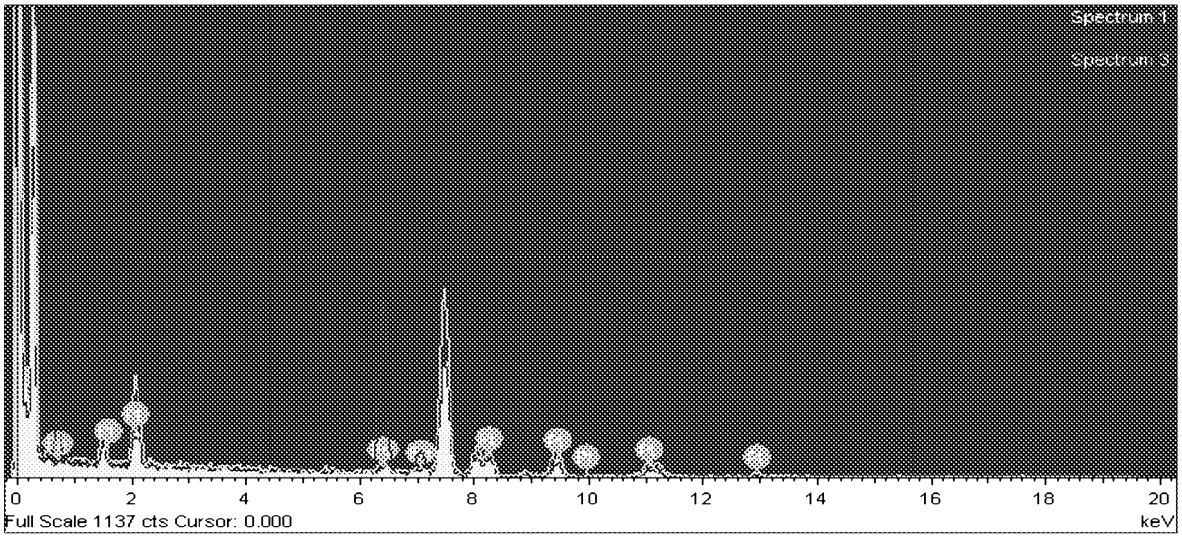


FIG. 133



FIG. 134

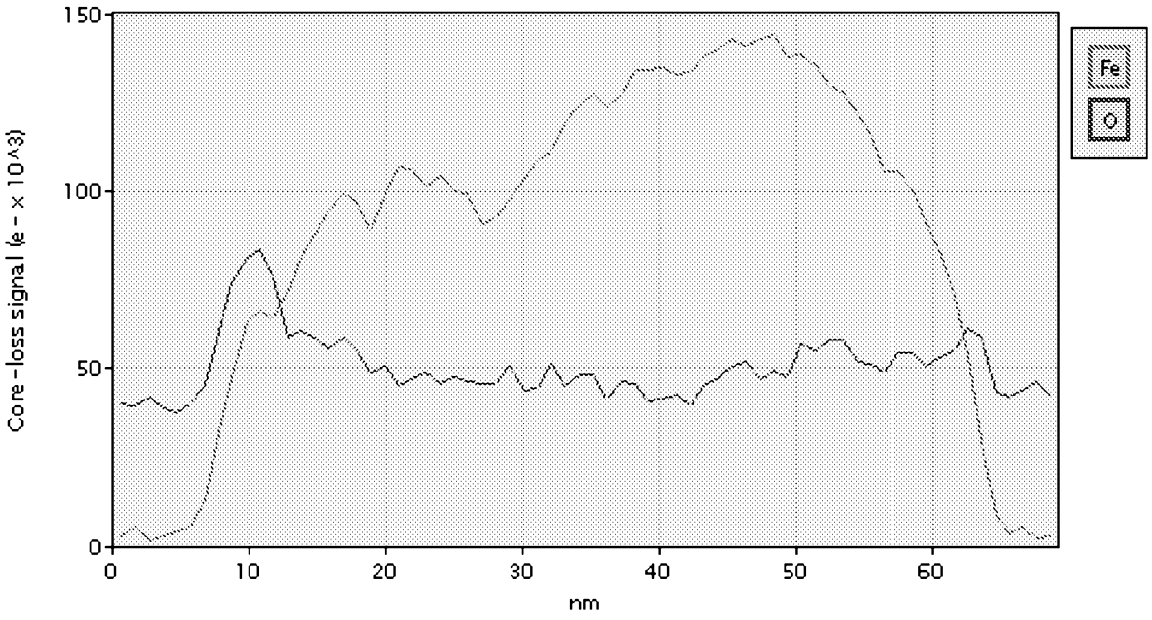


FIG. 135

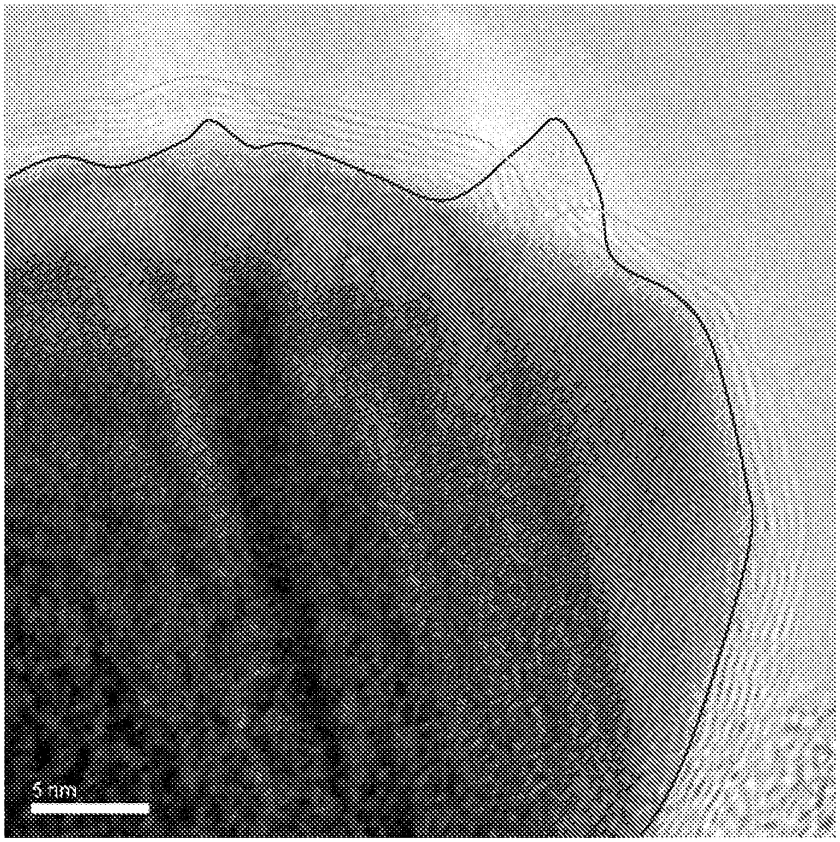


FIG. 136

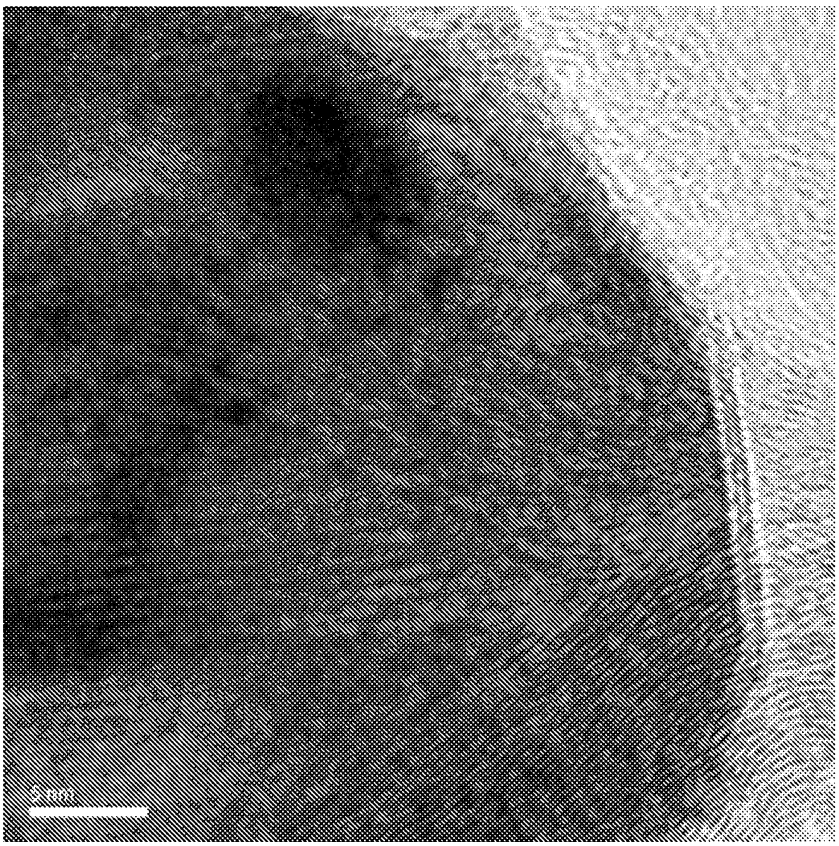


FIG. 137

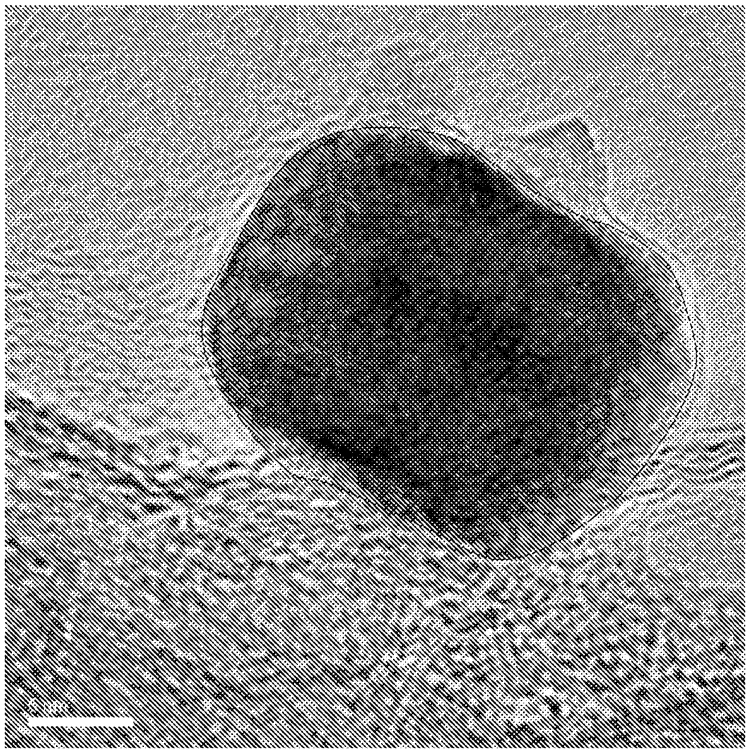


FIG. 138

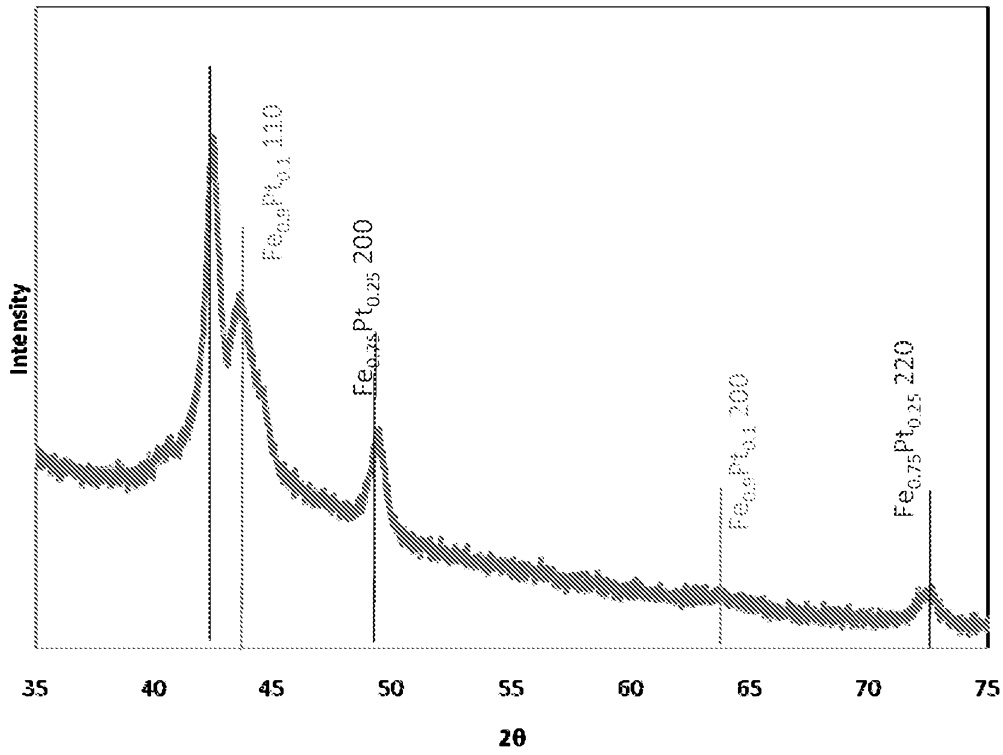


FIG. 139

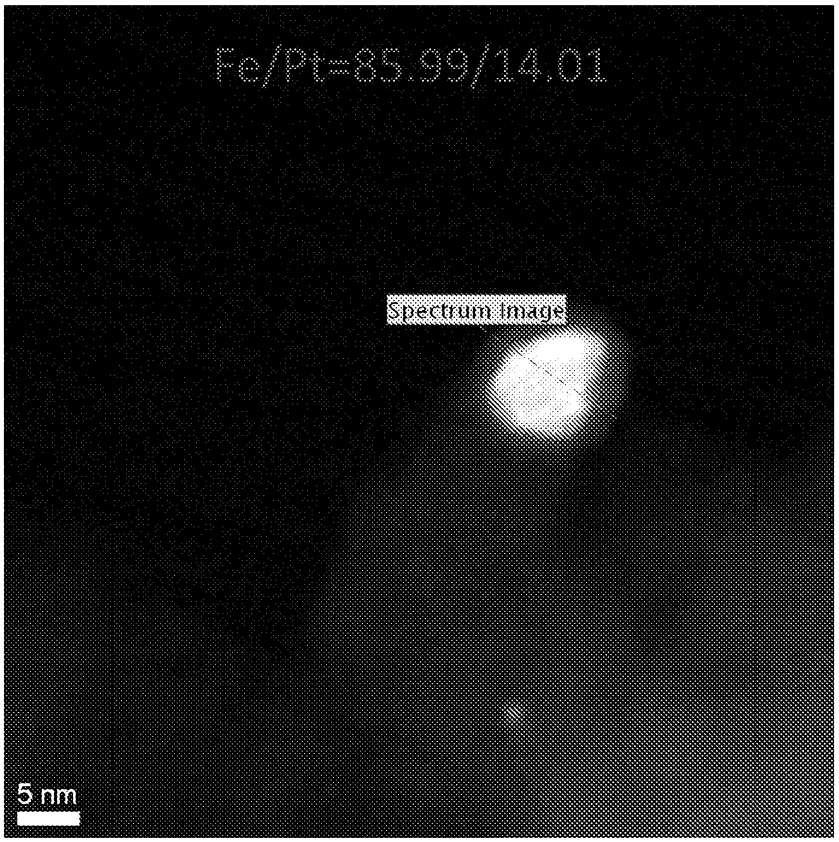


FIG. 140

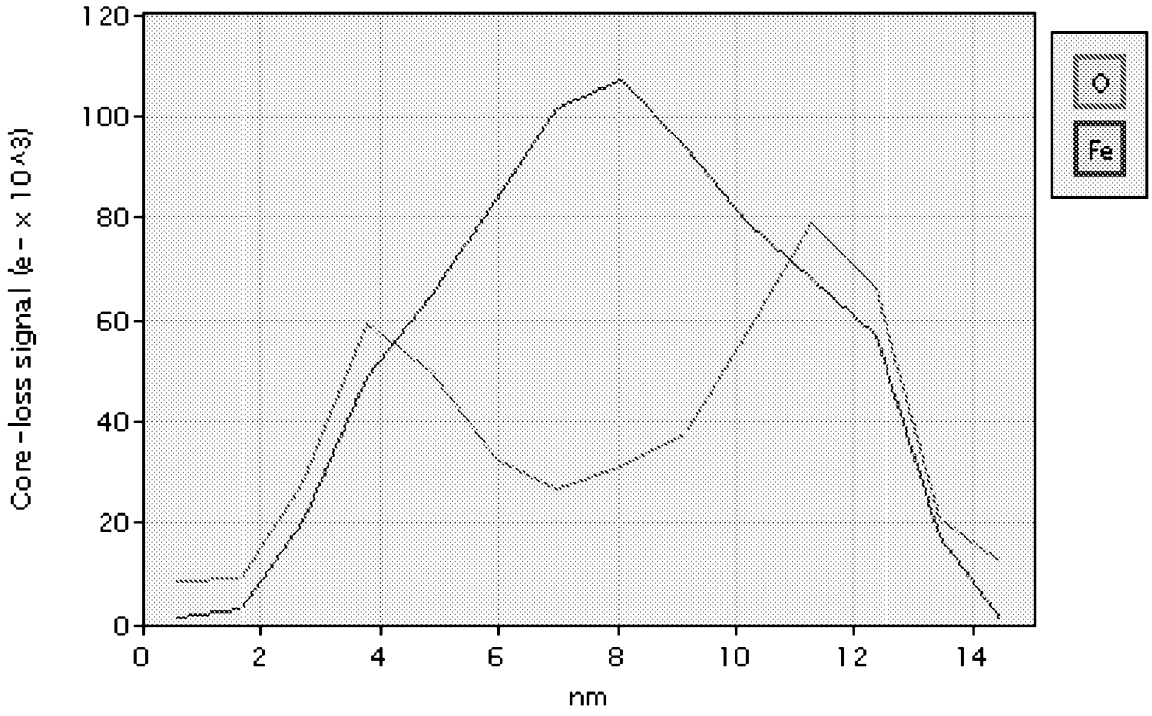


FIG. 141

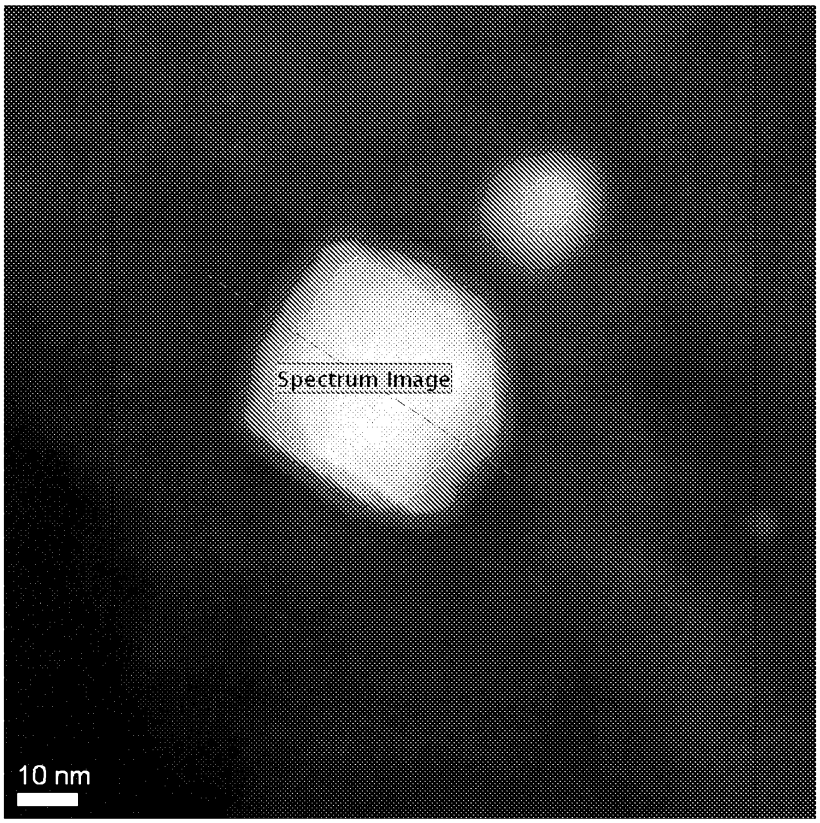


FIG. 142

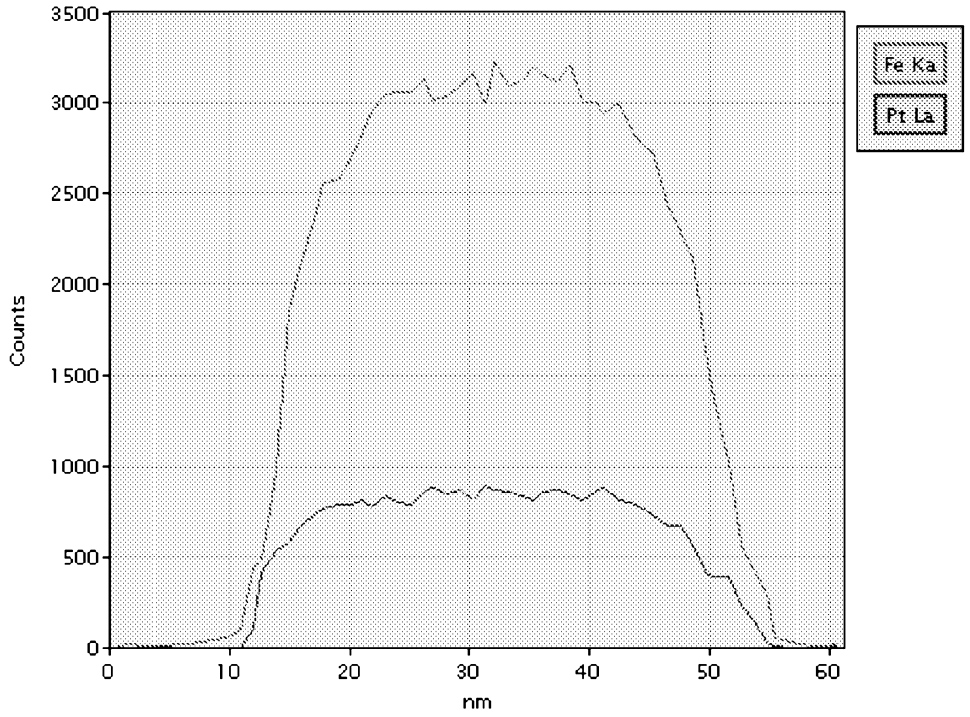


FIG. 143

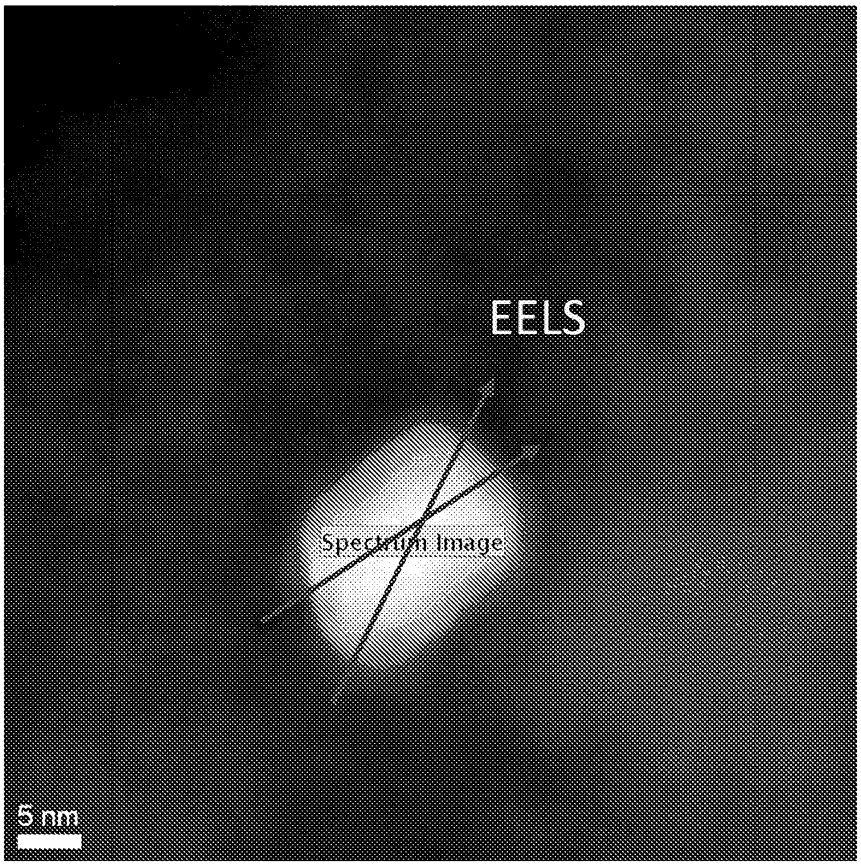


FIG. 144

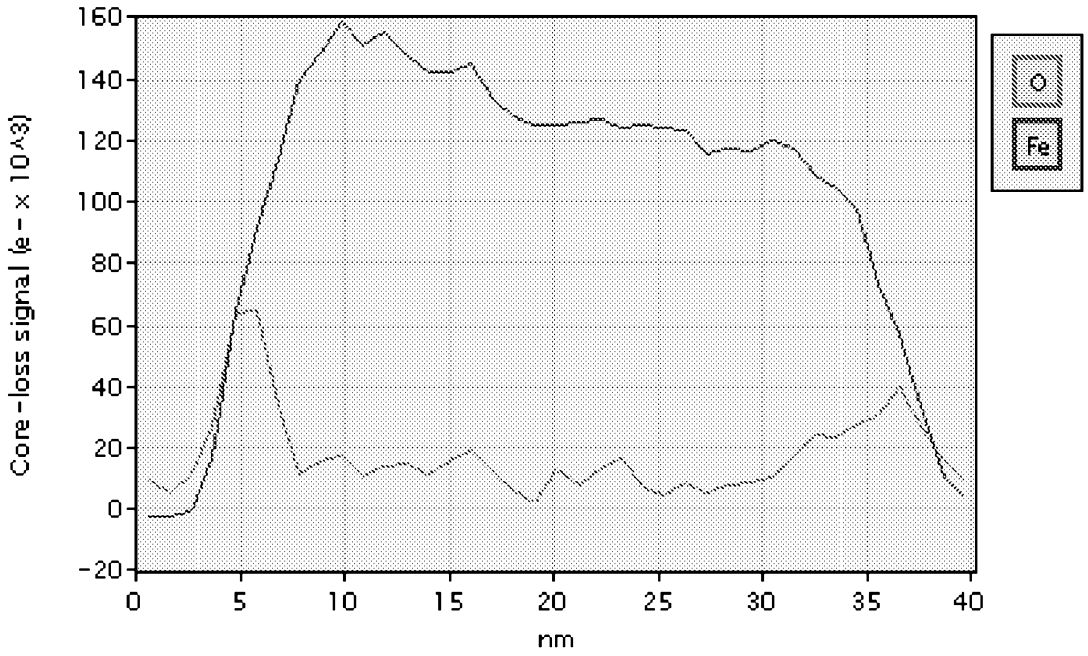


FIG. 145

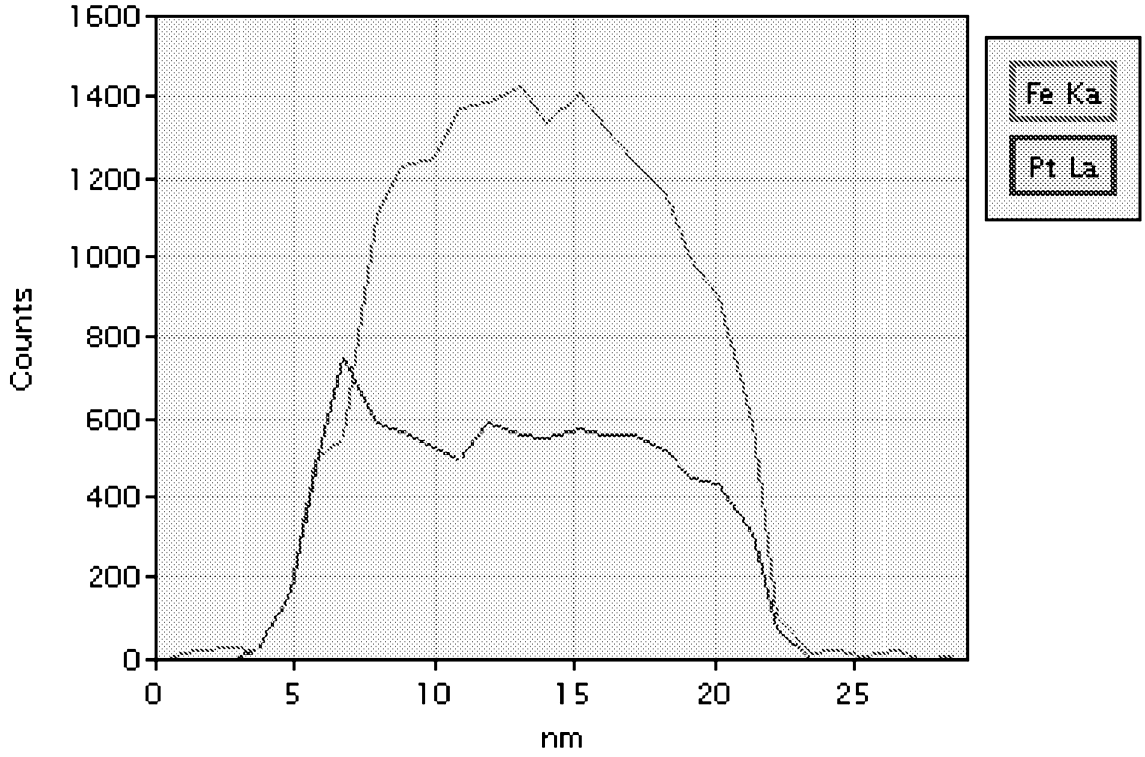


FIG. 146

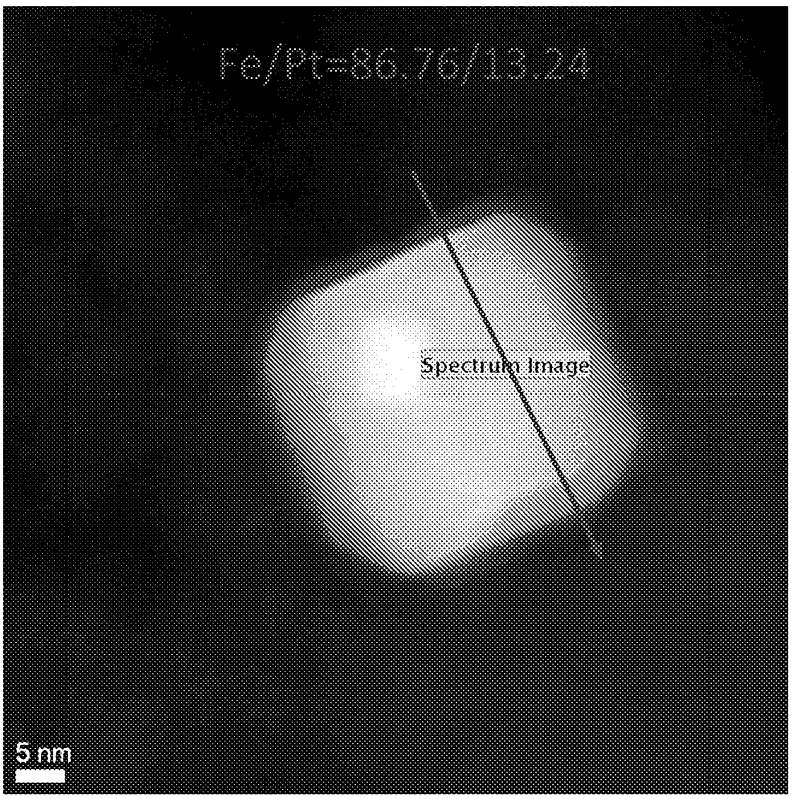


FIG. 147

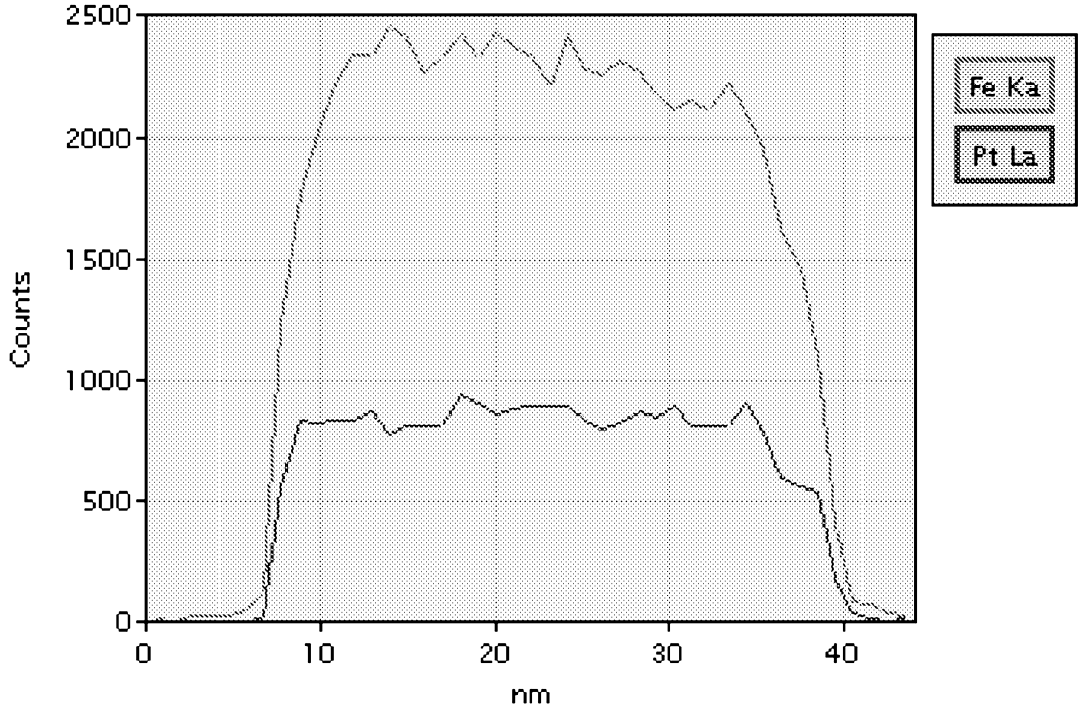


FIG. 148

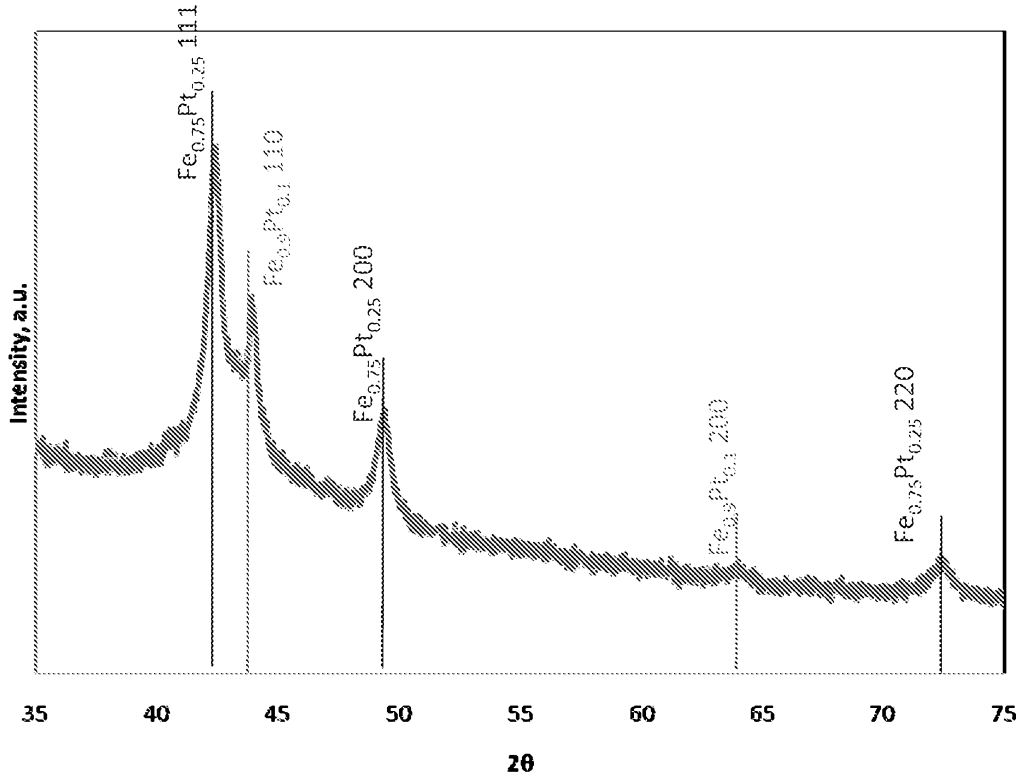


FIG. 149

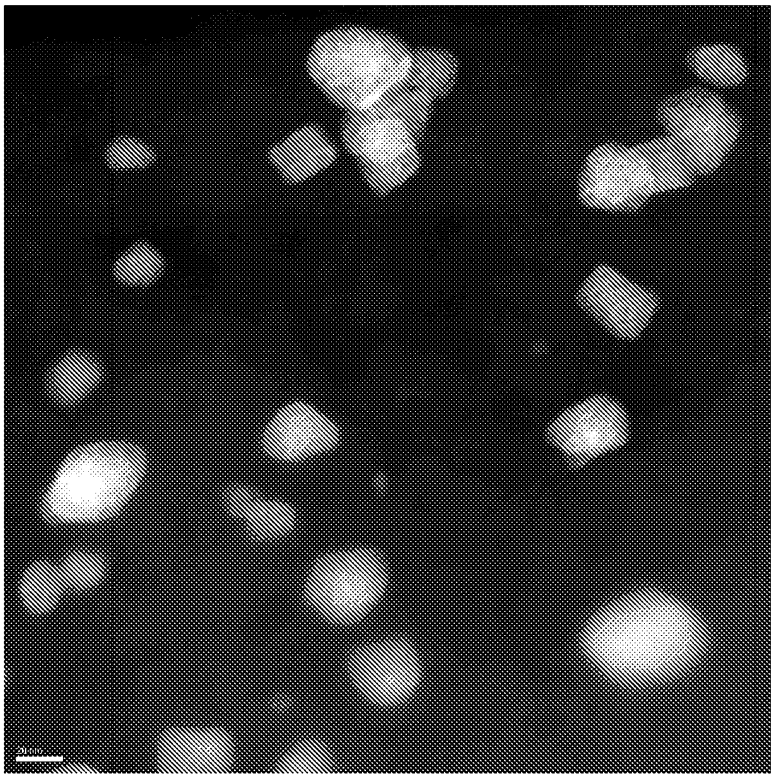


FIG. 150

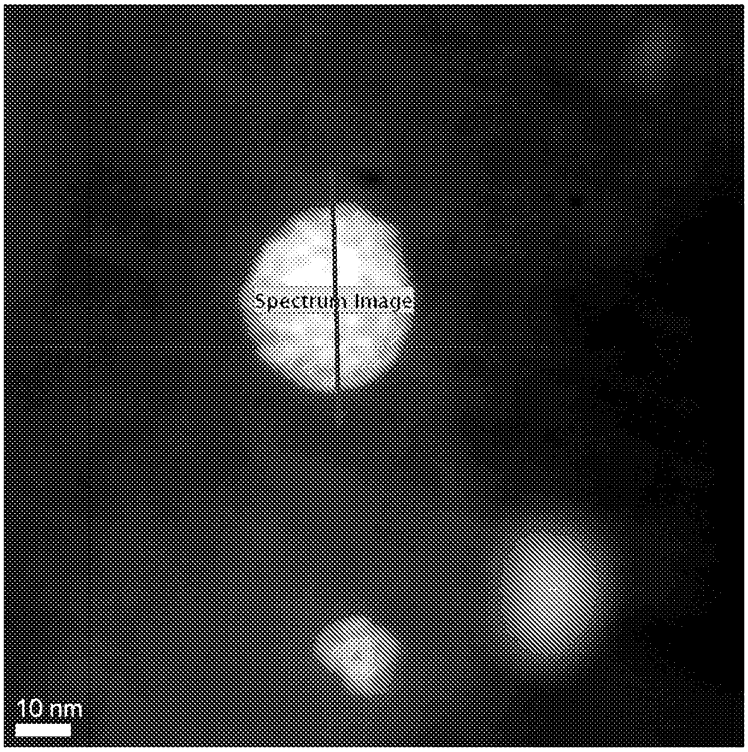


FIG. 151

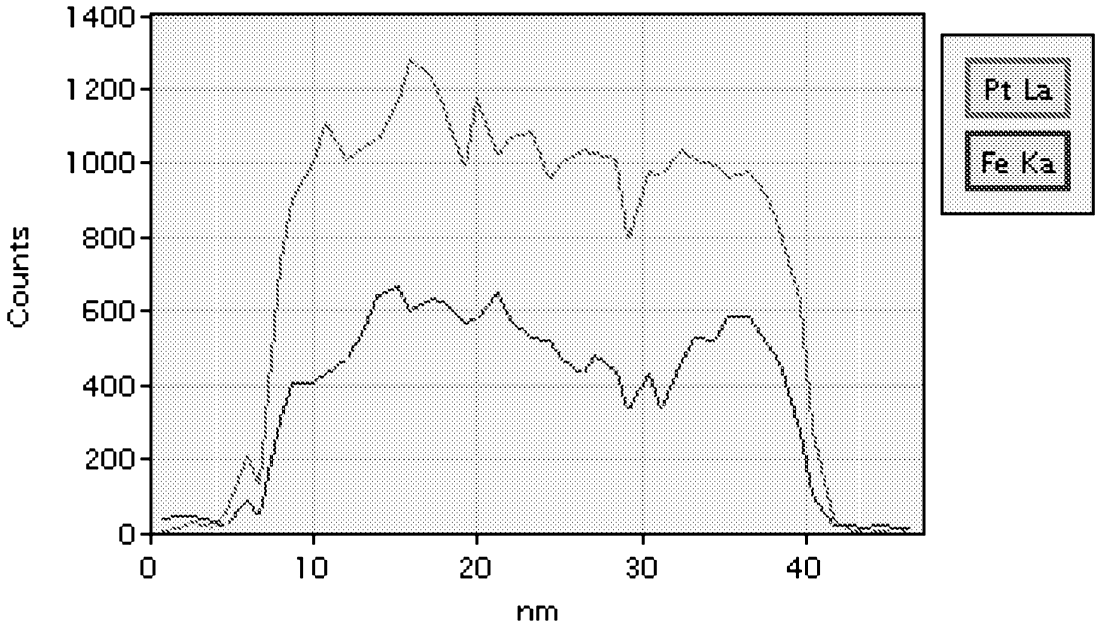


FIG. 152

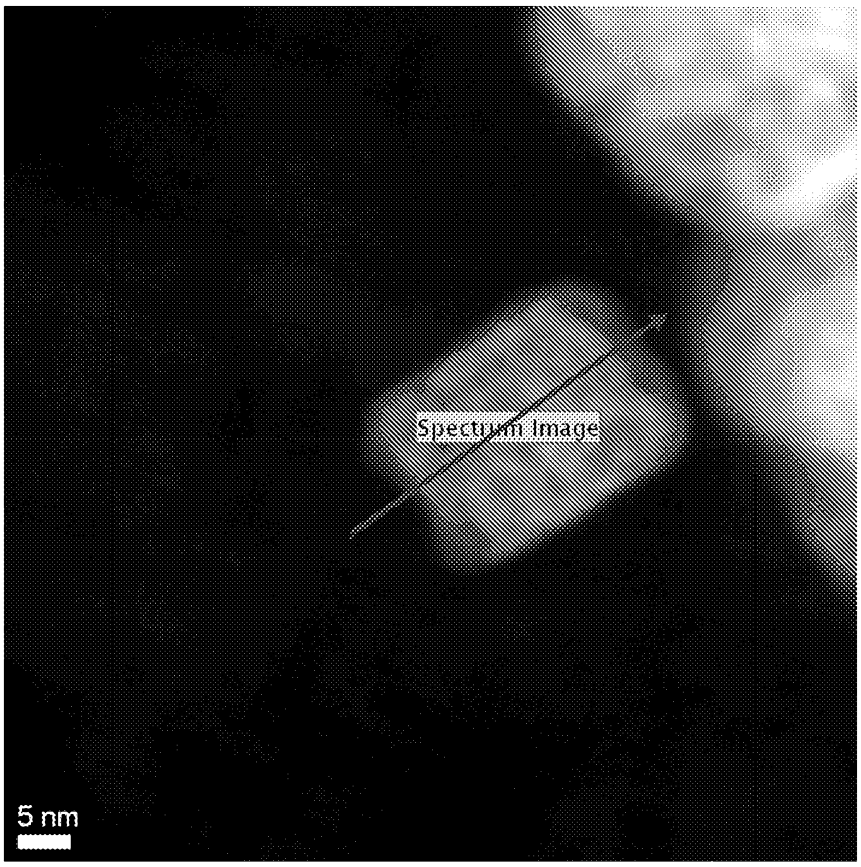


FIG. 153

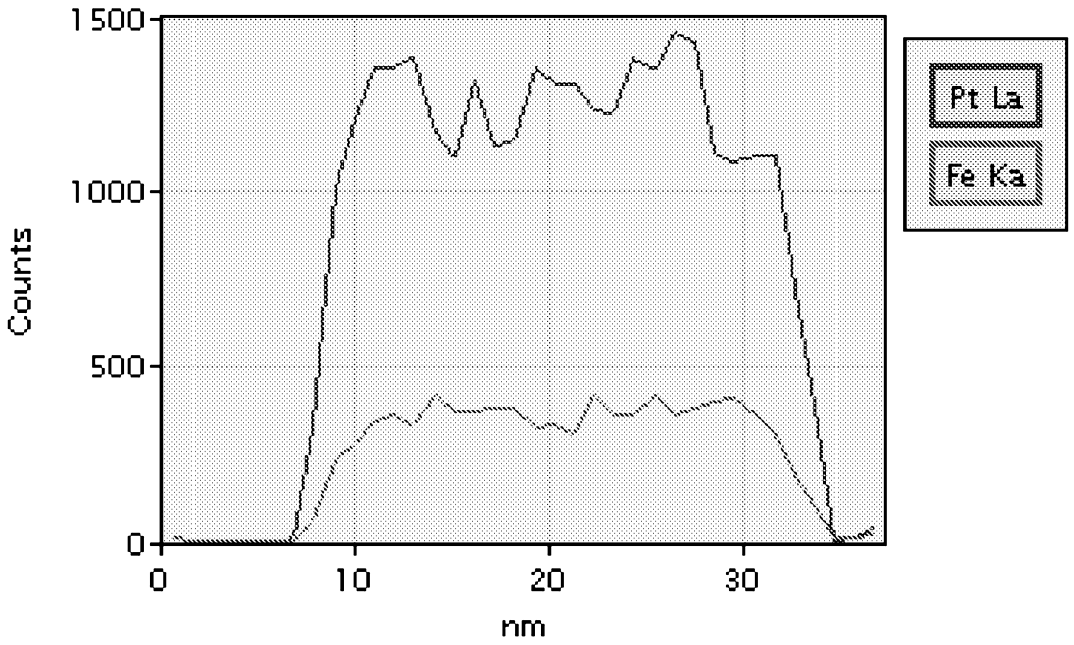


FIG. 154

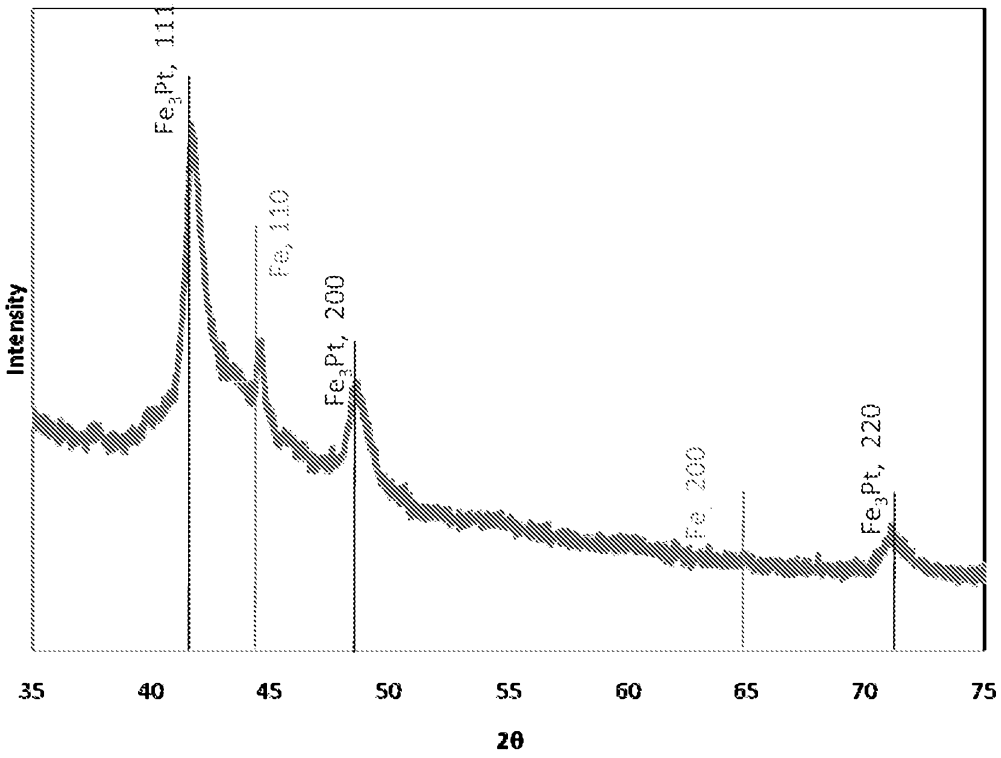


FIG. 155

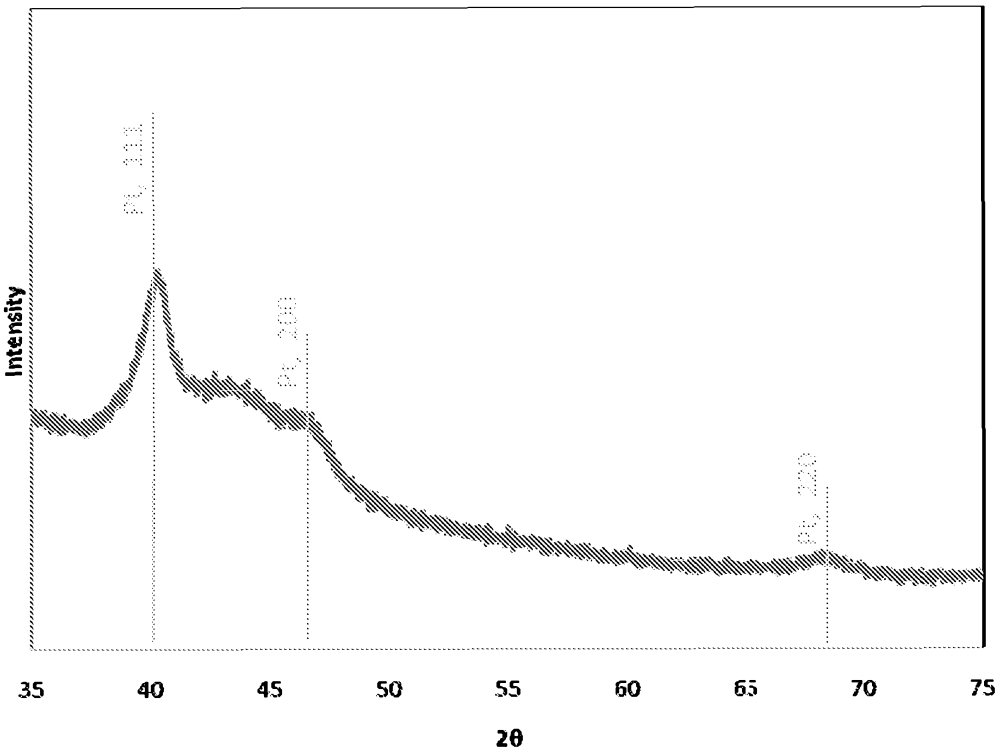


FIG. 155A

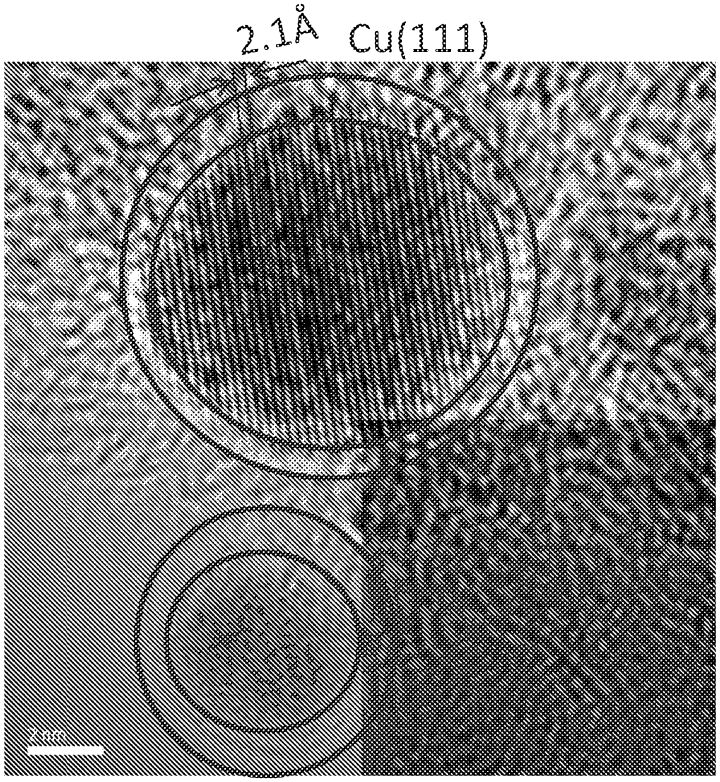


FIG. 155B

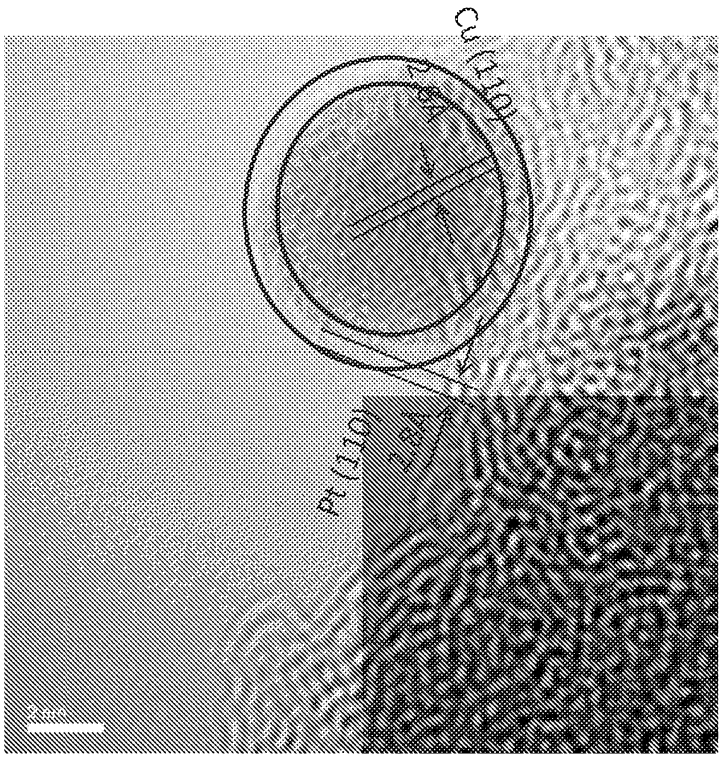


FIG. 155C

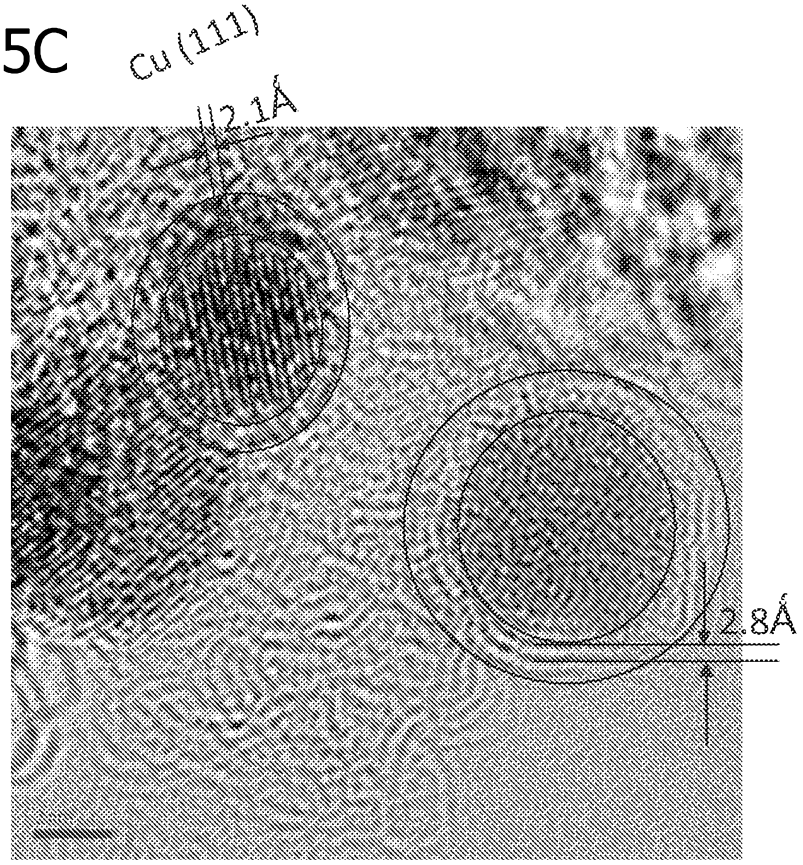


FIG. 155D

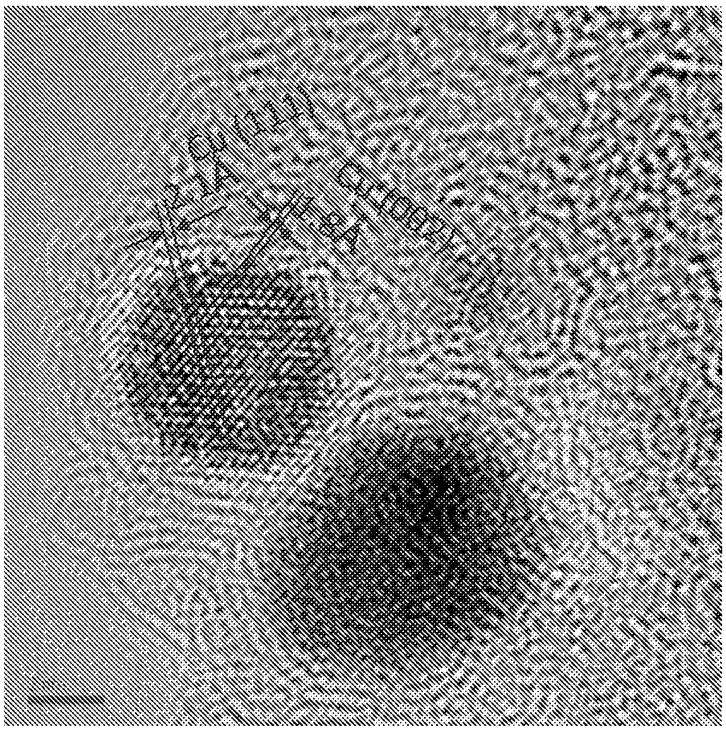


FIG. 155E

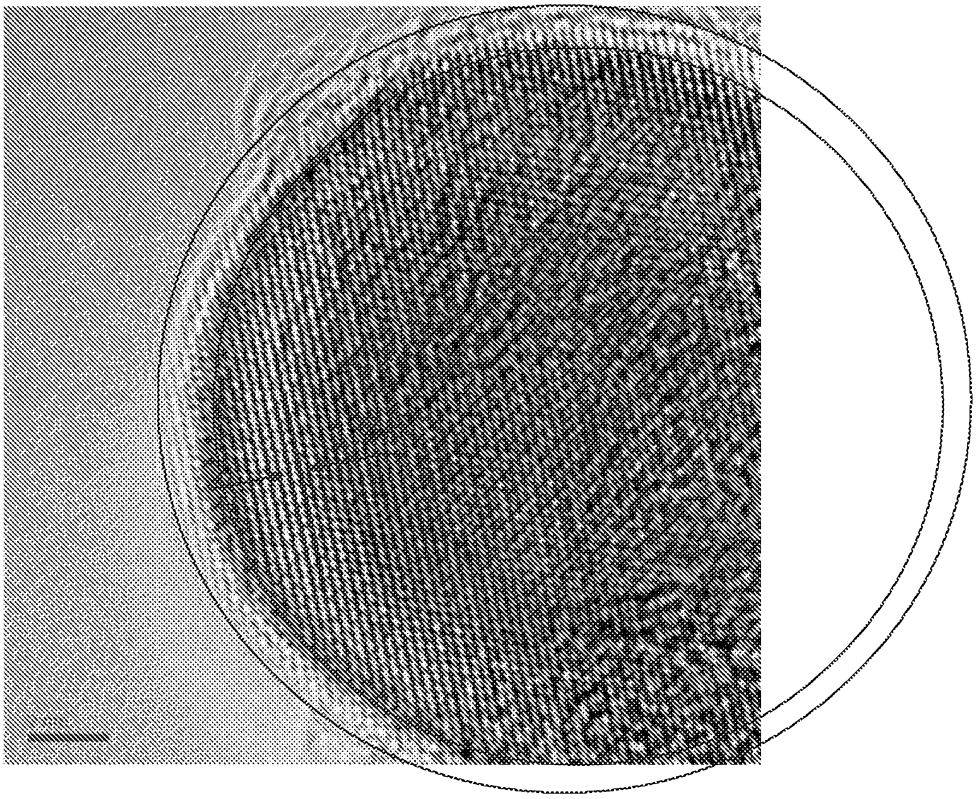


FIG. 155F

