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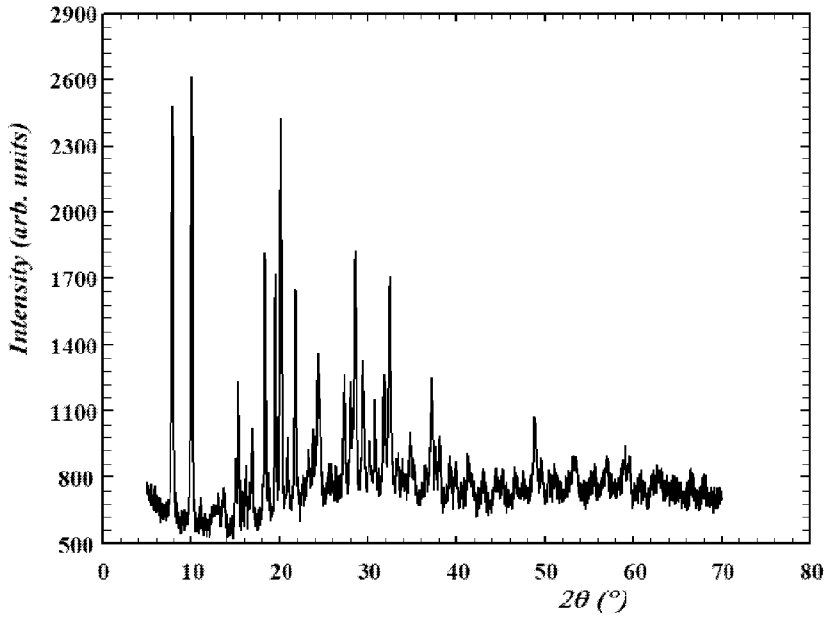
(54) Title: TRANSITION METAL TUNGSTATE MATERIAL



FIGURE

(57) Abstract: A hydroprocessing catalyst or catalyst precursor has been developed. The catalyst is a transition metal tungstate material or metal sulfides derived therefrom. The hydroprocessing using the crystalline ammonia transition metal tungstate material may include hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

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[Continued on next page]

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TRANSITION METAL TUNGSTATE MATERIAL

FIELD OF THE INVENTION

[0001] This invention relates to a new catalyst such as a hydroprocessing catalyst. More particularly this invention relates to a transition metal tungstate material and its use as a hydroprocessing catalyst. Hydroprocessing may include hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

BACKGROUND

[0002] In order to meet the growing demand for petroleum products there is greater utilization of sour crudes, which when combined with tighter environmental legislation regarding the concentration of nitrogen and sulfur within fuel, leads to accentuated refining problems. The removal of sulfur (hydrodesulfurization – HDS) and nitrogen (hydrodenitrification – HDN) containing compounds from fuel feed stocks is targeted during the hydrotreating steps of refining and is achieved by the conversion of organic nitrogen and sulfur to ammonia and hydrogen sulfide respectively.

[0003] Since the late 1940s the use of catalysts containing nickel (Ni) and molybdenum (Mo) or tungsten (W) have demonstrated up to 80% sulfur removal. See for example, V. N. Ipatieff, G. S. Monroe, R. E. Schaad, Division of Petroleum Chemistry, 115th Meeting ACS, San Francisco, 1949. For several decades now there has been an intense interest directed towards the development of materials to catalyze the deep desulfurization, in order to reduce the sulfur concentration to the ppm level. Some recent breakthroughs have focused on the development and application of more active and stable catalysts targeting the production of feeds for ultra low sulfur fuels. Several studies have demonstrated improved HDS and HDN activities through elimination of the support such as, for example, Al_2O_3. Using bulk unsupported materials provides a route to increase the active phase loading in the reactor as well as providing alternative chemistry to target these catalysts.

[0004] More recent research in this area has focused on the ultra deep desulfurization properties achieved by a Ni-Mo/W unsupported 'trimetallic' material reported in, for example, US 6,156,695.

The controlled synthesis of a broadly amorphous mixed metal oxide consisting of molybdenum, tungsten and nickel, significantly outperformed conventional hydrotreating catalysts. The structural chemistry of the tri-metallic mixed metal oxide material was likened to the hydrotalcite family of materials, referring to literature articles detailing the synthesis and characterization of a layered nickel molybdate material, stating that the partial substitution of molybdenum with tungsten leads to the production of a broadly amorphous phase which, upon decomposition by sulfidation, gives rise to superior hydrotreating activities.

[0005] The chemistry of these layered hydrotalcite-like materials was first reported by H. Pezerat, contribution à l'étude des molybdates hydrates de zinc, cobalt et nickel, *C. R. Acad. Sci.*, *261*, 5490, who identified a series of phases having ideal formulas $MMoO_4.H_2O$, $EHM_2O(MoO_4)_2.H_2O$, and $E_{2-x}(H_3O)_xM_2O(MoO_4)_2$ where E can be NH_4^+, Na^+ or K^+ and M can be Zn^{2+}, Co^{2+} or Ni^{2+}.

[0006] Pezerat assigned the different phases he observed as being Φc, Φx or Φy and determined the crystal structures for Φx and Φy, however owing to a combination of the small crystallite size, limited crystallographic capabilities and complex nature of the material, there were doubts raised as to the quality of the structural assessment of the materials. During the mid 1970s, Clearfield *et al* attempted a more detailed analysis of the Φx and Φy phases, see examples A. Clearfield, M. J. Sims, R. Gopal, *Inorg. Chem.*, *15*, 335; A. Clearfield, R. Gopal, C. H. Saldarriaga-Molina, *Inorg. Chem.*, *16*, 628. Single crystal studies on the product from a hydrothermal approach allowed confirmation of the Φx structure, however they failed in their attempts to synthesize Φy and instead synthesized an alternative phase, Na-Cu(OH)(MoO_4), see A. Clearfield, A. Moini, P. R. Rudolf, *Inorg. Chem.*, *24*, 4606.

[0007] The structure of Φy was not confirmed until 1996 by Ying *et al.* Their investigation into a room temperature *chimie douce* synthesis technique in the pursuit of a layered ammonium zinc molybdate led to a metastable aluminum-substituted zincite phase, prepared by the calcination of Zn/Al layered double hydroxide ($Zn_4Al_2(OH)_{12}CO_3.zH_2O$). See example D. Levin, S. L. Soled, J. Y. Ying, *Inorg. Chem., 1996*, *35*, 4191-4197. This material was reacted with a solution of ammonium heptamolybdate at room temperature to produce a highly crystalline compound, the structure of which could not be determined through conventional *ab-initio* methods. The material was indexed,

yielding crystallographic parameters which were the same as that of an ammonium nickel molybdate, reported by Astier, see example M. P. Astier, G. Dji, S. Teichner, J. *Ann. Chim. (Paris)*, 1987, *12*, 337, a material belonging to a family of ammonium-amine-nickel-molybdenum oxides closely related to Pezerat's materials. Astier did not publish any detailed structural data on this family of materials, leading to Ying *et al* reproducing the material to be analyzed by high resolution powder diffraction in order to elucidate the structure. Ying *et al* named this class of materials 'layered transition-metal molybdates' or LTMs.

[0008] Since the initial reports of unsupported Ni-Mo/W oxidic precursors, US 6,156,695, there have been several reports describing materials which, when sulfided, claim to have enhanced hydrotreating activities. US 6,534,437 discloses a process for preparing a mixed metal catalyst having a powder x-ray diffraction pattern showing reflections at 2.53 Angstroms and 1.70 angstroms. US 6,534,437 differentiates itself from US 3,678,124 and WO 9903578 based on characteristic full width half maximum line widths of more resolved reflections, present in WO 9903578, claiming that the invention of US 6,534,437 possesses a 'different microstructure' from prior work, WO 9903578.

[0009] U.S. Pat. 8,722,563 describes preparing a series of catalyst precursors with compositions comprising at least one Group VI metal and one metal from Group VIII through Group X. One of the comparative examples described in the patent yields a comparable powder x-ray diffraction pattern to that obtained in U.S. Pat. 6,534,437 and is described as the as-synthesized and dried hexagonal $NiWO_4$ catalyst precursor.

[0010] U.S. Pat. 7,648,941 discloses synthetic examples of a series of different bimetallic materials and states that the bulk bimetallic catalyst of the invention has a metastable structure and further assert that the crystalline 2θ structure of the metastable hexagonal $NiW0_4$ phase in the preferred catalysts of the invention have lattice parameters a=2.92Å, b=2.93Å, and c=4.64Å and that bulk catalyst has a metastable hexagonal structure having an X-ray diffraction pattern with a single reflection between 58 and 65°. As a point of reference, the largest two d-spacings which can be generated in an x-ray diffraction pattern by a hexagonal cell with lattice parameters a=2.92Å, b=2.93Å, and c=4.64Å are 4.64Å and 2.53Å.

[0011] A. Dias and V.S.T. Ciminelli, *J. Eur. Ceramic. Soc*, 2001, **21**, 2061-2065 reported on the thermodynamic calculations and modeling of hydrothermally synthesized nickel tungstates. They present a series of calculated yield diagrams at various synthesis temperatures highlighting the pH and reagent concentrations which yield $NiWO_4$. All of their calculations predict the formation of a nickel tungstate between pH 2 and 7.5, with nickel hydroxide being the main product at higher pH's. The authors show the x-ray diffraction patterns for the samples produced at 200, 230 and 260°C within and without their predicted yield zones. The x-ray diffraction pattern for the $NiWO_4$ material synthesized at 200°C can be described as poorly crystalline and the reference asserts that it is important to note that a crystallized material was obtained at 200°C, but with extremely fine particle size indicated by broad X-ray diffraction peaks. The reference asserts this can be explained by the energy barrier for the precipitation, which is closely related to the nature of the rate-controlling step in the dominant formation process. The reference puts forth that higher reaction temperatures accelerate the crystallization process because of greater thermal energy to overcome the energy barrier for transformation, and a consequence, materials with higher crystallinity and/or particle size can be obtained. The reference suggests that the phase obtained at 200°C is essentially a poorly crystalline, nano-wolframite ($NiWO_4$), and this conclusion is consistent with calculated yield diagrams of the reference.

[0012] Y. Bi, H. Nie, D. Li, S. Zeng, Q. Yang and M. Li, Chemical Communications, 2010, 46, 7430-7432 discuss the preparation of $NiWO_4$ nanoparticles as a promising hydrodesulfurization catalyst, stating that all the reflections in a typical powder x-ray diffraction pattern can be indexed undisputedly to the monoclinic $NiWO_4$, Wolframite, phase. The reference asserts that Fig. 1 shows the typical X-ray diffraction (XRD) pattern of the as-made sample and all reflections can be indexed undisputedly to the monoclinic $NiWO_4$ phase (JCPDS card 72-1189). The reference concludes that a close examination reveals that the reflections in the XRD pattern are a little broad, indicating the characteristic feature of nanosized materials.

SUMMARY OF THE INVENTION

[0013] A transition metal tungstate material has been produced and optionally sulfided, to yield an active catalyst or catalyst precursor for a hydroprocessing catalyst. The transition metal

tungstate material has a x-ray powder diffraction pattern showing peaks at 11.3, 8.9, 5.93, 5.65, 5.26 and 4.84Å. The transition metal tungstate material has the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is selected from NH_3, H_2O, or combinations thereof; m varies from 0.001 to 50, or from 1 to 25, or from 2 to 12; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn, and combinations thereof; 'y' varies from 0.5 to 2; or from 0.75 to 1.5, or from 0.9 to 1.25; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material; the material is further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

[0014] Another embodiment involves a method of making a transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is selected from NH_3, H_2O, or combinations thereof; m varies from 0.001 to 50, or from 1 to 25, or from 2 to 12; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn, and combinations thereof; 'y' varies from 0.5 to 2, or from 0.75 to 1.5, or from 0.9 to 1.25; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material;

the material is further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

the method comprising forming a reaction mixture containing NH_3, H_2O, or combinations thereof, sources of M and W, and reacting the mixture at elevated temperatures in an open or sealed vessel and then recovering the transition metal tungstate material. The method may further comprise drying the recovered transition metal tungstate material at a temperature from 100°C to 350 for 30 minutes to 48 hours.

[0015] Yet another embodiment involves a conversion process comprising contacting a sulfiding agent with a material to generate metal sulfides which are contacted with a feed at conversion conditions to generate at least one product, the material comprising: a transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is selected from NH_3, H_2O, or combinations thereof, m varies from 0.001 to 50, or from 1 to 25, or from 2 to 12; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn, and combinations thereof; 'y' varies from 0.5 to 2, or from 0.75 to 1.5, or from 0.9 to 1.25; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material;

the material is further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

[0016] Additional features and advantages of the invention will be apparent from the description of the invention, figures and claims provided herein.

BRIEF DESCRIPTION OF THE DRAWING

[0017] The Figure is the x-ray powder diffraction pattern of a transition metal tungstate material prepared by the method as described in the Examples.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The present invention relates to a transition metal tungstate composition and a process for preparing the composition. The material has the designation UPM-24. This composition has an empirical formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is selected from NH_3, H_2O, or combinations thereof, m varies from 0.001 to 50, or from 1 to 25, or from 2 to 12; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V,

Cu, Zn and combinations thereof; 'y' varies from 0.5 to 2, or from 0.75 to 1.5, or from 0.9 to 1.25; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material

[0019] The transition metal tungstate composition of the invention is characterized by having an extended network of M-O-M, where M represents a metal, or combination of metals listed above. The structural units repeat itself into at least two adjacent unit cells without termination of the bonding. The composition can have a one-dimensional network, such as, for example, linear chains.

[0020] The transition metal tungstate composition is further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A.

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

[0021] The transition metal tungstate composition of the invention is further characterized by the x-ray powder diffraction pattern shown in the Figure.

[0022] The transition metal tungstate composition can be prepared by solvothermal crystallization of a reaction mixture, typically by mixing reactive sources of tungsten with the appropriate metal 'M'.

[0023] Sources of M, and W include, but are not limited to, the respective halide, sulfide, acetate, nitrate, carbonate, sulfate, oxalate, thiols, hydroxide salts, and oxides of M, or W. Specific examples of sources of M include, but are not limited to, manganese nitrate, manganese chloride, manganese bromide, manganese sulfate, manganese carbonate, manganese sulfide, manganese hydroxide, manganese oxide, copper nitrate, copper chloride, copper bromide, copper sulfate, copper carbonate, copper acetate, copper oxalate, copper sulfide, copper hydroxide, copper oxide, zinc nitrate, zinc chloride, iron bromide, zinc sulfate, zinc carbonate, zinc acetate, zinc oxalate, zinc sulfide, zinc hydroxide, zinc oxide, and any mixture thereof. Additional specific sources include nickel chloride, nickel bromide, nickel nitrate, nickel acetate, nickel carbonate, nickel hydroxide, cobalt chloride, cobalt bromide, cobalt nitrate, cobalt acetate, cobalt carbonate, cobalt hydroxide, cobalt sulfide, nickel chloride, cobalt oxide, nickel bromide, nickel sulfide, nickel oxide, iron acetate, iron oxalate, iron nitrate, iron chloride, iron bromide, iron sulfate, iron carbonate, iron oxalate, iron sulfide, iron oxide, magnesium chloride, titanium oxide, vanadium chloride and any mixture thereof. Yet additional sources include, but are not limited to, tungstates and thiotungstates, such as tungsten trioxide, tungstic acid, tungsten oxytetrachloride, tungsten hexachloride, hydrogen tungstate, ammonium ditungstate, sodium ditungstate, ammonium metatungstate, ammonium paratungstate, sodium ditungstate, sodium ditungstate, sodium metatungstate, sodium paratungstate, and any mixture thereof.

[0024] Generally, the process used to prepare the composition of this invention involves forming a reaction mixture wherein the components, such as for example, Ni, W, NH_4OH and H_2O are mixed together. By way of specific examples, a reaction mixture may be formed which in terms of molar ratios of the oxides is expressed by the formula:

$$MO_x : AWO_z : B(NH_3) : H_2O$$

where 'M' is selected from the group consisting of iron, cobalt, nickel, manganese, vanadium, copper, zinc, and combinations thereof; 'x' is a number which satisfies the valency of 'M'; 'A' represents the ratio of 'W' relative to 'M' and varies from 0.4 to 2, or from 0.4 to 1.5, or from 0.5 to 1.25; 'z' is a number satisfies the valency of 'W'; 'B' represents the molar ratio of 'NH_3' and may vary from 0.1 to 100, or from 1 to 50, or from 2.5 to 25; the molar ratio of H_2O varies from 1 to 5000, or from 10 to 300, or from 20 to 100.

[0025] The reaction mixture, comprising NH_3, H_2O, or combinations thereof, and sources of M and W is reacted at temperatures ranging from 90°C to 250°C for a period of time ranging from 30 minutes to around 14 days. In one embodiment, the temperate range for the reaction is from 90°C to 120°C and in another embodiment the temperature is in the range of from 200°C to 250°C. In one embodiment, the reaction time is from 2 to 4 hours, and in another embodiment the reaction time is from 4 to 7 days. The reaction is carried out under atmospheric pressure or in a sealed vessel under autogenous pressure. In one embodiment, the synthesis may be conducted in an open vessel. The transition metal tungstate compositions are recovered as the reaction product. Optionally, the recovered transition metal tungstate material may be dried at a temperature from 100°C to 350°C for 30 minutes to 48 hours. The recovery may be by evaporation of solvent, decantation, filtration, or centrifugation. The transition metal tungstate compositions are characterized by the x-ray powder diffraction pattern as shown in Table A above and the Figure.

[0026] In the art of hydrothermal synthesis of metal oxides, it is well known that hydroxide defects occur in metal oxides made by this route and are located either internally as defects or externally as a result of often large external surface areas that are at least partially hydroxylated. These nonstoichiometric amounts of hydroxide moieties additively, together with the oxide ions, account for the collective valences of the metal ions in the compositions.

[0027] In one embodiment, an intermediate may be formed before reacting the reaction mixture. The intermediate is formed by removing at least some of the NH_3, H_2O, or a combination thereof to generate the intermediate which may be a precipitate, or at least a portion of the reaction mixture, or both a precipitate and a portion of the reaction mixture. The intermediate is then reacted as the reaction mixture at a temperature from 25°C to 500°C for a period of from 30 minutes to 14 days to generate the transition metal tungstate material.

[0028] Once formed, the transition metal tungstate may have a binder incorporated, where the selection of binder includes but is not limited to, anionic and cationic clays such as hydrotalcites, pyroaurite-sjogrenite-hydrotalcites, montmorillonite and related clays, kaolin, sepiolites, silicas, alumina such as (pseudo) boehomite, gibbsite, flash calcined gibbsite, eta-alumina, zirconia, titania, alumina coated titania, silica-alumina, silica coated alumina, alumina coated silicas and mixtures thereof, or other materials generally known as particle binders in order to maintain particle integrity.

These binders may be applied with or without peptization. The binder may be added to the bulk crystalline transition metal tungstate composition, and the amount of binder may range from 1 to 30 wt % of the finished catalysts or from 5 to 26 wt % of the finished catalyst. The binder may be chemically bound to the transition metal tungstate composition, or may be present in a physical mixture with the transition metal tungstate composition.

[0029] At least a portion of the transition metal tungstate, with or without a binder, or before or after inclusion of a binder, can be sulfided in situ in an application or pre-sulfided to form metal sulfides which in turn are used in an application as a catalyst. The sulfidation may be conducted under a variety of sulfidation conditions such as through contact of the transition metal tungstate with a sulfiding agent such as sulfur containing stream or feedstream or through contact with a gaseous mixture of H_2S / H_2, or both. The sulfidation of the transition metal tungstate may be performed at elevated temperatures, typically ranging from 50°C to 600°C, or from 150°C to 500°C, or from 250°C to 450°C. The materials resulting from the sulfiding step, the decomposition products, are referred to as metal sulfides which can be used as catalysts in conversion processes. As noted above, the metal sulfides may be present in a mixture with at least one binder. The sulfiding step can take place at a location remote from other synthesis steps, remote from the location of the conversion process, or remote from both the location of synthesis and remote from location of the conversion process.

[0030] At least a portion of the transition metal tungstate, with or without a binder, or before or after inclusion of a binder, can be sulfided in situ in an application or pre-sulfided to form metal sulfides which in turn are used in an application as a catalyst. The sulfidation may be conducted under a variety of sulfidation conditions such as through contact of the transition metal tungstate with a sulfiding agent such as sulfur containing stream or feedstream or through the use of a gaseous mixture of H_2S / H_2, or both. The sulfidation of the transition metal tungstate may be performed at elevated temperatures, typically ranging from 50°C to 600°C, or from 150°C to 500°C, or from 250°C to 450°C. The materials resulting from the sulfiding step, the decomposition products, are referred to as metal sulfides which can be used as catalysts in conversion processes. As noted above, at least a portion of the metal sulfides may be present in a mixture with at least one binder. The sulfiding step can take place at a location remote from other synthesis steps, remote from the

location of the conversion process, or remote from both the location of synthesis and remote from location of the conversion process.

[0031] As discussed, at least a portion of the transition metal tungstate of this invention can be sulfided and the resulting metal sulfides used as catalysts in conversion processes such as hydrocarbon conversion processes. Hydroprocessing is one class of hydrocarbon conversion processes in which the transition metal tungstate, or metal sulfides derived therefrom, is useful as a catalyst. Examples of specific hydroprocessing processes are well known in the art and include hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking. In one embodiment, a conversion process comprises contacting the transition metal tungstate with a sulfiding agent to generate metal sulfides which are contacted with a feed stream at conversion conditions to generate at least one product.

[0032] The operating conditions of the hydroprocessing processes listed above typically include reaction pressures from 2.5 MPa to 17.2 MPa, or in the range of 5.5 to 17.2 MPa, with reaction temperatures in the range of 245°C to 440°C, or in the range of 285°C to 425°C. Time with which the feed is in contact with the active catalyst, referred to as liquid hour space velocities (LHSV), should be in the range of 0.1 h^{-1} to 10 h^{-1}, or 2.0 h^{-1} to 8.0 h^{-1}. Specific subsets of these ranges may be employed depending upon the feedstock being used. For example, when hydrotreating a typical diesel feedstock, operating conditions may include from 3.5 MPa to 8.6 MPa, from 315°C to 410°C, from 0.25/h to 5/h, and from 84 Nm^3 H_2/m^3 to 850 Nm^3 H_2/m^3 feed. Other feedstocks may include gasoline, naphtha, kerosene, gas oils, distillates, and reformate.

[0033] Any of the lines, conduits, units, devices, vessels, surrounding environments, zones or similar used in the process may be equipped with one or more monitoring components including sensors, measurement devices, data capture devices or data transmission devices. Signals, process or status measurements, and data from monitoring components may be used to monitor conditions in, around, and on process equipment. Signals, measurements, and/or data generated or recorded by monitoring components may be collected, processed, and/or transmitted through one or more networks or connections that may be private or public, general or specific, direct or indirect, wired or

wireless, encrypted or not encrypted, and/or combination(s) thereof; the specification is not intended to be limiting in this respect.

[0034] Signals, measurements, and/or data generated or recorded by monitoring components may be transmitted to one or more computing devices or systems. Computing devices or systems may include at least one processor and memory storing computer-readable instructions that, when executed by the at least one processor, cause the one or more computing devices to perform a process that may include one or more steps. For example, the one or more computing devices may be configured to receive, from one or more monitoring component, data related to at least one piece of equipment associated with the process. The one or more computing devices or systems may be configured to analyze the data. Based on analyzing the data, the one or more computing devices or systems may be configured to determine one or more recommended adjustments to one or more parameters of one or more processes described herein. The one or more computing devices or systems may be configured to transmit encrypted or unencrypted data that includes the one or more recommended adjustments to the one or more parameters of the one or more processes described herein.

[0035] Examples are provided below so that the invention may be described more completely. These examples are only by way of illustration and should not be interpreted as a limitation of the broad scope of the invention, which is set forth in the appended claims.

[0036] Patterns presented in the following examples were obtained using standard x-ray powder diffraction techniques. The radiation source was a high-intensity, x-ray tube operated at 45 kV and 35 mA. The diffraction pattern from the copper K-alpha radiation was obtained by appropriate computer based techniques. Powder samples were pressed flat into a plate and continuously scanned from 3° and 70° (2θ). Interplanar spacings (d) in Angstrom units were obtained from the position of the diffraction peaks expressed as θ, where θ is the Bragg angle as observed from digitized data. Intensities were determined from the integrated area of diffraction peaks after subtracting background, "I_O" being the intensity of the strongest line or peak, and "I" being the intensity of each of the other peaks. As will be understood by those skilled in the art the determination of the parameter 2θ is subject to both human and mechanical error, which in combination can impose an uncertainty of ±0.4° on each reported value of 2θ. This uncertainty is

also translated to the reported values of the d-spacings, which are calculated from the 2θ values. In some of the x-ray patterns reported, the relative intensities of the d-spacings are indicated by the notations vs, s, m, and w, which represent very strong, strong, medium, and weak, respectively. In terms of $100(I/I_0)$, the above designations are defined as:

w=0.01-15, m=15-60: s=60-80 and vs=80-100

[0037] In certain instances, the purity of a synthesized product may be assessed with reference to its x-ray powder diffraction pattern. Thus, for example, if a sample is stated to be pure, it is intended only that the x-ray pattern of the sample is free of lines attributable to crystalline impurities, not that there are no amorphous materials present. As will be understood to those skilled in the art, it is possible for different poorly crystalline materials to yield peaks at the same position. If a material is composed of multiple poorly crystalline materials, then the peak positions observed individually for each poorly crystalline material would be observed in the resulting summed diffraction pattern. Likewise it is possible to have some peaks appear at the same positions within different, single phase, crystalline materials, which may be simply a reflection of a similar distance within the materials and not that the materials possess the same structure.

EXAMPLE 1

[0038] Nickel nitrate hexahydrate (29.1g, 0.1 moles of Ni) Ammonium metatungstate hydrate (25.3g, 0.1 moles of W) and urea (7.5g, 0.125 moles) were thoroughly mixed in DI H_2O (5g) and heat treated for 24 hrs at 65°C in a sealed PTFE bottle. The resultant mixture was then transferred to a ceramic crucible and heat treated at 100°C for a further 16 hours. The resulting product was analyzed by X-ray powder diffraction, and the X-ray powder diffraction pattern is shown in the Figure.

EXAMPLE 2

[0039] Cobalt nitrate hexahydrate (11.64g, 0.04 moles of Co), Nickel nitrate hexahydrate (11.63g, 0.04 moles of Ni), ammonium metatungstate hydrate (17.71g, 0.07 moles of W) and ammonium carbonate (30.76g, 0.64 moles of NH_3) were mixed thoroughly in DI H_2O (2.5g) before being heat treated for 12 hours at 100°C in a PTFE-lined stainless steel digestion vessel. The resultant slurry was filtered and the product was dried at 250°C for 24 hours. The resulting product

was analyzed by X-ray powder diffraction, and the X-ray powder diffraction pattern is shown in the Figure.

EXAMPLE 3

[0040] Nickel nitrate hexahydrate (26.1g, 0.09moles of Ni), zinc oxide (1.63g, 0.02 moles of Zn), ammonium metatungstate hydrate (17.71g, 0.07 moles of W) and ammonium carbonate (8.3g, 0.17 moles of NH_3) were mixed together in a PTFE bottle. The mixture was heated at 70°C for 48 hours after which the resultant green slurry was transferred to a ceramic dish and dried at 150°C for 48 hours. The resulting product was analyzed by X-ray powder diffraction, and the X-ray powder diffraction pattern is shown in the Figure.

EXAMPLE 4

[0041] Nickel nitrate hexahydrate (29.75g, 0.1moles of Ni) and ammonium metatungstate hydrate (17.71g, 0.07 moles of W) and urea (10g, 0.167 moles) and DI H_2O (5g, 0.278 moles) were mixed together in a sealed PTFE bottle. The mixture heat treated for 30 hours at 65°C with intermittent mixing, prior to being transferred to a ceramic dish and heat treated at 200°C. The resulting product was analyzed by X-ray powder diffraction, and the X-ray powder diffraction pattern is shown in the Figure.

EMBODIMENTS

[0042] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0043] A first embodiment of the invention is a transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is NH_3, H_2O, or combinations thereof; m varies from 0.001 to 50; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn and combinations thereof; 'y' varies from 0.5 to 2; 'z' is a number which satisfies the sum of the valency of the cationic species present in

the material; the material further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

[0044] An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the transition metal tungstate material is present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt-% binder. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the binder is selected from the group consisting of silicas, aluminas, and silica-aluminas. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein M is nickel or cobalt. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein M is nickel.

[0045] A second embodiment of the invention is a method of making a transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is NH_3, H_2O, or combinations thereof; m varies from 0.001 to 50; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn and combinations thereof; 'y' varies

from 0.5 to 2; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material; the material further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

the method comprising: forming a reaction mixture containing NH_3, H_2O, or a combination thereof, and sources of M and W; reacting the reaction mixture at a temperature of from 50°C to and 250°C in an autogenous environment; and recovering the transition metal tungstate material. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising removing at least some of the NH_3, the H_2O, or the combination thereof to form an intermediate before reacting the mixture at a temperature from 50°C to 250°C in an autogenous environment. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the reacting is conducted at a temperature of from 50°C to 250°C for a period of time from 30 minutes to 14 days. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the recovering is by filtration or centrifugation. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising drying the recovered crystalline transition metal tungstate material at a temperature from 100°C to 350°C for 30 minutes to 48 hours. An embodiment of the invention is one, any or all of prior embodiments in this

paragraph up through the second embodiment in this paragraph further comprising adding a binder to the recovered transition metal tungstate material. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the binder is selected from the group consisting of aluminas, silicas, and alumina-silicas. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising decomposing the recovered transition metal tungstate material by sulfidation to form metal sulfides.

[0046] A third embodiment of the invention is a conversion process comprising contacting a material with a sulfiding agent to convert at least a portion of the material to metal sulfides and contacting the metal sulfides with a feed at conversion conditions to generate at least one product, wherein the material comprises a transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is NH_3, H_2O or combinations thereof; m varies from 0.001 to 50; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn and combinations thereof; 'y' varies from 0.5 to 2; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material; the material further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph wherein the conversion process is hydroprocessing. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph wherein the conversion process is selected from the group consisting of hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph wherein the transition metal tungstate material, or at least a portion of the the metal sulfides, or both are present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt-% binder. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph further comprising at least one of: sensing at least one parameter of the process and generating a signal or data from the sensing; or generating and transmitting a signal; or generating and transmitting data.

[0047] Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

[0048] In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS:

1. A transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is NH_3, H_2O, or combinations thereof; m varies from 0.001 to 50; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn and combinations thereof; 'y' varies from 0.5 to 2; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material; the material further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

2. The transition metal tungstate material of claim 1 wherein the transition metal tungstate material is present in a mixture with at least one binder selected from silicas, aluminas, and silica-aluminas and wherein the mixture comprises up to 25 wt-% binder.
3. A method of making a transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is NH_3, H_2O, or combinations thereof; m varies from 0.001 to 50; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn and combinations thereof; 'y' varies from 0.5 to 2; 'z' is a number which satisfies the sum of the valency of the cationic species present in

the material; the material further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

the method comprising:

a. forming a reaction mixture containing NH_3, H_2O, or a combination thereof, and sources of M and W;

b. reacting the reaction mixture at a temperature of from 50°C to and 250°C in an autogenous environment; and

c. recovering the transition metal tungstate material.

4. The method of claim 3 further comprising removing at least some of the NH_3, the H_2O, or the combination thereof to form an intermediate before reacting the mixture at a temperature from 50°C to 250°C in an autogenous environment.

5. The method of claim 3 wherein the reacting is conducted at a temperature of from 50°C to 250°C for a period of time from 30 minutes to 14 days.

6. The method of claim 3 further comprising drying the recovered transition metal tungstate material at a temperature from 100°C to 350°C for 30 minutes to 48 hours.

7. The method of Claim 3 further comprising decomposing the recovered transition metal tungstate material by sulfidation to form metal sulfides.

8. A conversion process comprising contacting a material with a sulfiding agent to convert at least a portion of the material to metal sulfides and contacting the metal sulfides with a feed at conversion conditions to generate at least one product, wherein the material comprises a transition metal tungstate material having the formula:

$$A_mM(OH)_n(W)_yO_z$$

where 'A' is NH_3, H_2O or combinations thereof; m varies from 0.001 to 50; 'n' varies from 0.001 to 10; 'M' is a metal selected from Mn, Fe, Co, Ni, V, Cu, Zn and combinations thereof; 'y' varies from 0.5 to 2; 'z' is a number which satisfies the sum of the valency of the cationic species present in the material; the material further characterized by a x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

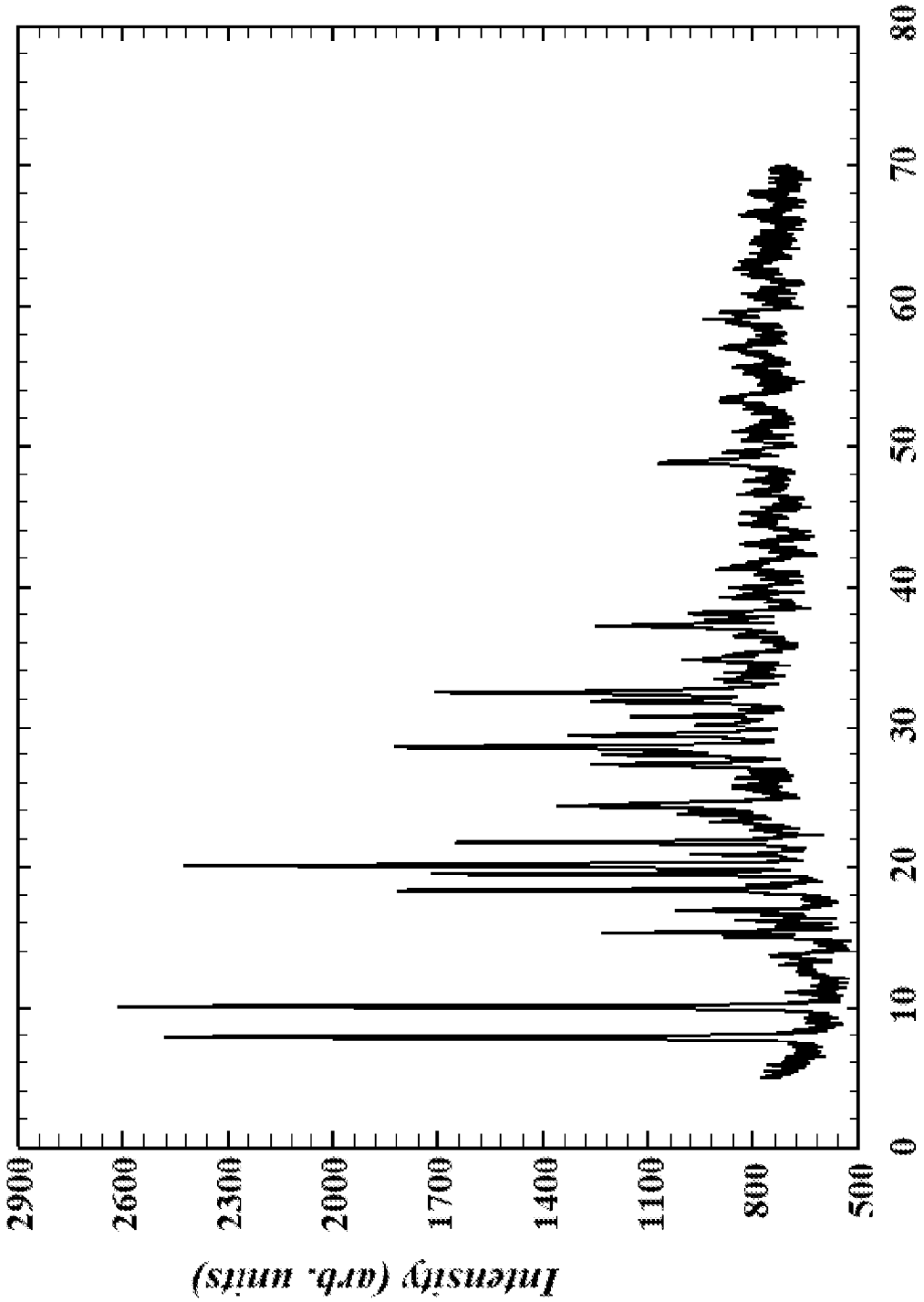
TABLE A

d(Å)	I/I_0 (%)
11.29	s
8.9	vs
5.93	vs
5.65	w
5.26	m
4.84	m
4.44	m
4.27	w
4.1	m
3.77	m
3.66	m

9. The process of claim 8 wherein the conversion process is selected from the group consisting of hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

10. The process of claim 8 wherein the transition metal tungstate material, or at least a portion of the the metal sulfides, or both are present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt-% binder.

5


Intensity (arb. units)
2900
2600
2300
2000
1700
1400
1100
800
500
0
10
20
30
40
50
60
70
80
2θ (°)

FIGURE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 2019/038134

A. CLASSIFICATION OF SUBJECT MATTER
(see extra sheet)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
B01J, C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Espacenet, PatSearch, USPTO, RUPTO, WIPO, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2018/0169633 A1 (UOP LLC) 21.06.2018	1-10
A	US 2017/0165645 A1 (UOP LLC) 15.06.2017	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 September 2019 (17.09.2019)	07 November 2019 (07.11.2019)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	Authorized officer M. Golubzova Telephone No. (8499)240-25-91

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INTERNATIONAL SEARCH REPORT
Classification of subject matter

International application No.
PCT/US 2019/038134

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B01J37/08(2006.01)
C10G45/08(2006.01)
C10G45/50(2006.01)
C10G45/60(2006.01)