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(71) Applicant (for all designated States except US): **EXXON-MOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SHIH, Stuart, S.** [US/US]; 11737 Villa Avenue, Baton Rouge, LA 70810 (US). **SOLED, Stuart, Leon** [US/US]; 21 Cooks Cross Road, Pittstown, NJ 08867 (US). **MISEO, Sabato** [US/US]; 770 County Road #579, Pittstown, NJ 08867 (US).

(74) Agents: **HUGHES, Gerard, J.** et al.; ExxonMobil Research and Engineering Company, 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

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(54) Title: A BULK METAL HYDROTREATING CATALYST USED IN THE PRODUCTION OF LOW SULFUR DIESEL FUELS

(57) Abstract: The instant invention relates to a bulk metal hydrotreating catalyst used for hydrotreating diesel boiling range feed-streams to produce low sulfur diesel products.



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**A BULK METAL HYDROTREATING CATALYST USED
IN THE PRODUCTION OF LOW SULFUR DIESEL FUELS**

FIELD OF THE INVENTION

[0001] The instant invention relates to a bulk metal catalyst used for upgrading hydrocarbon feedstreams boiling within the diesel range. More particularly, the instant invention relates to a bulk metal hydrotreating catalyst comprising Co, Mo, and Nb used for hydrotreating diesel boiling range feedstreams to produce low sulfur diesel products.

BACKGROUND OF THE INVENTION

[0002] Environmental and regulatory initiatives are requiring ever lower levels of both sulfur and aromatics in distillate fuels. For example, proposed sulfur limits for distillate fuels to be marketed in the European Union for the year 2005 is 50 wppm or less. There are also proposed limits that would require lower levels of total aromatics as well as lower levels of multi-ring aromatics found in distillate fuels and heavier hydrocarbon products. Further, the maximum allowable total aromatics level for CARB reference diesel and Swedish Class I diesel are 10 and 5 vol.%, respectively. Further, the CARB reference fuels allow no more than 1.4 vol.% polyaromatics (PNAs). Consequently, much work is presently being done in the hydrotreating art because of these proposed regulations.

[0003] However, as the supply of low sulfur, low nitrogen crudes decreases, refineries are processing crudes with greater sulfur and nitrogen contents at the same time that environmental regulations are mandating lower levels of these heteroatoms in products. Consequently, a need exists for increasingly efficient diesel desulfurization and denitrogenation processes. Therefore, processes and

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catalysts have been developed to reduce the concentration of sulfur and nitrogen contaminants in these streams.

[0004] In one approach, a family of compounds, related to hydrotalcites, e.g., ammonium nickel molybdates, has been prepared as catalysts to be used in such processes. Whereas X-ray diffraction analysis has shown that hydrotalcites are composed of layered phases with positively charged sheets and exchangeable anions located in the galleries between the sheets, the related ammonium nickel molybdate phase has molybdate anions in interlayer galleries bonded to nickel oxyhydroxide sheets. See, for example, Levin, D., Soled, S. L., and Ying, J. Y., Crystal Structure of an Ammonium Nickel Molybdate prepared by *Chemical Precipitation, Inorganic Chemistry*, Vol. 35, No. 14, p. 4191-4197 (1996). The preparation of such materials also has been reported by Teichner and Astier, *Appl. Catal.* 72, 321-29 (1991); *Ann. Chim. Fr.* 12, 337-43 (1987), and *C. R. Acad. Sci.* 304 (II), #11, 563-6 (1987) and Mazzocchia, *Solid State Ionics*, 63-65 (1993) 731-35.

[0005] Also, processes to produce fuels to meet the ever more restrictive Environmental regulations, such as hydrotreating, are well known in the art and typically requires treating the petroleum streams with hydrogen in the presence of a supported catalyst at hydrotreating conditions. The catalyst is usually comprised of a Group VI metal with one or more Group VIII metals as promoters on a refractory support. Hydrotreating catalysts that are particularly suitable for hydrodesulfurization, as well as hydrodenitrogenation, generally contain molybdenum or tungsten on alumina promoted with a metal such as cobalt, nickel, iron, or a combination thereof. Cobalt promoted molybdenum on alumina catalysts

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are most widely used when the limiting specifications are hydrodesulfurization, while nickel promoted molybdenum on alumina catalysts are the most widely used for hydrodenitrogenation, partial aromatic saturation, as well as hydrodesulfurization.

[0006] However, there still exists a need in the art for catalysts effective at reducing the sulfur and nitrogen content in diesel boiling range hydrocarbon streams.

SUMMARY OF THE INVENTION

[0007] The instant invention is directed at a bulk metal hydrotreating catalyst that is used in the production of low sulfur diesel products. The bulk metal hydrotreating catalyst comprises:

- a) 0 to 50 wt.% Co;
- b) 0 to 60 wt.% Mo; and
- c) 0 to 50 wt.% Nb.

BRIEF DESCRIPTION OF THE FIGURES

[0008] Figure 1 compares the hydrodesulfurization activity of various CoMoNb bulk hydrotreating catalysts to the hydrodesulfurization activity of a commercial hydrotreating catalyst.

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[0009] Figure 2 compares the hydrodenitrogenation activity of various CoMoNb bulk hydrotreating catalysts to the hydrodenitrogenation activity of a commercial hydrotreating catalyst.

[0010] Figure 3 compares the hydrogenation activity of various CoMoNb bulk hydrotreating catalysts to the hydrogenation activity of a commercial hydrotreating catalyst.

[0011] Figure 4 compares the hydrodesulfurization and hydrodenitrogenation activity of a CoNiMo bulk hydrotreating catalyst to the hydrodesulfurization activity of a commercial hydrotreating catalyst and a CoMo bulk hydrotreating catalyst.

[0012] Figure 5 compares the hydrodesulfurization and hydrodenitrogenation activity of a CoNiMoNb bulk hydrotreating catalyst to the hydrodesulfurization activity of a commercial hydrotreating catalyst and a CoMoNb bulk catalyst.

DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0013] It should be noted that the terms "bulk" and "unsupported" when used in conjunction with the hydrotreating catalysts disclosed herein are synonymous and are sometimes used interchangeably.

[0014] The present invention is a bulk metal hydrotreating catalyst used in processes to produce low sulfur diesel products. The catalyst comprises 0 to 50 wt.% Co, 0 to 60 wt.% Mo, and 0 to 50 wt.% Nb. In a typical process utilizing

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the presently claimed bulk metal hydrotreating catalysts a diesel boiling range feedstream containing organically bound sulfur contaminants is contacted with the above-described bulk metal catalysts in a reaction stage. The contacting of the diesel boiling range feedstream and the hydrotreating catalyst occurs in the presence of a hydrogen-containing treat gas, and the reaction stage is operated under hydrotreating conditions effective at removing at least a portion of the organically bound sulfur contaminants. The contacting of the diesel boiling range feedstream with the bulk metal hydrotreating catalyst produces a liquid diesel boiling range product having a lower concentration of organically bound sulfur contaminants than the diesel boiling range feedstream.

[0015] As stated above, the invention disclosed herein is a bulk metal hydrotreating catalyst that is used in the production of low sulfur diesel fuels. By bulk metal, it is meant that the catalysts used in the present invention are unsupported. The catalyst comprises from 0 to 50 wt.% Nb, based on the catalyst, preferably 2 to 45 wt.%, more preferably 10 to 35 wt.%, and most preferably 15 to 20 wt.%. The bulk metal hydrotreating catalyst also contains Mo present in amounts ranging from 0 to 60 wt.%, based on the catalyst, preferably 1 to 50 wt.%, more preferably 10 to 40 wt.%, and most preferably 15 to 30 wt.%. The bulk metal hydrotreating catalyst also contains Co present in amounts ranging from 0 to 50 wt.%, based on the catalyst, preferably 10 to 45 wt.%, more preferably 20 to 40 wt.%, and most preferably 30 to 40 wt.%. Thus, the bulk metal hydrotreating that are disclosed and claimed herein are bulk metal hydrotreating catalysts having the nomenclature CoMoNb wherein each metal is present in amounts specified above. The inventors hereof have unexpectedly discovered that these bulk metal catalysts, when used in hydrotreating diesel

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boiling range feedstreams, are more active for desulfurization, denitrogenation, and hydrogenation than conventional hydrotreating catalysts.

[0016] It is also useful to describe the bulk metal hydrotreating catalysts as having specific molar concentrations of each metal. Therefore, in one embodiment the finished catalysts have the metals concentrations described above and are also described as those bulk metal hydrotreating catalysts in the oxide state having a composition of $\text{Mo}_x\text{Co}_y\text{Nb}_z$, excluding the oxygen, wherein x , y , and z describe relative molar quantities. Thus, the bulk metal hydrotreating catalysts used herein comprise 0.1 to 2.0 moles Nb, denoted by " z ", preferably 0.2 to 1.5 moles, more preferably 0.2 to 0.8 moles. The moles of Mo, denoted by " x ", are present in amounts ranging from 0.1 to 2 moles, preferably 0.2 to 1.5 moles, more preferably 0.2 to 0.8 moles. The moles of Co, denoted by " y ", are present in amounts ranging from 0.5 to 2 moles, preferably 0.8 to 1.5 moles, more preferably 1 to 1.5 moles. Thus, particularly preferred catalyst compositions comprise CoMoNb having the wt.% and molar concentration of each metal as outlined above.

[0017] The bulk metal hydrotreating catalysts disclosed herein can be prepared by any methods known in the catalyst art for forming bulk metal catalysts. Non-limiting examples of these methods include those outlined in Teichner and Astier, *Appl. Catal.* 72, 321-29 (1991); *Ann. Chim. Fr.* 12, 337-43 (1987), and *C. R. Acad. Sci.* 304 (II), #11, 563-6 (1987) and Mazzocchia, *Solid State Ionics*, 63-65 (1993) 731-35, which are hereby incorporated by reference. The bulk metal hydrotreating catalysts used herein are preferably made by reacting insoluble or partially insoluble metal salts of the metals in the presence

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of a protic liquid. Preferably, at least one of the metal components remains at least partly in the solid state during the entire catalyst making process. It is also preferred that the at least one Group VIII and at least one Group VIB metals comprise from 50 wt.% to 100 wt.%, calculated as oxides, of the total weight of the bulk catalyst particles. The preferred methods of making the catalyst compositions used herein are described in more detail in U.S. Patent 6,156,695, U.S. Patent 6,534,437, U.S. Patent 6,162,350, U.S. Patent 6,299,760, and PCT published application WO00/41810, which are incorporated herein by reference for all purposes to the extent that they are not inconsistent with the present invention disclosure and claims. The bulk metal hydrotreating catalyst is preferably sulfided prior to use, and most preferably made by the methods outlined in U.S. Patent 6,534,437 and U.S. Patent 6,162,350.

[0018] As stated above, the bulk metal hydrotreating catalysts disclosed herein are typically used in processes to produce low sulfur diesel products. Feedstreams suitable for treatment with the presently disclosed bulk metal catalysts boil within the diesel range. The diesel boiling range includes streams boiling in the range of 300°F (148.89°C) to 775°F (412.78°C), preferably 350°F (176.67°C) to 750°F (398.89°C), more preferably 400°F (204.44°C) to 700°F (371.11°C), most preferably 450°F (232.22°C) to 650°F (343.33°C). These include diesel boiling range feedstreams that are not hydrotreated, are a blend of non-hydrotreated diesel boiling range feedstreams, previously hydrotreated diesel boiling range feedstreams, blends of hydrotreated diesel boiling range feedstreams, and blends of non-hydrotreated and hydrotreated diesel boiling range feedstreams.

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[0019] The diesel boiling range feedstreams suitable for treatment with the presently disclosed bulk metal catalysts also contain nitrogen. Typically, the nitrogen content of such streams is 50 to 1000 wppm nitrogen, preferably 75 to 800 wppm nitrogen, and more preferably 100 to 700 wppm nitrogen. The nitrogen appears as both basic and non-basic nitrogen species. Non-limiting examples of basic nitrogen species may include quinolines and substituted quinolines, and non-limiting examples of non-basic nitrogen species may include carbazoles and substituted carbazoles. The sulfur content of the diesel boiling range feedstream will generally range from 50 wppm to 7000 wppm, more typically from 100 wppm to 5000 wppm, and most typically from 100 to 3000 wppm. The sulfur will usually be present as organically bound sulfur. That is, as sulfur compounds such as simple aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and polysulfides and the like. Other organically bound sulfur compounds include the class of heterocyclic sulfur compounds such as thiophene, tetrahydrothiophene, benzothiophene and their higher homologs and analogs. Aromatics are typically present in an amount ranging from 0.05 wt.%, to 2.5 wt.%, based on the diesel boiling range feedstream.

[0020] As stated above, in a typical process utilizing the presently claimed bulk metal hydrotreating catalysts a diesel boiling range feedstream containing organically bound sulfur contaminants is contacted with the above-described bulk metal catalysts in a reaction stage. Hydrogen-containing treat gasses suitable for use in these processes can be comprised of substantially pure hydrogen or can be mixtures of other components typically found in refinery hydrogen streams. It is typically preferred that the hydrogen-containing treat gas stream contains little, more preferably no, hydrogen sulfide. The hydrogen-

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containing treat gas purity should be at least 50% by volume hydrogen, preferably at least 75% by volume hydrogen, and more preferably at least 90% by volume hydrogen for best results. It is most preferred that the hydrogen-containing stream be substantially pure hydrogen.

[0021] The reaction stage can be comprised of one or more reactors or reaction zones each of which can comprise one or more catalyst beds of the same or different bulk metal hydrotreating catalyst described above. Although other types of catalyst beds can be used, fixed beds are typically preferred. Such other types of catalyst beds include fluidized beds, ebullating beds, slurry beds, and moving beds. Interstage cooling or heating between reactors, reaction zones, or between catalyst beds in the same reactor, can be employed since some olefin saturation can take place, and olefin saturation and the hydrotreating reaction are generally exothermic. A portion of the heat generated during hydrotreating can be recovered. Where this heat recovery option is not available, conventional cooling may be performed through cooling utilities such as cooling water or air, or through use of a hydrogen quench stream. In this manner, optimum reaction temperatures can be more easily maintained.

[0022] The diesel boiling range feedstream is contacted with the above-described bulk metal hydrotreating catalyst in the reaction stage under effective hydrotreating conditions. These conditions typically include temperatures ranging from 150°C to 425°C, preferably 200°C to 370°C, more preferably 230°C to 350°C. Typical weight hourly space velocities ("WHSV") range from 0.1 to 20hr⁻¹, preferably from 0.5 to 5hr⁻¹. Any effective pressure can be utilized,

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and pressures typically range from 4 to 70 atmospheres, preferably 10 to 40 atmospheres.

[0023] The contacting of the diesel boiling range feedstream with the above-described bulk metal hydrotreating catalysts produces a reaction product comprising at least a vapor product and a liquid diesel boiling range product. The vapor product typically comprises gaseous reaction products such as H_2S , and the liquid reaction product typically comprises a liquid diesel boiling range product having a reduced level of nitrogen, aromatics, and sulfur contaminants. Thus, it is typically preferred to separate the vapor product and the liquid diesel boiling range product, and recover the liquid diesel boiling range product. The method of separating the vapor product from the liquid diesel boiling range product is generally accomplished by any means known to be effective at separating gaseous and liquid reaction products. For example, a stripping tower or reaction zone can be used to separate the vapor product from the liquid diesel boiling range product. The diesel boiling range product thus recovered will have a sulfur concentration lower than that of the diesel boiling range feedstream, and will preferably have a sulfur level low enough to meet regulatory requirements imposed at the time of production.

[0024] The above description is directed to several embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

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[0025] The following examples will illustrate the improved effectiveness of the present invention, but are not meant to limit the present invention in any fashion.

EXAMPLES

EXAMPLE 1

[0026] The unexpected results achieved by utilizing a Nb-containing catalyst as described above was illustrated by comparing the hydrotreating activity of CoMoNb catalysts to a commercial supported hydrotreating catalyst. The commercial hydrotreating catalyst was obtained from Akzo Nobel and is marketed as KF-757. The weight percent and molar ratio of each element of the bulk metal hydrotreating catalysts used in this experiment are contained in Table 1 below. It should be noted that the molar ratios contained in Table 1 exclude oxygen.

TABLE 1
CoMoNb Bulk Hydrotreating Catalyst Compositions

Catalyst	Co (molar ratio)	Mo (molar ratio)	Nb (molar ratio)	Co (wt. %)	Mo (wt. %)	Nb (wt. %)
	x	y	z			
CoMo	1.50	1.00		34.50	37.40	0.00
CoMoNb	1.50	0.75	0.25	34.90	28.40	9.20
CoMoNb	1.50	0.50	0.50	35.20	19.10	18.50
CoMoNb	1.50	0.75	0.25	35.60	9.70	28.10
CoNb	1.50		1.00	36.00	0.00	37.90

[0027] Each of the catalysts described in Table 1, along with the commercial hydrotreating catalyst, was evaluated for hydrodesulfurization ("HDS") activity, hydrodenitrogenation ("HDN") activity, and hydrogenation activity. A total of 6cc of each of the catalysts was placed in a fixed bed down-flow reactor and contacted with a diesel boiling range distillate having 1.6 wt.% sulfur, an API Gravity of 32.3, 100 wppm nitrogen, and an initial and final boiling point of 396°F (202.22°C) and 779°F (415°C), respectively. The diesel boiling range distillate and the catalysts were contacted under hydrotreating conditions including temperatures of 625°F (329.44°C), hydrogen treat rates of 2000 scf/bbl substantially pure hydrogen, pressures of 400 psig (27.58 bar), and liquid hourly space velocities ("LHSV") of 1.0 hr⁻¹.

[0028] The HDS activity, expressed as a 1.5 order rate constant k_{HDS} , of each of the CoMoNb catalysts was then calculated by an apparent 1.5 order reaction respected to sulfur concentration and compared to the HDS activity of the conventional catalyst. The k_{HDS} equation used was $k_{\text{HDS}} = [(1/C_p^{0.5}) - (1/C_f^{0.5})] \times$

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LHSV/0.5. Where C_f and C_p are sulfur concentrations expressed as wt.% for feed and product, respectively. The results are contained in Figure 1.

[0029] As can be seen in Figure 1, the $\text{Co}_{1.5}\text{Mo}_{1.0}$, $\text{Co}_{1.5}\text{Mo}_{0.74}\text{Nb}_{0.25}$, and $\text{Co}_{1.5}\text{Mo}_{0.5}\text{Nb}_{0.5}$ catalysts were more active for HDS than the commercial catalyst. Figure 1 also demonstrates that the Nb promoted $\text{Co}_{1.5}\text{Mo}_{0.74}\text{Nb}_{0.25}$, and $\text{Co}_{1.5}\text{Mo}_{0.5}\text{Nb}_{0.5}$ catalysts were the most active for HDS.

[0030] The HDN activity, expressed as a 1.5 order rate constant k_{HDN} , of each of the CoMoNb catalysts was then calculated by an apparent 1.5 order reaction respected to sulfur concentration and compared to the HDN activity of the conventional catalyst. The k_{HDS} equation used was $k_{\text{HDN}} = \text{LHSV} \times \ln(C_f/C_p)$. Where C_f and C_p are nitrogen concentrations expressed as wppm for feed and product, respectively. The results are contained in Figure 2.

[0031] As can be seen in Figure 2, the $\text{Co}_{1.5}\text{Mo}_{1.0}$, $\text{Co}_{1.5}\text{Mo}_{0.74}\text{Nb}_{0.25}$, and $\text{Co}_{1.5}\text{Mo}_{0.5}\text{Nb}_{0.5}$ catalysts were more active for HDN than the commercial catalyst. Figure 2 also demonstrates that the Nb promoted $\text{Co}_{1.5}\text{Mo}_{0.74}\text{Nb}_{0.25}$, and $\text{Co}_{1.5}\text{Mo}_{0.5}\text{Nb}_{0.5}$ catalysts were the most active for HDN.

[0032] The hydrogenation activity of each catalyst, expressed as API gravity, was then calculated and compared to the hydrogenation activity of the commercial catalyst. API gravity is a reliable method of comparing hydrogenation activity because it is known that the hydrogenation of aromatics will increase the API gravity of a hydrocarbon stream. The results are contained

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in Figure 3. It should be noted that the hydrogenation activity is expressed in terms of the API density of the desulfurized product.

[0033] As can be seen in Figure 3, the $\text{Co}_{1.5}\text{Mo}_{1.0}$, $\text{Co}_{1.5}\text{Mo}_{0.74}\text{Nb}_{0.25}$, and $\text{Co}_{1.5}\text{Mo}_{0.5}\text{Nb}_{0.5}$ catalysts were more active for hydrogenation than the commercial catalyst. Figure 3 also demonstrates that the Nb promoted $\text{Co}_{1.5}\text{Mo}_{0.74}\text{Nb}_{0.25}$, and $\text{Co}_{1.5}\text{Mo}_{0.5}\text{Nb}_{0.5}$ catalysts were the most active for hydrogenation.

EXAMPLE 2

[0034] The unexpected results achieved by utilizing a Nb-containing catalyst as described above was illustrated by comparing the hydrotreating activity of CoNiMoNb hydrotreating catalysts having a compositional formula of $\text{Co}_a\text{Ni}_b\text{Mo}_c\text{Nb}_d$, wherein a, b, c, and d are the respective molar ratios of each component, to a commercial supported hydrotreating catalyst, also. The commercial hydrotreating catalyst was obtained from Akzo Nobel and is marketed as KF-757. The weight percent of each element of the bulk metal hydrotreating catalysts used in this experiment are contained in Table 2 below.

TABLE 2
CoNiMoNb Bulk Hydrotreating Catalyst Compositions

Catalyst	Co (molar ratio)	Ni (molar ratio)	Mo (molar ratio)	Nb (molar ratio)	Co (wt.%)	Ni (wt.%)	Mo (wt.%)	Nb (wt.%)
	a	b	c	d				
CoNiMo	0.75	0.25	1.00	0.00	20.60	6.80	44.79	0.00
CoNiMoNb	0.20	1.00	0.50	0.50	7.50	27.30	46.19	14.90

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[0035] Each of the catalysts described in Table 2, along with the commercial hydrotreating catalyst, was evaluated for hydrodesulfurization ("HDS") activity, hydrodenitrogenation ("HDN") activity, and hydrogenation activity. A total of 6cc of each of the catalysts was placed in a fixed bed down-flow reactor and contacted with the same diesel boiling range distillate used in Example 1 above. The diesel boiling range distillate and the catalysts were contacted under hydrotreating conditions including temperatures of 625°F (329.44°C), hydrogen treat rates of 2000 scf/bbl substantially pure hydrogen, pressures of 400 psig (27.58 bar), and liquid hourly space velocities ("LHSV") of 1.0 hr⁻¹.

[0036] The HDN and HDN activity of the CoNiMo catalyst was then calculated as described above, and compared to the HDS and HDN activity of the commercial catalyst. The results are contained in Figure 4.

[0037] As can be seen in Figure 4, compared to Co_{1.5}M_{1.0}, Co_{0.75}Ni_{0.25}Mo_{1.0} was more active for denitrogenation but less active for desulfurization (Figure 4). However, it was more active than the commercial hydrotreating catalyst.

[0038] The HDN and HDN activity of the CoNiMoNb catalyst was then calculated as described above, and compared to the HDS and HDN activity of the commercial catalyst. The results are contained in Figure 5.

[0039] As can be seen in Figure 5, compared to Co_{1.5}Mo_{0.5}Nb_{0.5}, Co_{0.2}Ni_{1.0}Mo_{0.5}Nb_{0.5} was less active for both desulfurization and denitrogenation. However, it was still more active than the KF-757 commercial catalyst.

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CLAIMS:

1. A bulk metal hydrotreating catalyst comprising:
 - a) 0 to 50 wt.% Co;
 - b) 0 to 60 wt.% Mo; and
 - c) 0 to 50 wt.% Nb.
2. The bulk metal hydrotreating catalyst according to claim 1 wherein Nb is present in an amount ranging from 2 to 45 wt.%, Mo is present in an amount ranging from 1 to 50 wt.%, and Co is present in an amount ranging from 10 to 45 wt.%.
3. The bulk metal hydrotreating catalyst according to any preceding claim wherein said bulk metal hydrotreating catalyst is a bulk metal catalyst in the oxide state having a composition of $\text{Mo}_x\text{Co}_y\text{Nb}_z$, excluding the oxygen, wherein x ranges from 0.1 to 2, y ranges from 0.5 to 2, and z ranges from 0.1 to 2.
4. The bulk metal hydrotreating catalyst according to any preceding claim wherein the Co and Mo metals comprise from 50 wt.% to 100 wt.%, calculated as oxides, of the total weight of the bulk metal hydrotreating catalyst.
5. The bulk metal hydrotreating catalyst according to any preceding claim wherein Nb is present in amount from 10 to 35 wt.%, Mo is present in

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amounts ranging from 10 to 40 wt.%, and Co is present in amounts ranging from 20 to 40 wt.%, based on the weight of the catalyst.

6. The bulk metal hydrotreating catalyst according to any preceding claim wherein said bulk metal hydrotreating catalyst is a bulk metal catalyst in the oxide state having a composition of $\text{Mo}_x\text{Co}_y\text{Nb}_z$, excluding the oxygen, wherein x ranges from 0.2 to 1.5, y ranges from 0.8 to 1.5, and z ranges from 0.2 to 1.5.
7. The bulk metal hydrotreating catalyst according to any preceding claim wherein Nb is present in amount from 15 to 20 wt.%, Mo is present in amounts ranging from 15 to 30 wt.%, and Co is present in amounts ranging from 30 to 40 wt.%, based on the weight of the catalyst.
8. The bulk metal hydrotreating catalyst according to any preceding claim wherein said bulk metal hydrotreating catalyst is a bulk metal catalyst in the oxide state having a composition of $\text{Mo}_x\text{Co}_y\text{Nb}_z$, excluding the oxygen, wherein x ranges from 0.2 to 0.8, y ranges from 0.8 to 1.5 and z ranges from 1 to 1.5.
9. The bulk metal hydrotreating catalyst of any preceding claim, wherein Co is present in an amount ranging from 0 to 45 wt.%, Mo is present in an amount ranging from 1 to 50 wt.%, and Nb is present in an amount ranging from 2 to 45 wt.%, wherein said bulk metal hydrotreating catalyst is a bulk metal catalyst in the oxide state having a composition of $\text{Mo}_x\text{Co}_y\text{Nb}_z$, excluding the oxygen, wherein x ranges from 0.1 to 2, y

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ranges from 0.5 to 2, and z ranges from 0.1 to 2, and wherein the wt.% of the Co, Mo, and Nb are based on the weight of the catalyst.

10. The bulk metal hydrotreating catalyst of any preceding claim, wherein Co is present in an amount ranging from 20 to 40 wt.%, Mo is present in an amount ranging from 10 to 40 wt.%, and Nb is present in an amount ranging from 10 to 35 wt.%, wherein the Co and Mo metals comprise from 50 wt.% to 100 wt.%, calculated as oxides, of the total weight of the bulk metal hydrotreating catalyst, and wherein said bulk metal hydrotreating catalyst is a bulk metal catalyst in the oxide state having a composition of $\text{Mo}_x\text{Co}_y\text{Nb}_z$, excluding the oxygen, wherein x ranges from 0.2 to 1.5, y ranges from 0.8 to 1.5, and z ranges from 0.2 to 1.5.
11. The bulk metal hydrotreating catalyst of any preceding claim, wherein Co is present in an amount ranging from 30 to 40 wt.%, Mo is present in an amount ranging from 15 to 30 wt.%, and Nb is present in an amount from 15 to 20 wt.%, wherein the Co and Mo metals comprise from 50 wt.% to 100 wt.%, calculated as oxides, of the total weight of the bulk metal hydrotreating catalyst, and wherein said bulk metal hydrotreating catalyst is a bulk metal catalyst in the oxide state having a composition of $\text{Mo}_x\text{Co}_y\text{Nb}_z$, excluding the oxygen, wherein x ranges from 0.2 to 0.8, y ranges from 0.8 to 1.5, and z ranges from 1 to 1.5.

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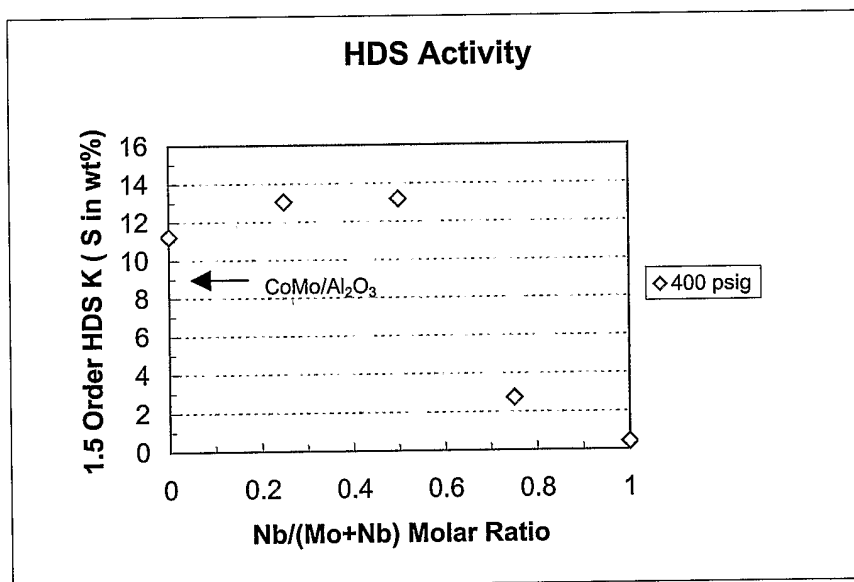


FIGURE 1

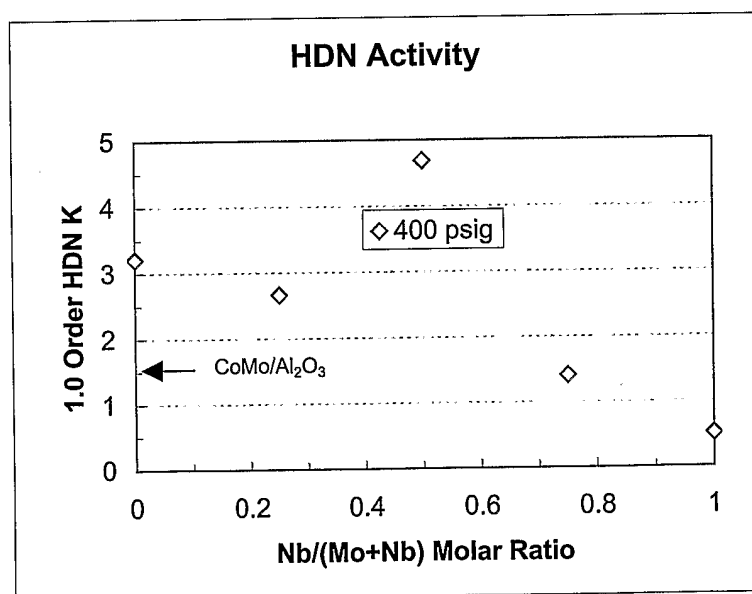


FIGURE 2

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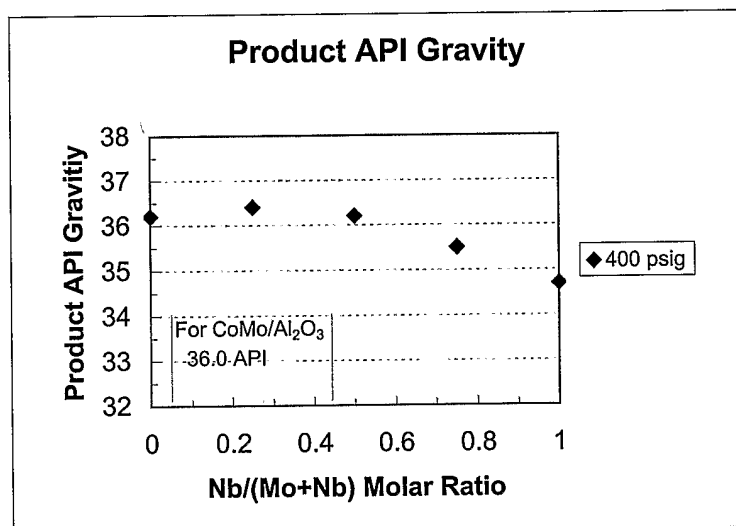


FIGURE 3

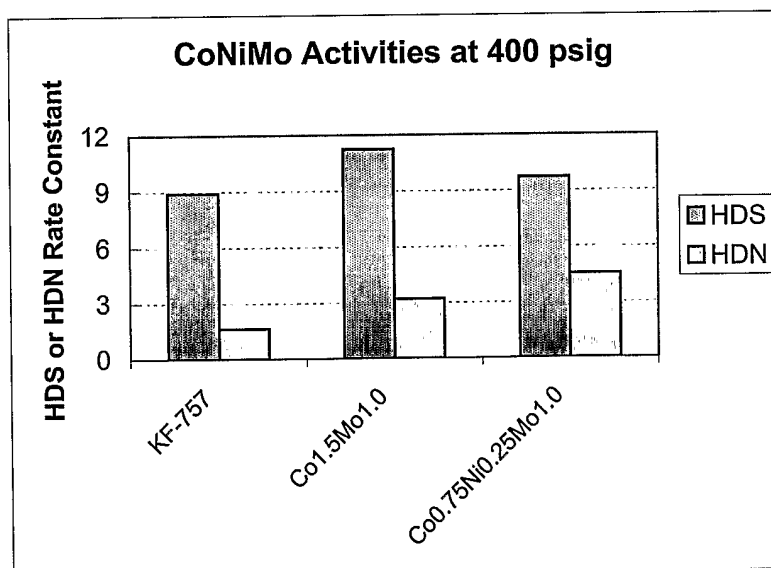


FIGURE 4

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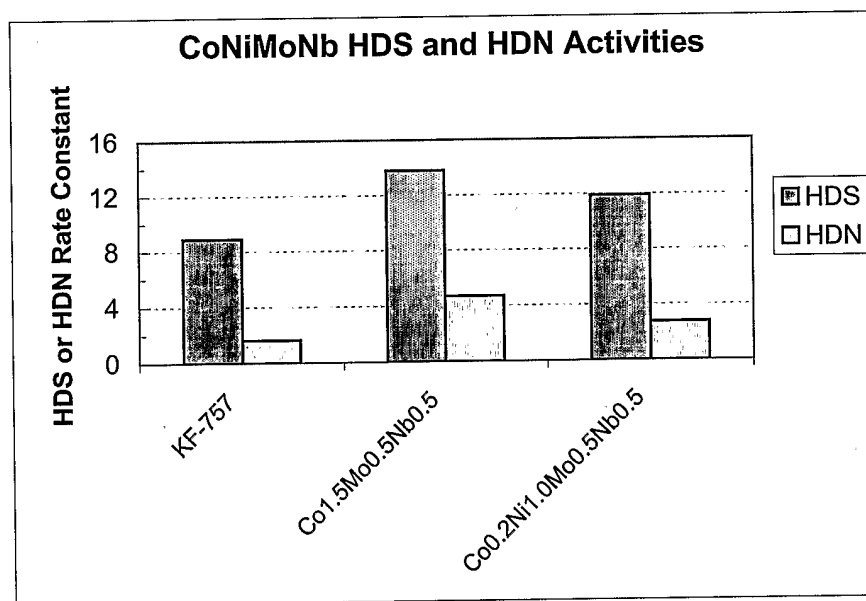


FIGURE 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/013513

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/887 B01J23/20 C10G45/08

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)

IPC 7 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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 156 694 A (HARPER ET AL) 5 December 2000 (2000-12-05) example 1 -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in 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

15 July 2005

Date of mailing of the international search report

07. 10. 2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schoofs, B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2005/013513

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 (part) and 2-11 as far as they relate to the first invention

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1(part) and 2-11 as far as they relate to the first invention

a bulk metal hydrotreating catalyst comprising:

- a) Co,
- b) no Mo, and
- c) no Nb

2. claims: 1(part) and 2-11 as far as they relate to the second invention

a bulk metal hydrotreating catalyst comprising:

- a) no Co,
- b) Mo, and
- c) no Nb

3. claims: 1(part) and 2-11 as far as they relate to the third invention

a bulk metal hydrotreating catalyst comprising:

- a) no Co,
- b) no Mo, and
- c) Nb

4. claims: 1(part) and 2-11 as far as they relate to the fourth invention

a bulk metal hydrotreating catalyst comprising:

- a) Co,
- b) Mo, and
- c) no Nb

5. claims: 1(part) and 2-11 as far as they relate to the fifth invention

a bulk metal hydrotreating catalyst comprising:

- a) Co,
- b) no Mo, and
- c) Nb

6. claims: 1(part) and 2-11 as far as they relate to the sixth invention

a bulk metal hydrotreating catalyst comprising:

- a) no Co,
- b) Mo, and
- c) Nb

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

7. claims: 1(part) and 2-11 as far as they relate to the seventh invention

a bulk metal hydrotreating catalyst comprising:

- a) Co,
- b) Mo, and
- c) Nb

8. claims: 1(part) and 2-11 as far as they relate to the eighth invention

a bulk metal hydrotreating catalyst comprising:

- a) no Co,
- b) no Mo, and
- c) no Nb

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/013513

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6156694	A	05-12-2000	BR 9915248 A 30-10-2001
		CA 2345523 A1 18-05-2000	
		CN 1325320 A 05-12-2001	
		DE 69911643 D1 30-10-2003	
		DE 69911643 T2 08-07-2004	
		EP 1137484 A1 04-10-2001	
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		JP 2002529227 T 10-09-2002	
		TW 590800 B 11-06-2004	
		WO 0027526 A1 18-05-2000	
