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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 5017, 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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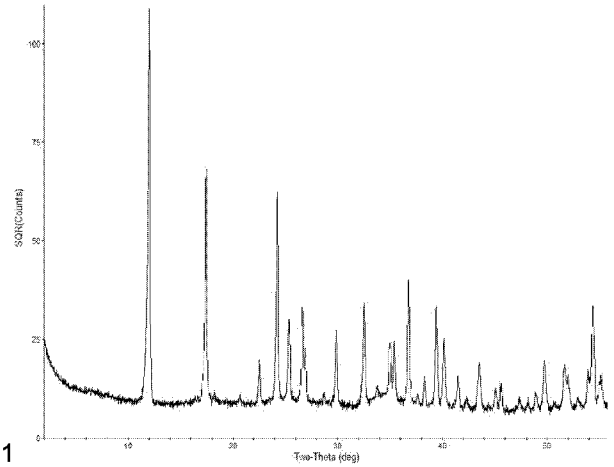

FIG. 1

(57) Abstract: A unique crystalline bis-ammonia metal molybdate material has been developed. The material may be used as a hydroprocessing catalyst. The hydroprocessing may include hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodearomatization, hydrodesilication, hydroisomerization, hydrotreating, hydrofining, and hydrocracking.

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CRYSTALLINE BIS-AMMONIA METAL MOLYBDATE

PRIORITY CLAIM OF EARLIER NATIONAL APPLICATION

[0001] This application claims priority to U.S. Application No. 62/267,857 filed December 15, 2015, the contents of which are hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention relates to a new hydroprocessing catalyst. More particularly this invention relates to a unique crystalline bis-ammonia metal molybdate 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. 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.

[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 bis-ammonia metal molybdate material has been produced and optionally sulfided, to yield an active hydroprocessing catalyst. The crystalline bis-ammonia metal molybdate material has a unique x-ray powder diffraction pattern showing strong peaks at d-spacings 7.33, 5.06 and 3.93Å. The crystalline bis-ammonia metal molybdate material has the formula:

$$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$$

where '*n*' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5, or between 0.6 to 1.3, or from 0.8 to 1.2; 'y' is a number which satisfies the sum of the valences of M and Mo, the material is further characterized by a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

[0010] Another embodiment involves a method of making a crystalline bis-ammonia metal molybdate material having the formula:

$$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$$

where '*n*' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5, or between 0.6 to 1.3, or from 0.8 to 1.2; 'y' is a number which satisfies the sum of the valences of M and Mo, the material is further characterized by a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A, the method comprising forming a reaction mixture containing NH_3, H_2O, and sources of M and Mo; adjusting the pH of the reaction mixture to a pH of from 8.5 to 10; and recovering the crystalline bis-ammonia metal molybdate material.

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

[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 bis-ammonia metal molybdate material having the formula:

$$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$$

where '*n*' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5, preferably between 0.6 to 1.3, or from 0.8 to 1.2; 'y' is a number which satisfies the sum of the valences of M and Mo, the material is further characterized by a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	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, the drawing and claims provided herein.

BRIEF DESCRIPTION OF THE DRAWING

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

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention relates to a crystalline bis-ammonia metal molybdate composition, a process for preparing the composition, and a conversion process using the composition as the catalyst. The composition has been given the designation UPM-4. This composition has an empirical formula:

$$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$$

where '*n*' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5, or between 0.6 to 1.3, or from 0.8 to 1.2; 'y' is a number which satisfies the sum of the valences of M and Mo.

[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. Decomposition products from these one-dimensional chains may result in one-dimensional chains or a two dimensional network i.e. layers or a three dimensional framework solid.

[0016] The crystalline bis-ammonia metal molybdate composition is further characterized by a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A.

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

[0017] The crystalline bis-ammonia metal molybdate composition of the invention is further characterized by the x-ray powder diffraction pattern shown in FIG. 1.

[0018] The crystalline bis-ammonia metal molybdate composition is prepared by solvothermal crystallization of a reaction mixture typically prepared by mixing reactive sources of molybdenum with the appropriate metal 'M' 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. 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, zinc chloride, nickel nitrate, cobalt nitrate, iron nitrate, manganese nitrate, zinc nitrate, nickel acetate, cobalt acetate, iron acetate, nickel carbonate, cobalt carbonate, zinc hydroxide, 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. In general, one or more sources of Ni, one or more sources of Mo, NH_3 and H_2O are mixed in solution together to form the material. Examples of suitable sources of Ni and Mo include metal oxides of Ni or Mo, metal halides of Ni and Mo, and alkali metals of Ni and Mo.

[0021] By way of a specific example, the sources of Ni and Mo may be Ni-oxides and Mo-oxides. In this specific example, a reaction mixture may be formed which in terms of molar ratios of the oxides is expressed by the formula:

$$AMO_x : BMoO_y : C(NH_3): H_2O$$

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 may vary from 0.5 to 3, or from 0.75 and 2.0,, or from 1.0 and 1.5; 'x' is a number that satisfies the valency of M; 'B' represents the molar ratio of 'Mo' and may vary from is from 0.5 to 3, or from 0.75 and 2.0,, or from 1.0 and 1.5 ; and 'y' is a number that satisfies the valency of Mo; 'C' represents the molar ratio of NH_3 and may vary from is from 0.1 to 5, or from 0.5 and 3,, or from 1 and 2; the molar ratio of H_2O may vary from 10 to 1000, or from 20 and 500, , or from 25 and 100. It is necessary to adjust the pH of the mixture the pH of the reaction mixture to a pH of 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 90°C to 100°C for a period of time ranging from 30 minutes to around 8 hours. In one embodiment the temperate range for the reaction is from 95°C to 100°C and in another embodiment the temperature range of from 97°C to 100°C. In one embodiment, the reaction time is from 4 to 6 hours, and in another embodiment the reaction time is from 4.5 to 5.5 hours. Beyond 8 hours the yield suffers. 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 bis-ammonia metal molybdate compositions are characterized by their unique x-ray powder diffraction pattern as shown in Table A above and FIG. 1.

[0023] Once formed, the crystalline bis-ammonia metal molybdate 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 bis-ammonia metal molybdate 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 bis-ammonia metal molybdate composition, or may be present in a physical mixture with the crystalline bis-ammonia metal molybdate composition.

[0024] The crystalline bis-ammonia metal molybdate 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 bis-ammonia metal molybdate 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 bis-ammonia metal molybdate 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 bis-ammonia metal molybdate material of this invention can be used as a catalyst or catalyst support in various hydrocarbon conversion processes. Hydroprocessing processes are one class of hydrocarbon conversion processes in which the crystalline bis-ammonia metal molybdate material is useful as a catalyst. Examples of specific hydroprocessing processes are well known in the art and include hydrotreating or hydrofining, hydrogenation, hydrodearomatization, hydrodemetallation, hydrodesilication, hydrocracking, hydrodenitrogenation, and hydrodesulfurization.

[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 Nm3 H2/m3 to 850 Nm3 H2/m3 feed. Other feedstocks may include gasoline, naphtha, kerosene, gas oils, distillates, and reformate.

[0027] The unsupported crystalline bis-ammonia metal molybdate 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 bis-ammonia metal molybdate material is useful as a catalyst. Examples of specific hydroprocessing processes are well known in the art and include hydrotreating or hydrofining, hydrogenation, hydrodearomatization, hydrodemetallation, hydrodesilication hydrocracking, hydrodenitrogenation, and hydrodesulfurization.

[0028] 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 Nm3 H2/m3 to 850 Nm3 H2/m3 feed. Other feedstocks may include gasoline, naphtha, kerosene, gas oils, distillates, and reformate.

[0029] 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. X-ray powder diffraction 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=0-15, m=15-60: s=60-80 and vs=80-100

[0030] 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 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

[0031] In a 3 liter flask, 35.61g of nickel carbonate (0.3 moles Ni) and 43.17g molybdenum trioxide (0.3 moles Mo) were added to 300 ml of water forming a slurry. To this slurry, 90 ml of a concentrated NH_4OH solution was added in order to adjust the pH to 9.1. The solution was refluxed at 100°C. During the heating the precipitates dissolved to give a clear deep blue solution prior to the formation of a lime green precipitate. After 5 hours, a

green precipitate was observed suspended in the blue pH 9 solution. This precipitate was cooled to room temperature, filtered, washed with 90 ml of 90°C water and then dried at 100°C. The dried precipitate was analyzed by x-ray powder diffraction as described above, and the X-ray powder diffraction pattern is shown in FIG. 1; the phase was identified as $(NH_3)_2Ni(MoO_4)$.

EXAMPLE 2

[0032] In a 3 liter flask, 29.67g of nickel carbonate (0.25 moles Ni) and 2.87g of manganese nitrate hexahydrate (0.01moles of Mn) and 43.17g molybdenum trioxide (0.30 moles Mo) were added to 300 ml of water forming a slurry. To this slurry, 90 ml of a concentrated NH_4OH solution was added in order to adjust the pH to 9.1. The solution was refluxed at 100°C. During the heating the precipitates dissolved to give a clear deep blue solution prior to the formation of the lime green precipitate. After 5hrs, a green precipitate was observed suspended in the blue pH 9 solution. This precipitate was cooled to room temperature, filtered, washed with 90 ml of 90°C water and then dried at 100°C. The dried precipitate was analyzed by x-ray powder diffraction as described above, and the X-ray powder diffraction pattern is shown in FIG. 1; the phase was identified as $(NH_3)_2Ni(MoO_4)$.

EXAMPLE 3

[0033] In a 1 liter flask, 10.14g of basic nickel carbonate hydrate (0.1 moles Ni) and 17.66g of ammonium heptamolybdate (0.1 moles Mo) were added to 200 ml of water and mixed thoroughly, after which 39.53g ammonium bicarbonate was added and the solution was refluxed at 100°C. During the heating the precipitates dissolved to give a clear deep blue solution prior to the formation of the lime green precipitate. After 2hrs, a green precipitate was observed suspended in the blue pH 8 solution, this precipitate was cooled to room temperature, filtered, washed with 90 ml of 90°C water and then dried at 100°C. The dried precipitate was analyzed by x-ray powder diffraction as described above, and the X-ray powder diffraction pattern is shown in FIG. 1; the phase was identified as $(NH_3)_2Ni(MoO_4)$.

EMBODIMENTS OF THE INVENTION

[0034] One embodiment includes a crystalline bis-ammonia metal molybdate material having the formula:

$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$

where '*n*' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5, or between 0.6 to 1.3, or from 0.8 to 1.2; 'y' is a number which satisfies the sum of the valences of M and Mo, the material is further characterized by a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

[0035] The crystalline bis-ammonia metal molybdate material may be present in a mixture with at least one binder and wherein the mixture comprises up to 25 wt% binder.

[0036] The binder may be selected from the group consisting of silicas, aluminas, and silica-aluminas.

[0037] M of the crystalline bis-ammonia metal molybdate material may be nickel or cobalt.

[0038] M of the crystalline bis-ammonia metal molybdate material may be nickel.

[0039] The crystalline bis-ammonia metal molybdate material may be sulfided.

[0040] One embodiment includes a method of making a crystalline bis-ammonia metal molybdate material having the formula:

$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$

where '*n*' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5, or between 0.6 to 1.3, or from 0.8 to 1.2; 'y' is a number which satisfies the sum of the valences of M and Mo, the material is further characterized by a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

[0041] The method comprising forming a reaction mixture containing NH_3, H_2O, and sources of M and Mo; adjusting the pH of the reaction mixture to a pH of from 8.5 to 10; heating the solution to between 85 – 100°C until the resultant pH is between 8.5 and 9.5 and then recovering the crystalline bis-ammonia metal molybdate material.

[0042] The recovering may be by filtration or centrifugation.

[0043] A binder may be added to the recovered crystalline bis-ammonia metal molybdate material.

[0044] The binder may be selected from the group consisting of aluminas, silicas, and alumina-silicas.

[0045] The recovered crystalline bis-ammonia metal molybdate material may be sulfided.

[0046] One embodiment includes a conversion process comprising contacting a feed with a catalyst at conversion conditions to give at least one product, the catalyst comprising: a crystalline bis-ammonia metal molybdate material having the formula:

$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$

where 'n' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5, or between 0.6 to 1.3, or from 0.8 to 1.2; 'y' is a number which satisfies the sum of the valences of M and Mo, the material is further characterized by a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

[0047] The process may be hydroprocessing.

[0048] The process may be selected from the group consisting of hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodearomatization, hydroisomerization, hydrodesilication, hydrotreating, hydrofining, and hydrocracking.

[0049] The process may use the crystalline bis-ammonia metal molybdate material in a mixture with at least one binder and wherein the mixture comprises up to 25 wt% binder.

[0050] The process may use the crystalline bis-ammonia metal molybdate material that has been sulfided.

CLAIMS:

1. A crystalline bis-ammonia metal molybdate material having the formula:

$$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$$

where 'n' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5; 'y' is a number which satisfies the sum of the valences of M and Mo, the material having a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
5.1-5.05	s
4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

2. The crystalline bis-ammonia metal molybdate material of claim 1 wherein the crystalline bis-ammonia metal molybdate 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 bis-ammonia metal molybdate material of claim 1 wherein the crystalline bis-ammonia metal molybdate material is sulfided.

4. A method of making a crystalline bis-ammonia metal molybdate material having the formula:

$$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$$

where 'n' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5; 'y' is a number which satisfies the sum of the valences of M and Mo, the material having a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
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4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	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 and Mo;

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

(c) heating the reaction mixture to between 85° and 100°C until the resultant pH is between 8.5 and 9.5; and

(d) recovering the crystalline bis-ammonia metal molybdate material.

5. 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 bis-ammonia metal molybdate material.

6. The method of claim 4 further comprising sulfiding the recovered crystalline bis-ammonia metal molybdate material.

7. A conversion process comprising contacting a feed with a catalyst at conversion conditions to give at least one product, the catalyst comprising: a crystalline bis-ammonia metal molybdate material having the formula:

$(NH_3)_{2-n}M(OH_2)_nMo_xO_y$

where 'n' varies from 0.1 to 2.0; 'M' is a metal selected from Mg, Mn, Fe, Co Ni, Cu, Zn, and mixtures thereof; 'x' varies from 0.5 to 1.5; 'y' is a number which satisfies the sum of the valences of M and Mo, the material having a unique x-ray powder diffraction pattern showing the peaks at the d-spacings listed in Table A:

TABLE A

d(Å)	I/I_0 %
7.49-7.28	vs
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4.4-4.257	w
3.966-3.915	m
3.69-3.645	s
3.52-3.48	m
3.35-3.32	m
3.31-3.29	m
3.12-3.097	w
3-2.97	m
2.76-2.73	m

8. The process of claim 7 wherein the conversion process is hydroprocessing and wherein the hydroprocessing process is selected from the group consisting of hydrodenitrification, hydrodesulfurization, hydrodemetallation, hydrodearomatization, hydroisomerization, hydrodesilication, hydrotreating, hydrofining, and hydrocracking.

9. The process of claim 7 wherein the crystalline bis-ammonia metal molybdate 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 7 wherein the crystalline bis-ammonia metal molybdate material is sulfided.

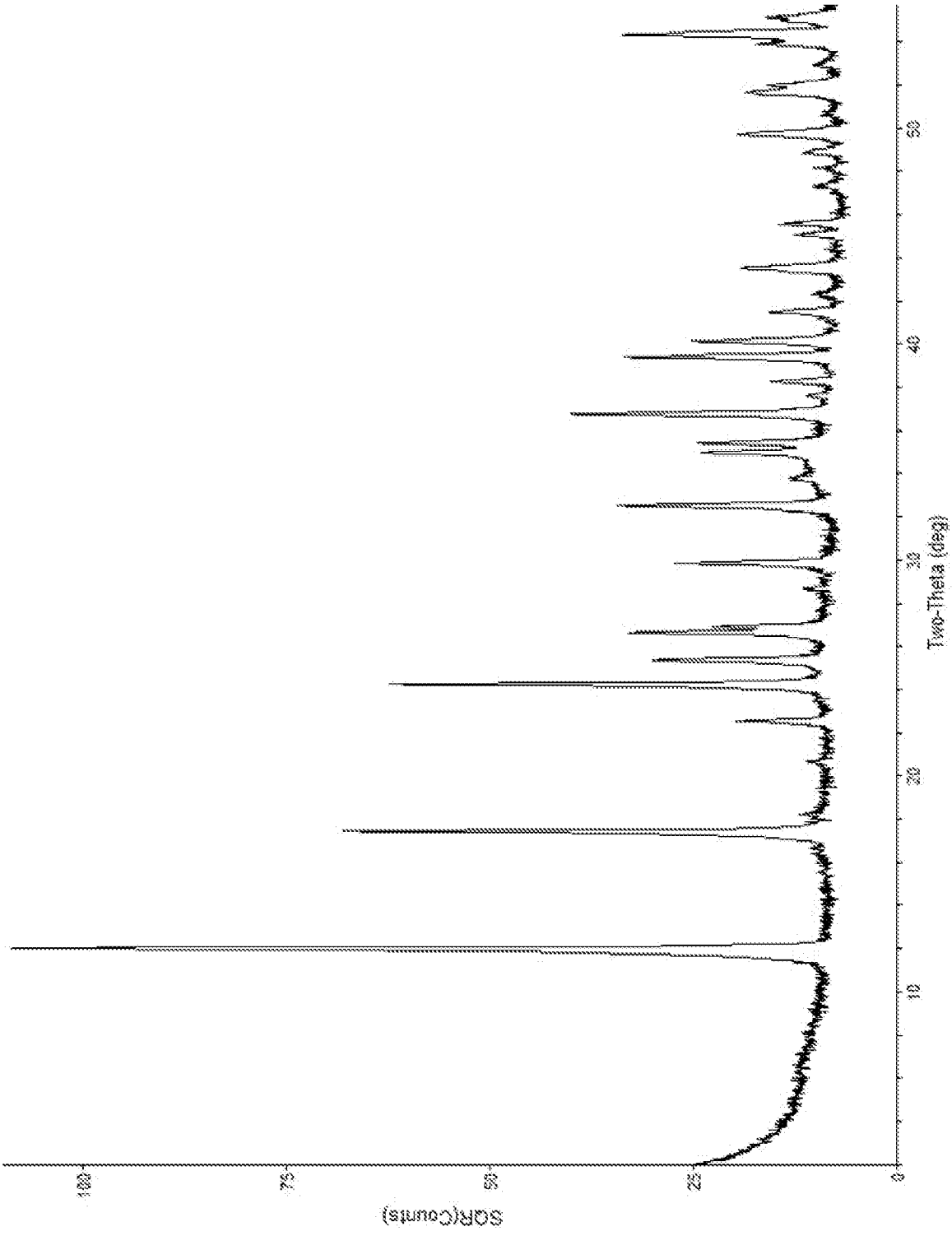

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/066283

A. CLASSIFICATION OF SUBJECT MATTER

C01G 39/00 *(2006.01)*
C01G 49/02 *(2006.01)*
C01G 99/00 *(2010.01)*
C01G 51/04 *(2006.01)*
C01G 45/02 *(2006.01)*
C01G 53/04 *(2006.01)*
C01G 1/00 *(2006.01)*

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)

C01G 39/00, 49/00-49/02, 99/00, 51/00-51/04, 45/00-45/02, 53/00-53/04, 1/00

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)

PatSearch (RUPTO internal), USPTO, PAJ, K-PION, Esp@cenet, Information Retrieval System of FIPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Doron Levin. Novel Transition Metal Molybdates for Catalytic Oxidative Dehydrogenation. Submitted to the Department of Chemical Engineering in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemical Engineering at the Massachusetts Institute of Technology. June 1997	1-10
A	US 3678124 A (GENNADY ARKADIEVICH STEPANOV et al) 18.07.1972	1-10
A	US 5010049 A (MARIA A.VILLA-GARCIA) 23.04.1991	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)

"O" document referring to an oral disclosure, use, exhibition or other means

"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
21 March 2017 (21.03.2017)	30 March 2017 (30.03.2017)

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

E. Zelenina

Telephone No. (499) 240-25-91