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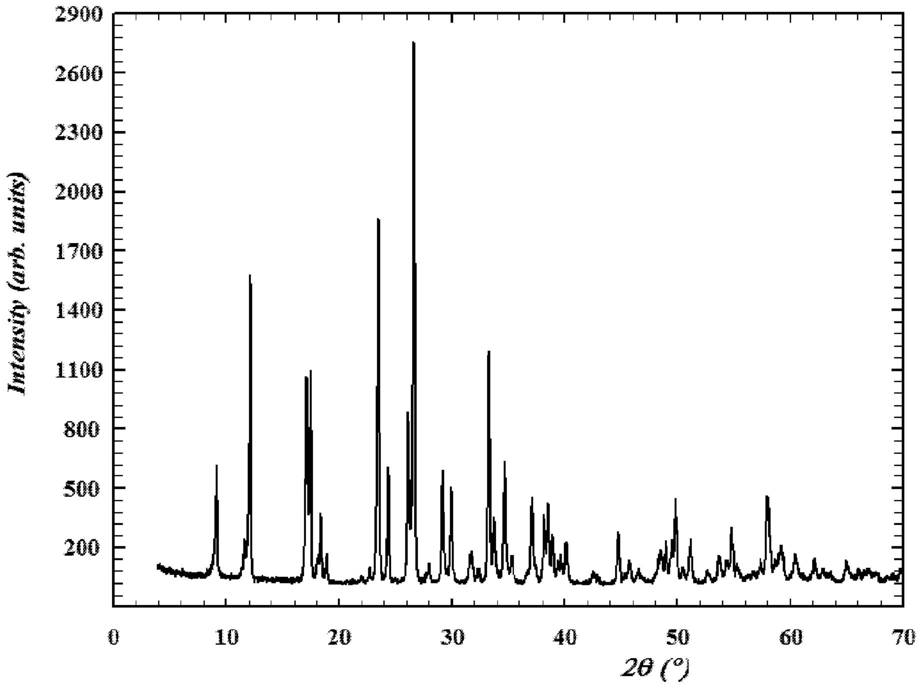
(72) Inventeurs/Inventors:
MILLER, STUART, US;
KOSTER, SUSAN C., US

(73) Propriétaire/Owner:
UOP LLC, US

(74) Agent: MACRAE & CO.

(54) Titre : MATERIAU TUNGSTOMOLYBDIQUE, OXYHYDROXYDE DE METAL DE TRANSITION A STRUCTURE CRISTALLINE
(54) Title: CRYSTALLINE TRANSITION METAL OXY-HYDROXIDE MOLYBDOTUNGSTATE



(57) Abrégé/Abstract:
A hydroprocessing catalyst has been developed. The catalyst is a unique crystalline transition metal oxy-hydroxide molybdotungstate material. The hydroprocessing using the crystalline ammonia transition metal oxy-hydroxide molybdotungstate material may include hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

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(71) Applicant: **UOP LLC** [US/US]; 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(72) Inventors: **MILLER, Stuart**; Uop Llc, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **KOSTER, Susan C.**; Uop Llc, 25 East Algonquin Road, P. O. Box 5, Des Plaines, Illinois 60017-5017 (US).

(74) Agent: **ROMANO, Ashley E.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

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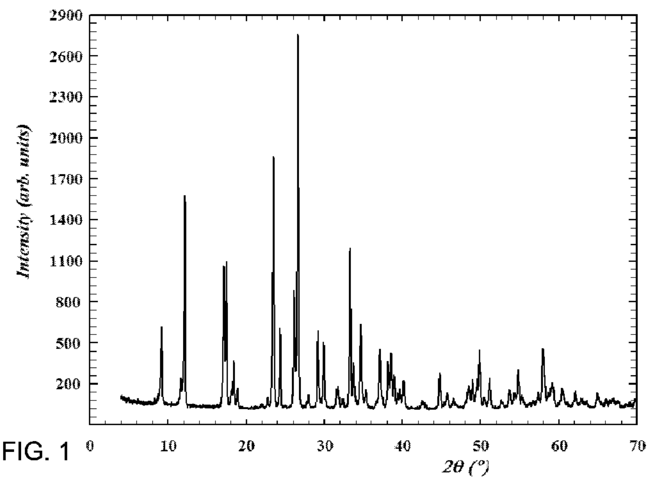

FIG. 1

(57) **Abstract**: A hydroprocessing catalyst has been developed. The catalyst is a unique crystalline transition metal oxy-hydroxide molybdotungstate material. The hydroprocessing using the crystalline ammonia transition metal oxy-hydroxide molybdotungstate material may include hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

WO 2017/106133 A1

CRYSTALLINE TRANSITION METAL OXY-HYDROXIDE MOLYBDOTUNGSTATE

[0001]

FIELD OF THE INVENTION

[0002] This invention relates to a new hydroprocessing catalyst. More particularly this invention relates to a unique crystalline transition metal oxy-hydroxide molybdotungstate and its use as a hydroprocessing catalyst. The hydroprocessing may include hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

BACKGROUND

[0003] 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.

[0004] Since the late 1940s the use of catalysts containing nickel (Ni) and molybdenum (Mo) or tungsten (W) have demonstrated up to 80% sulfur removal. 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.

[0005] 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.

[0006] 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+}.

[0007] Pezerat assigned the different phases he observed as being Φc, Φy 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.

[0008] The structure of Φy was not confirmed until 1996 when 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.

SUMMARY OF THE INVENTION

[0009] A unique crystalline transition metal oxy-hydroxide molybdotungstate material has been produced and optionally sulfided, to yield an active hydroprocessing catalyst. The crystalline transition metal oxy-hydroxide molybdotungstate material has a unique x-ray powder diffraction pattern showing strong peaks at 9.65, 7.3 and 5.17Å. The crystalline transition metal oxy-hydroxide molybdotungstate material has the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

where "a" varies from 0.1 to 10, or from 0.5 to 5, or from 0.75 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5, or from 0.75 to 1.5, or from 0.8 to 1.2; 'y' varies from 0.01 to 0.4, or from 0.01 to 0.25; where the sum of (x+y) must be $\leq$ 1.501, or $\leq$1.2 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

[0010] Another embodiment involves a method of making a crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

where "a" varies from 0.1 to 10, or from 0.5 to 5, or from 0.75 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5, or from 0.75 to 1.5, or from 0.8 to 1.2; 'y' varies from 0.01 to 0.4, or from 0.01 to 0.25; where the sum of (x+y) must be $\leq$ 1.501, or $\leq$1.2 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

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10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

the method comprising forming a reaction mixture containing NH_3, H_2O, and sources of M, W, and Mo; adjusting the pH of the reaction mixture to a pH of from 8.5 to 10; reacting the mixture together at elevated temperature with an autogenous pressure and then recovering the crystalline transition metal oxy-hydroxide molybdotungstate material. The reacting may be conducted at a temperature of from 70°C to 200°C for a period of time from 30 minutes to 14 days.

[0011] Yet another embodiment involves a conversion process comprising contacting a feed with a catalyst at conversion conditions to give at least one product, the catalyst comprising: a crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

where "a" varies from 0.1 to 10, or from 0.5 to 5, or from 0.75 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5, or from 0.75 to 1.5, or from 0.8 to 1.2; 'y' varies from 0.01 to 0.4, or from 0.01 to 0.25; where the sum of (x+y) must be ≤ 1.501, or ≤1.2 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

[0012] Additional features and advantages of the invention will be apparent from the description of the invention, and the drawing provided herein.

BRIEF DESCRIPTION OF THE DRAWING

[0013] FIG. 1 is the x-ray powder diffraction pattern of a crystalline transition metal oxy-hydroxide molybdotungstate prepared by boiling crystallization as described in Examples 1 to 3.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention relates to a crystalline transition metal oxy-hydroxide molybdotungstate material and a process for preparing the material. The material has the designation UPM-9. The crystalline transition metal oxy-hydroxide molybdotungstate material has an empirical formula:

$(NH_4)_aM(OH)_bMo_xW_yO_z$

where "a" varies from 0.1 to 10, or from 0.5 to 5, or from 0.75 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5, or from 0.75 to 1.5, or from 0.8 to 1.2; 'y' varies from 0.01 to 0.4, or from 0.01 to 0.25; where the sum of (x+y) must be $\leq$ 1.501, or $\leq$1.2 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W.

[0015] The crystalline 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.

[0016] The crystalline transition metal oxy-hydroxide molybdotungstate composition having an x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A.

TABLE A

d(Å)	**I/I_0 %**
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

[0017] The crystalline transition metal oxy-hydroxide molybdotungstate composition of the invention having the x-ray powder diffraction pattern shown in FIG. 1.

[0018] The crystalline transition metal oxy-hydroxide molybdotungstate composition is prepared by solvothermal crystallization of a reaction mixture typically prepared by mixing reactive sources of molybdenum and tungsten with a solvent as well as a source of ammonia. Specific examples of the molybdenum source which may be utilized in this invention include but are not limited to molybdenum trioxide, ammonium dimolybdate, ammonium thiomolybdate, and ammonium heptamolybdate. Specific examples of the tungsten source which may be utilized in this invention include but are not limited to tungsten trioxide, ammonium ditungstate, ammonium thiotungstate, and ammonium metatungstate. Sources of other metals "M" include but are not limited to the respective halide, acetate, nitrate, carbonate, thiols and hydroxide salts. Specific examples include nickel chloride, cobalt chloride, nickel bromide, cobalt bromide, magnesium chloride, nickel nitrate, cobalt nitrate, iron nitrate, manganese nitrate, zinc nitrate, nickel acetate, cobalt acetate, iron acetate, nickel carbonate, cobalt carbonate, zinc carbonate, nickel hydroxide and cobalt hydroxide.

[0019] The source of ammonia may include but is not limited to ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, ammonium chloride, ammonium fluoride or a combination thereof.

[0020] Generally, the solvothermal process used to prepare the composition of this invention involves forming a reaction mixture wherein all of the components, such as for example, Ni, Mo, NH_3 and H_2O are mixed in solution together. By way of one specific example, a reaction mixture may be formed which in terms of molar ratios of the oxides is expressed by the formula:

$$AMO_X : BMoO_Y : CWO_Z : D(NH_3) : H_2O$$

where 'M' is selected from the group consisting of iron, cobalt, nickel, manganese, copper, zinc and mixtures thereof; 'A' represents the molar ratio of 'M' and varies from 0.1 to 3 or from 0.5 to 2 or from 0.75 to 1.25; 'x' is a number which satisfies the valency of 'M'; 'B' represents the molar ratio of 'Mo' and varies from 0.1 to 3 or from 0.5 to 2 or from 0.75 to 1.25; 'y' is a number satisfies the valency of 'Mo'; 'B' represents the molar ratio of 'W' and varies from 0.01 to 1 or from 0.05 to 0.8 or from 0.1 to 0.6; 'D' represents the molar ratio of NH_3 and varies from 0.01 to 50 or from 0.1 to 40 or from 1 to 30 ; the molar ratio of H_2O and varies from 10 to 1000 or from 50 to 500 or from 90 to 300.

CA 3004607 2020-02-13

[0021] The pH of the mixture is adjusted to a value ranging from 7.5 to 11, or from 8.5 to 10. The pH of the mixture can be controlled through the addition of a base such as NH_4OH, quaternary ammonium hydroxides, amines, and the like.

[0022] Once the reaction mixture is formed, the reaction mixture is reacted at temperatures ranging from 70°C to 230°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 110°C to 120°C and in another embodiment the temperature is in the range of from 150°C to 180°C. In one embodiment, the reaction time is from 4 to 6 hours, and in another embodiment the reaction time is from 7 to 10 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 under reflux conditions. The crystalline transition metal oxy-hydroxide molybdotungstate compositions are recovered as the reaction product. The crystalline transition metal oxy-hydroxide molybdotungstate compositions are further characterized by their x-ray powder diffraction pattern as shown in Table A above and FIG. 1.

[0023] Once formed, the crystalline transition metal oxy-hydroxide molybdotungstate composition 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, zicronica, 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 oxy-hydroxide molybdotungstate 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 crystalline transition metal oxy-hydroxide molybdotungstate composition, or may be present in a physical mixture with the crystalline transition metal oxy-hydroxide molybdotungstate composition.

[0024] The crystalline transition metal oxy-hydroxide molybdotungstate composition, with or without an incorporated binder can then be sulfided or pre-sulfided under a variety of sulfidation conditions, these include through contact of the crystalline transition metal oxy-hydroxide molybdotungstate composition with a sulfur containing feed as well as the use of a gaseous mixture of H_2S / H_2. The sulfidation of the crystalline transition metal oxy-hydroxide molybdotungstate composition is performed at elevated temperatures, typically ranging from 50 to 600°C, or from 150 to 500°C, or from 250 to 450°C.

[0025] The unsupported crystalline transition metal oxy-hydroxide molybdotungstate material of this invention can be used as a catalyst or catalyst support in various hydrocarbon conversion processes. Hydroprocessing processes is one class of hydrocarbon conversion processes in which the crystalline transition metal oxy-hydroxide molybdate material 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

[0026] 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.

[0027] 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.

[0028] 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, "Io" 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 powder diffraction 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=0-15, M=15-60: S=60-80 AND VS=80-100

[0029] 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 powder diffraction 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 a 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 materials 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

[0030] In a 2 liter flask, 125.71g of nickel nitrate hexahydrate (0.43 moles of Ni), 23.2g of molybdenum trioxide (0.16 moles of Mo) and 77g of ammonium metatungstate (0.31 moles of W) were dissolved in 1200ml of water. The pH of the solution was increased to 9 using concentrated NH_4OH (300ml). At this point the solution was transferred to a 2-liter stainless steel autoclave, the heat was ramped to 180°C over a period of 2 hours and held at 180°C for 24 hours, after which time the autoclave was cooled to room temperature, filtered, washed with 90 ml of 90°C water and then dried at 100°C. The x-ray powder diffraction spectra of the phase matches the spectra shown in FIG. 1.

CA 3004607 2019-11-22

EXAMPLE 2

[0031] In a 2 liter flask, 104.76g of nickel nitrate hexahydrate (0.36 moles of Ni), 126.96g of ammonium heptamolybdate (0.72 moles of Mo) and 53.28g of ammonium metatungstate (0.21 moles of W) were dissolved in 1008ml of water. The pH of the solution was increased to 9 using concentrated NH_4OH (100ml). At this point the solution was transferred to a 2-liter stainless steel autoclave, the heat was ramped to 180°C over a period of 2 hours and held at 180°C for 24 hours, after which time the autoclave was cooled to room temperature, filtered, washed with 90 ml of 90°C water and then dried at 100°C. The x-ray powder diffraction spectra of the phase matches the spectra shown in FIG. 1.

EXAMPLE 3

[0032] In a 2 liter flask, 104.76g of nickel nitrate hexahydrate (0.36 moles of Ni), 95.22g of ammonium heptamolybdate (0.54 moles of Mo) and 53.28g of ammonium metatungstate (0.21 moles of W) were dissolved in 1008ml of water. The pH of the solution was increased to 9 using concentrated NH_4OH (100ml). At this point the solution was transferred to a 2-liter stainless steel autoclave, the heat was ramped to 180°C over a period of 2 hours and held at 150°C for 7 days, after which time the autoclave was cooled to room temperature, filtered, washed with 90 ml of 90°C water and then dried at 100°C. The x-ray powder diffraction spectra of the phase matches the spectra shown in FIG. 1.

EMBODIMENTS

[0033] Embodiment 1 is a crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

where "a" varies from 0.1 to 10, or from 0.5 to 5, or from 0.75 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5, or from 0.75 to 1.5, or from 0.8 to 1.2; 'y' varies from 0.01 to 0.4, or from 0.01 to 0.25; where the sum of (x+y) must be $\leq$ 1.501, or $\leq$1.2 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

[0034] The crystalline transition metal oxy-hydroxide molybdotungstate material of embodiment 1 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt% binder.

[0035] The crystalline transition metal oxy-hydroxide molybdotungstate material of embodiment 1 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt% binder and wherein the binder is selected from the group consisting of silicas, aluminas, and silica-aluminas.

[0036] The crystalline transition metal oxy-hydroxide molybdotungstate material of embodiment 1 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is sulfided.

[0037] Embodiment 2 is a method of making a crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$(NH_4)_aM(OH)_bMo_xW_yO_z$

where "a" varies from 0.1 to 10, or from 0.5 to 5, or from 0.75 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5, or from 0.75 to 1.5, or from 0.8 to 1.2; 'y' varies from 0.01 to 0.4, or from 0.01 to 0.25; where the sum of (x+y) must be ≤ 1.501, or ≤1.2 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

the method comprising: (a) forming a reaction mixture containing NH_3, H_2O, and sources of M, W, and Mo; (b) adjusting the pH of the reaction mixture to a pH of from 8.5 to 10; (c) reacting the reaction mixture between 100°C and 220°C in an autogenous environment, and (d) recovering the crystalline transition metal oxy-hydroxide molybdotungstate material.

[0038] The method of embodiment 2 wherein the reacting is conducted at a temperature of from 100°C to 200°C for a period of time from 30 minutes to 14 days.

[0039] The method of embodiment 2 wherein the recovering is by filtration or centrifugation.

CA 3004607 2019-11-22

[0040] The method of embodiment 2 further comprising adding a binder to the recovered crystalline transition metal oxy-hydroxide molybdotungstate material.

[0041] The method of embodiment 2 further comprising adding a binder to the recovered crystalline transition metal oxy-hydroxide molybdotungstate material wherein the binder is selected from the group consisting of aluminas, silicas, and alumina-silicas.

[0042] The method of embodiment 2 further comprising sulfiding the recovered crystalline transition metal oxy-hydroxide molybdotungstate material.

[0043] Embodiment 3 is a conversion process comprising contacting a feed with a catalyst at conversion conditions to give at least one product, the catalyst comprising: a crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

where "a" varies from 0.1 to 10, or from 0.5 to 5, or from 0.75 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5, or from 0.75 to 1.5, or from 0.8 to 1.2; 'y' varies from 0.01 to 0.4, or from 0.01 to 0.25; where the sum of (x+y) must be ≤ 1.501, or ≤ 1.2 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

[0044] The process of embodiment 3 wherein the conversion process is hydroprocessing.

[0045] The process of embodiment 3 wherein the conversion process is selected from the group consisting of hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodesilication, hydrodearomatization, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

[0046] The process of embodiment 3 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt% binder.

[0047] The process of embodiment 3 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is sulfided.

CA 3004607 2019-11-22

CLAIMS:

1. A crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

where "a" varies from 0.1 to 10, 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5; 'y' varies from 0.01 to 0.4; where the sum of (x+y) must be ≤ 1.501; 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

.

2. The crystalline transition metal oxy-hydroxide molybdotungstate material of claim 1 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is present in a mixture with at least one binder selected from the group consisting of silicas, aluminas, and silica-aluminas and wherein the mixture comprises up to 25 wt% binder.

3. The crystalline transition metal oxy-hydroxide molybdotungstate material of claim 1 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is sulfided.

4. A method of making a crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

where "a" varies from 0.1 to 10, 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5; 'y' varies from 0.01 to 0.4; where the sum of (x+y) must be $\leq$ 1.501; 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

the method comprising:

(a) forming a reaction mixture containing NH_3, H_2O, and sources of M, W, and Mo;

(b) adjusting the pH of the reaction mixture to a pH of from 8.5 to 10;

(c) reacting the reaction mixture between 100°C and 220°C in an autogenous environment; and

(d) recovering the crystalline transition metal oxy-hydroxide molybdotungstate material.

5. The method of claim 4 wherein the reacting is conducted at a temperature of from 100°C to 200°C for a period of time from 30 minutes to 14 days.

6. The method of claim 4 further comprising adding a binder selected from the group consisting of aluminas, silicas, and alumina-silicas to the recovered crystalline transition metal oxy-hydroxide molybdotungstate material.

7. The method of claim 4 further comprising sulfiding the recovered crystalline transition metal oxy-hydroxide molybdotungstate material.

8. A hydroprocessing process comprising contacting a feed with a catalyst at hydroprocessing conditions to give at least one product, the catalyst comprising: a crystalline transition metal oxy-hydroxide molybdotungstate material having the formula:

$$(NH_4)_aM(OH)_bMo_xW_yO_z$$

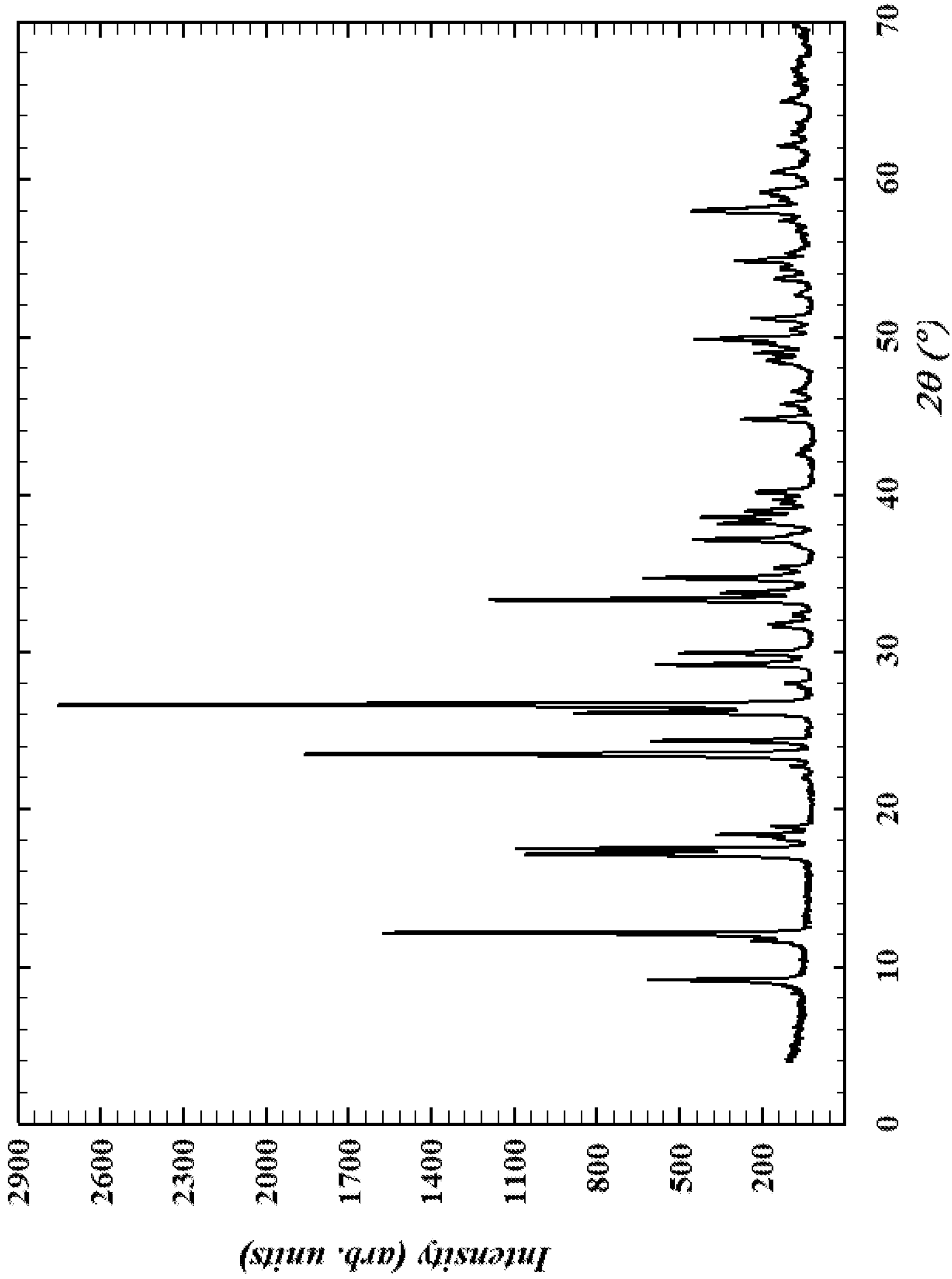
where "a" varies from 0.1 to 10, 'M' is a metal selected from Mg, Mn, Fe, Co, Ni, Cu, Zn and mixtures thereof; 'b' varies from 0.1 to 2; 'x' varies from 0.5 to 1.5; 'y' varies from 0.01 to 0.4; where the sum of (x+y) must be $\leq$ 1.501; 'z' is a number which satisfies the sum of the valencies of NH_4, M, OH, Mo and W; the material having a unique x-ray powder diffraction pattern showing peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
10.0-9.53	m
7.72-7.76	s
7.49-7.25	m
5.27-5.12	m
5.1-5.04	m
4.92-4.87	w
3.97-3.91	m
3.69-3.64	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.09	w
3-2.97	m
2.76-2.73	m

9. The process of claim 8 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt% binder.

10. The process of claim 8 wherein the crystalline transition metal oxy-hydroxide molybdotungstate material is sulfided.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40
50
60
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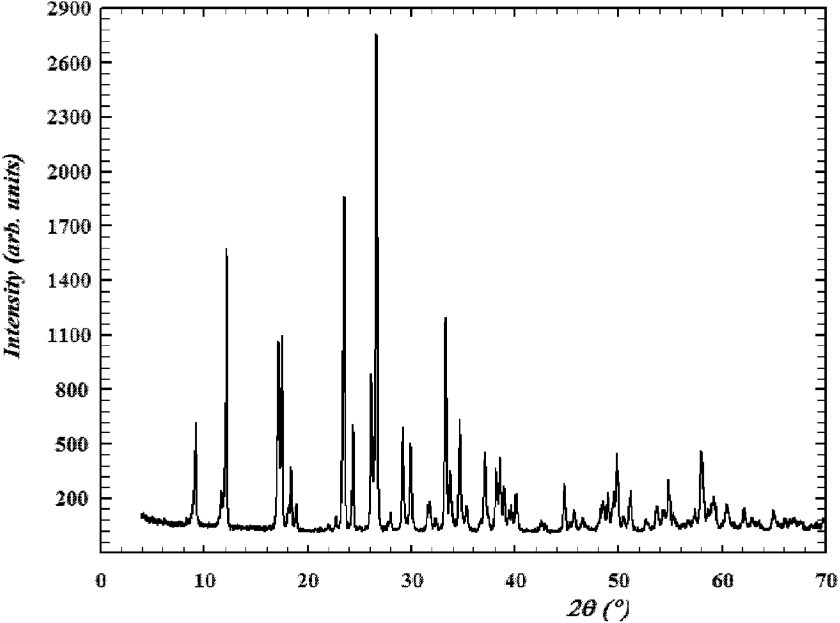
FIG. 1



Intensity (arb. units)
2900
2600
2300
2000
1700
1400
1100
800
500
200
0
10
20
30
40
50
60
70
2θ (°)