

[54] **PROCESS FOR OIL DEMETALATION AND
DESULFURIZATION WITH
COBALT-MOLYBDENUM IMPREGNATED
MAGNESIUM ALUMINATE SPINEL**
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[52] **U.S. Cl.**..... **208/216, 208/251 H**
[51] **Int. Cl.**..... **C10g 23/02**
[58] **Field of Search** **208/216, 217, 213, 251 H**

[56] **References Cited**
UNITED STATES PATENTS
2,781,295 2/1957 Teter et al. 208/216
2,840,512 6/1958 Burton et al. 208/216

2,853,429 9/1958 Gislou et al. 208/216
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[57] **ABSTRACT**
A catalyst composition is provided which comprises a cobalt-molybdenum impregnated magnesium aluminate spinel having a surface area of greater than about 50m²/g and a pore volume of greater than about 0.3 cc/g.
Also provided is a process for demetalation and desulfurization of oil stock which comprises contacting said oil stock in the presence of hydrogen with a catalytically effective amount of said cobalt-molybdenum impregnated magnesium aluminate spinel at a temperature of from about 600°F to about 1,000°F and a liquid hourly space velocity of from about 0.1 to about 2.

14 Claims, No Drawings

PROCESS FOR OIL DEMETALATION AND DESULFURIZATION WITH COBALT-MOLYBDENUM IMPREGNATED MAGNESIUM ALUMINATE SPINEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a catalyst composition and process for demetalation and desulfurization of oil stock, e.g. residua. More particularly, it relates to a catalyst composition of cobalt-molybdenum impregnated magnesium aluminate spinel and a process for residua demetalation and desulfurization which comprises contacting said residua with said catalyst of cobalt-molybdenum impregnated magnesium aluminate spinel in the presence of hydrogen.

2. Description of Prior Art

Residual petroleum oil fractions containing relatively high proportions of metals, such as those heavy fractions produced by atmospheric and vacuum crude distillation columns, would represent excellent charge stocks for a cracking process were it not for their high metals content. Principal metal contaminants are nickel and vanadium, with iron and copper also sometimes present. Additionally, trace amounts of zinc and sodium may be present. Since these metals, when present in crude oil, are associated with very large hydrocarbon molecules, the heavier fractions produced by crude distillation contain substantially all the metals present in the crude, such metals being particularly concentrated in the asphaltene residual fraction. The metal contaminants are typically large organo-metallic complexes such as metal porphyrins.

At present, cracking operations are performed on petroleum fractions lighter than residual fractions. Typical cracking charge stocks are coker and/or crude unit gas oil, vacuum tower overhead, etc., the feedstock having an API gravity range of between about 15 and about 45. Since these charge stocks are lighter than residual hydrocarbon fractions, such residual fractions being characterized as having an API gravity of less than about 25, they do not contain significant proportions of the heavy and large molecules in which the metals are concentrated.

When metals are present in a cracking unit charge stock, such metals are deposited on the cracking catalyst. The metals act as a catalyst poison and greatly decrease the efficiency of the cracking process by altering the catalyst so that it promotes increased hydrogen production.

Sulfur is also undesirable in a cracking unit charge stock. The sulfur contributes to corrosion of the unit's mechanical equipment and creates difficulties in treating products and flue gases. At typical cracking conversion rates, about one-half of the sulfur charge to such a unit is converted to H_2S gas which must be removed from the gasoline product, usually by scrubbing with an amine stream. A large portion of the remaining sulfur is deposited on the cracking catalyst itself. When the catalyst is regenerated, at least a portion of this sulfur is oxidized to form SO_2 or SO_3 gas which must be removed from the flue gas which is normally discharged into the atmosphere.

In the past, high molecular weight, e.g. residual, stocks containing sulfur and metals have often been processed in a cokerto effectively remove metals and

also some of the sulfur. However, there are limits to the amount of metals and sulfur which can be tolerated in the product coke if it is to be marketable. Hence, there is a considerable need to develop economically practicable means for effecting the removal and recovery of metallic and sulfur contaminants from high boiling fractions of petroleum oils so that conversion of such contaminated oils to more desirable product may be effectively accomplished. The present application is particularly concerned with the removal of metal and sulfur contaminants from residua.

It has been proposed to improve the salability of high sulfur and metal content residual-containing petroleum oils by a variety of hydroprocessing methods, e.g. hydrosulfurization and hydrometalation. However, difficulty has been experienced in achieving a commercially feasible catalytic hydroprocessing process. Short catalyst life in such processes is manifested by inability of a catalyst to maintain a relatively high capability for desulfurizing charge stock with increasing quantities of coke and/or metallic contaminants deposited thereon which act as catalyst poisons. Satisfactory catalyst life can be obtained relatively easily with distillate oils, but is especially difficult to obtain in desulfurizing residual oils, since the asphaltenic or porphyrinic components of an oil, which tend to form disproportionate amounts of coke, are concentrated in the residual fractions of a petroleum oil, and since a relatively high proportion of the metallic contaminants that normally tend to poison catalysts are commonly found in the asphaltene components of the oil. Further, on a commercial scale, these processes are rather costly due to high hydrogen consumption levels. It is, therefore, advantageous to provide a demetalation/desulfurization process such as the present invention which exhibits superior demetalation characteristics, good desulfurization benefits, low hydrogen consumption and satisfactory ageing properties.

U.S. Pat. Nos. 3,716,479 and 3,772,185 propose demetalation of a hydrogen charge stock by contacting the charge stock with added hydrogen in the presence of a catalyst material derived from a manganese nodule.

British Pat. Nos. 1,318,941 and 1,318,942 teach use of zinc, magnesium, beryllium or calcium aluminate spinels combined, after calcination, with a Group VIII metal, such as, for example, platinum, as a dehydrogenation catalyst.

Demetalation of hydrocarbon fractions is taught in U.S. Pat. No. 2,902,429 as contacting said fractions with a catalyst having a relatively small amount of a sulfur-resistant hydrogenation-dehydrogenation component disposed on a low surface area carrier, i.e. a carrier with a surface area of not more than $15m^2/g$, and preferably not more than about $3m^2/g$. Examples of such low surface area carriers include diatomaceous earth, natural clays and Alundum.

There are numerous references in the art showing various metals combined with carriers such as alumina, silica, zirconia or titania as catalysts for use in demetalation and/or desulfurization processes. No references are known to the applicants which teach the present invention with its attendant benefits.

SUMMARY OF THE INVENTION

In accordance with the present invention, an oil stock, e.g. residua, is demetalized and desulfurized by

contacting it in the presence of hydrogen with a particular porous solid material catalyst identified as a magnesium aluminate spinel having a relatively high surface area and pore volume and having impregnated thereon both cobalt and molybdenum, at a temperature of from about 600°F to about 1,000°F and a liquid hourly space velocity of from about 0.1 to about 2.

DESCRIPTION OF PREFERRED EMBODIMENTS

The process of the present invention comprises contacting an oil stock, e.g. residua, with a particular specified catalyst in the presence of hydrogen to produce an upgraded demetalized and desulfurized oil.

The oil stock which may be treated in accordance with this invention may generally be any residual oil comprising a total nickel and vanadium content of between about 1 ppm and about 150 ppm, or, more usually, between about 1 ppm and about 60 ppm. Said oil stock may also be found to be a high boiling range residual oil boiling above about 400°F. Such oil stock may include components obtained by, for example, fractionation, such as atmospheric or vacuum crude distillation, of crude oils. Non-limiting examples of said crude oils are Pennsylvania, Midcontinent, Gulf Coast, West Texas, Amal, Agha Jari, Kuwait, Barco, Arabian and others. Said oil stock may be one having a substantial portion thereof of the fractionation product of one or more of the above mentioned crude oils mixed with other oil stocks.

It is further observed that the present process may be effectively utilized for crude oil demetalation and desulfurization when said crude oil comprises a total nickel and vanadium content of between about ½ ppm and about 75 ppm. Also, the oil stock to be treated in accordance herewith may be comprised of a portion of an above defined crude oil with a portion of an above defined residua oil.

The catalyst material of the present invention is a cobalt-molybdenum impregnated magnesium aluminate spinel having a surface area of greater than about 50 m²/g and up to about 300 m²/g and higher and a pore volume of greater than about 0.3 cc/g and up to about 1.3 cc/g and higher.

The impregnated cobalt and molybdenum may be in the salt or oxide form or in elemental form with little or no effect upon the efficiency of the present process. The preferred form, however, is the oxide form of cobalt and molybdenum with the impregnated catalyst being comprised of from about 1 to about 5 weight percent cobalt oxide (CoO) and from about 8 to about 20 weight percent molybdenum oxide (MoO₃). A particularly preferred composition would have from about 2 to about 4 weight percent CoO and from about 10 to about 15 weight percent MoO₃.

These catalyst materials may be made according to procedures well known in the art (exemplified herein-after) and may be, if desired, dehydrated, at least partially, before use in the present process. Such dehydration can be accomplished by heating to a temperature in the range of 200° to 600°C in an inert atmosphere, such as air, nitrogen, etc. and at atmospheric or subatmospheric pressures for between 1 and 48 hours. Dehydration can also be performed at lower temperatures merely by placing the catalyst in a vacuum, but a longer time is required to obtain a like degree of dehydration under the latter conditions.

The operating parameters in the present process are critical to achieving the desired results of degrees of demetalation and desulfurization of the oil stock being treated thereby without substantial loss in yield. For example, the liquid hourly space velocity (LHSV) required for the instant invention is from about 0.1 to about 2, with a preferred range of from about 0.25 to about 1. The temperature of the present demetalation/desulfurization process must be within the range of from about 600°F to about 1,000°F, with a preferred temperature range of from about 675°F to about 800°F. The pressure of the reaction system of the present process must be between about 1,000 psig and about 3,000 psig, with a preferred pressure range being from about 1,800 psig to about 3,000 psig.

In order to more fully illustrate the process of the present invention, the following specific examples, which in no sense limit the invention, are presented.

EXAMPLE 1

A quantity of magnesium aluminate spinel was prepared by the following method:

Into a 1000 ml. two-neck flask, equipped with a reflux condenser and septum, was added 500 ml. anhydrous methanol and 12.2 grams of magnesium metal. The resulting reaction was complete in about 3 hours.

Into a 3,000 ml. four-neck flask, equipped with a heating mantle, stirrer, check valve and septum, was added 204 grams of aluminum isopropoxide and 1,500 ml. of isopropanol. This mixture was heated and stirred until nearly all of the isopropoxide was dissolved.

While the stirring was continued in the 3,000 ml. flask, it and the 1,000 ml. flask were connected by means of syringe needles and plastic small-bore tubing.

The reflux condenser on the 1,000 ml. flask was then replaced with a septum, into which a syringe needle was placed, said needle being connected to a source of nitrogen pressure. Nitrogen pressure was then applied so that the contents of the 1,000 ml. flask was transferred to the 3,000 ml. flask. This was accomplished in a way that heat evolution and boiling were kept at a minimum. Heating and stirring of the total contents of the 3,000 ml. flask was then continued for about 2-3 hours.

The contents of the 3,000 ml. flask were then cooled and the precipitate was filtered and spread on a paper. The alkoxide was in this manner allowed to hydrolyze in air moisture for 2-3 days.

The solid material product was then calcined in a furnace programmed for a temperature increase of 1°C per minute. It was kept at 650°C for two days, resulting in a lumped form (-10/+20 mesh) of magnesium aluminate spinel having a surface area of about 150 m²/g.

A solution of 11.3 grams of Co(NO₃)₆H₂O in 40 cc of water was brought in contact with 100 grams of the above spinel under vacuum. After 10 minutes of contact, the resulting product was dried in a vacuum oven at 230°F overnight. The resulting dried product was then contacted with a solution of 13.6 grams of (NH₄)₂MoO₃ in 40 cc of water under vacuum. Again, the resulting product was dried in a vacuum oven at 230°F overnight. The dried product was then calcined for 8 hours at 1,000°F, giving a lumped form (-10/+20 mesh) of cobaltmolybdenum impregnated magnesium aluminate spinel having the following properties determined by chemical and physical analysis:

MoO ₃	wt. %	=	10.20
CoO	wt. %	=	3.24
Ni	wt. %	=	0.03
V	wt. %	=	<0.01
Fe	wt. %	=	0.04
Al ₂ O ₃	wt. %	=	59.2
SiO ₂	wt. %	=	< 0.1
Ash	wt. %	=	99.3
Surface Area, m ² /g		=	124
Real Density		=	3.27
Particle Density		=	0.678
Pore Volume, cc/g		=	1.169
Pore Size Distribution in Angstrom Units			

<30	30-50	50-100	100-200	200-300	>300
4%	2%	9%	9%	6%	70%

EXAMPLE 2

A quantity of magnesium aluminate spinel was prepared as in Example 1 except that it was extruded as a 1/32 inch extrudate prior to calcination. The extruded spinel was then impregnated with cobalt-molybdenum as in Example 1 giving an extruded form (1/32 inch extrudate) of cobalt-molybdenum impregnated magnesium aluminate spinel having the following properties:

MoO ₃	wt. %	=	11.50
CoO	wt. %	=	4.20
Ni	wt. %	=	0.03
V	wt. %	=	<0.01
Fe	wt. %	=	0.04
Mg	wt. %	=	12.1
Al ₂ O ₃	wt. %	=	62.9
Ash	wt. %	=	96.3
Surface Area, m ² /g		=	206
Real Density		=	3.44
Particle Density		=	1.23
Pore Volume, cc/g		=	0.622
Pore Size Distribution in Angstrom Units			

<30	30-50	50-100	100-200	200-300	>300
21%	17%	29%	12%	7%	15%

EXAMPLE 3

The cobalt-molybdenum impregnated magnesium aluminate spinel materials prepared in Examples 1 and 2, along with two commercially available resid processing catalyst materials, hereinafter described, were tested for comparison purposes in a laboratory test simulating a standard fixed bed resid hydrodesulfurization process. The catalyst materials being tested were each evaluated in said test in a short-term, i.e. 10 days on stream, run using Kuwait atmospheric resid which had a sulfur content of 3.54 weight percent and a total vanadium and nickel content of 54 ppm (hereinafter "Resid X"), or a sulfur content of 3.56 weight percent and a total vanadium and nickel content of 51 ppm (hereinafter "Resid Y"). Test conditions such as temperature, pressure, liquid hourly space velocity and hydrogen circulation are listed in Table I hereinafter.

Properties of the two commercially available catalysts, designated "catalyst A" and "catalyst B," are listed below:

Property		Catalyst A	Catalyst B
MoO ₃	wt. %	13.40	12.10
CoO	wt. %	3.40	3.54
Ni	wt. %	0.18	0.04
V	wt. %	<0.01	<0.01
Fe	wt. %	0.06	0.06
Al ₂ O ₃	wt. %	82.7	85.2
SiO ₂	wt. %	4.91	1.69
Surface Area, m ² /g		286	268
Particle Density		1.28	1.374
Real Density		3.42	3.644
Pore Volume, cc/g		0.491	0.453
Pore Size Distribution in Angstrom Units			
<30		7%	7%
30-50		28%	34%
50-100		62%	56%
100-200		1%	1%
200-300		0%	0%
>300		2%	2%

The results of the test are recorded in Table I.

TABLE I

Catalyst		Example 1 (with Resid X)					Example 2 (with Resid Y)				
Operating Conditions		700	750	800	800	674	724	775	675	724	774
Temperature, °F.		2000	2000	2000	1000	2000	2000	2000	1000	1000	1000
Pressure, psig.		0.70	0.72	0.71	0.24	0.74	0.74	0.75	0.39	0.39	0.40
LHSV, V (oil)/hr/V (catalyst)		4013	3756	3562	3877	4703	4223	3883	4296	3993	3525
Hydrogen Circulation, SCF/B.		302	568	743	872	306	506	735	293	432	566
Hydrogen Consumption, SCF/B.		98.4	97.8	96.3	94.1	97.8	97.0	95.8	97.7	96.9	95.4
Yield of C ₃ +, wt. %		1.86	1.18	0.56	0.51	1.58	0.81	0.32	1.58	0.96	0.44
Sulfur, wt. %		48.3	67.4	84.8	86.5	55.6	77.2	91.0	55.6	73.0	87.6
% Desulfurization		5.0	1.6	0.3	0.4	5.0	2.3	0.1	5.3	2.6	0.2
Nickel, ppm		8.4	1.2	0.3	0.2	13.0	5.1	0.1	13.0	5.6	0.1
Vanadium, ppm		75	95	99	99	65	86	99+	64	84	99
% Demetalation											
Catalyst		Catalyst A (with Resid Y)					Catalyst B (with Resid X)				
Operating Conditions		676	725	774	676	727	776	700	750	800	
Temperature, °F.		2000	2000	2000	1000	1000	1000	2000	2000	2000	
Pressure, psig.		0.74	0.72	0.74	0.41	0.41	0.40	0.75	0.75	0.75	
LHSV					090.38						
Hydrogen Circulation, SCF/B.		4437	3649	3669	4523	3126	4129	5000	5000	5000	
Hydrogen Consumption, SCF/B.		336	599	1154	260	486	711	459	759	880	
Yield of C ₃ +, wt. %		97.3	96.9	96.5	97.0	96.5	94.8	98.2	97.5	96.2	
Properties of Yield											
Sulfur, wt. %		1.18	0.62	0.40	1.04	0.48	0.34	.91	.53	.45	
% Desulfurization		66.8	82.6	88.8	70.8	86.5	90.4	74.3	85.0	87.3	
Nickel, ppm		7.0	5.9	3.5	8.9	5.4	3.6	7.3	5.4	3.7	
Vanadium, ppm		20.0	16.0	8.4	23.0	14.0	9.2	20	14	10	
% Demetalation		47	57	77	37	62	75	49	64	80	

EXAMPLES 4-7

A quantity of magnesium aluminate spinel (Example 4) and a quantity of cobalt-molybdenum impregnated magnesium aluminate spinel (Example 5) were prepared as in Example 1. Further, a quantity of platinum impregnated magnesium aluminate spinel (Example 6) and a quantity of molybdenum impregnated magnesium aluminate spinel (Example 7) were prepared for comparison as follows:

Material of Example 6

A 100 gram quantity of the spinel of Example 4 was washed with 150 cc of 1:10 acetic acid:acetone mixture, followed by washing with acetone. It was then suspended in 200 cc of acetone and 1.3 grams of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ dissolved in 25 cc of acetone was slowly added to the suspension. After 15 minutes, the acetone of the total suspension was driven off slowly by carefully heating it on a hot plate. The final product was dried for 8 hours at 250°F and calcined for 8 hours at 1,050°F.

Material of Example 7

A 13.6 gram quantity of $(\text{NH}_4)_2\text{MoO}_3$ dissolved in 40cc of water was mixed with 100 grams of the spinel of Example 4 under vacuum. The resulting product was dried overnight in a vacuum oven at 230°F and calcined for 8 hours at 1,000°F.

EXAMPLE 8

A Shaker Bomb test under severe resid hydrotreating conditions was conducted using the catalyst materials of Examples 4-7 wherein a batch-type reaction vessel was filled with catalyst material, oil (Resid X, hereinbefore defined) and hydrogen and brought quickly to the desired temperature and pressure (see Table II) while being agitated at 200 rpm. The particular Shaker Bomb apparatus used is described fully by J. W. Payne et al. in *Industrial and Engineering Chemistry*, volume 50, 1958, page 47. The test conditions and results are summarized in Table II.

It is readily observed from the data presented in Table II that the catalyst for use in the present invention, i.e. Example 5, provides substantially better demetalation and desulfurization than other similar but different catalyst compositions, i.e. Examples 4, 6 and 7.

TABLE II

Catalyst	Example 4	Example 5	Example 6	Example 7
Operating Conditions				
Temperature, °F.	800	800	700	800
Pressure, psig	2000	2000	2000	2000
Oil/Catalyst, weight ratio	20	20	20	20
Properties of Yield				
Gravity, °API	26.1	28.4	13.9	25.0
Viscosity, KV ₁₀₀	8.25	12.13	—	—
Sulfur, wt. %	2.66	0.81	3.14	1.89
Hydrogen, wt. %	11.60	12.40	11.25	11.90
Nickel, ppm	4.2	0.4	—	2.4
Vanadium, ppm	16.0	0.3	—	5.3
% Desulfurization	28	78	13	49
% Demetalation	62	99	—	87

What is claimed is:

1. A process for demetalation and desulfurization of an oil stock which comprises contacting said oil stock with hydrogen and with a cobalt-molybdenum impregnated magnesium aluminate spinel at a temperature of from about 600°F to about 1,000°F, a pressure of from about 1,000 psig to about 3,000 psig and a liquid hourly space velocity of from about 0.1 to about 2, said spinel having a surface area of greater than about 50 m²/g and a pore volume of greater than about 0.3 cc/g.

2. The process of claim 1 wherein the temperature is from about 675°F to about 800°F, the pressure is from about 1,800 psig to about 3,000 psig and the liquid hourly space velocity is from about 0.25 to about 1.

3. The process of claim 1 wherein said oil stock is a residual oil comprising a total nickel and vanadium content of between about 1 ppm and about 150 ppm.

4. The process of claim 3 wherein the temperature is from about 675°F to about 800°F, the pressure is from about 1,800 psig to about 3,000 psig and the liquid hourly space velocity is from about 0.25 to about 1.

5. The process of claim 3 wherein said residual oil comprises a total nickel and vanadium content of between about 1 ppm and about 60 ppm.

6. The process of claim 5 wherein the temperature is from about 675°F to about 800°F, the pressure is from about 1,800 psig to about 3,000 psig and the liquid hourly space velocity is from about 0.25 to about 1.

7. The process of claim 1 wherein said oil stock is a high boiling range residual oil boiling above about 400°F.

8. The process of claim 7 wherein the temperature is from about 675°F to about 800°F, the pressure is from about 1,800 psig to about 3,000 psig and the liquid hourly space velocity is from about 0.25 to about 1.

9. The process of claim 1 wherein said oil stock includes components obtained by fractionation of crude oils.

10. The process of claim 9 wherein the temperature is from about 675°F to about 800°F, the pressure is from about 1,800 psig to about 3,000 psig and the liquid hourly space velocity is from about 0.25 to about 1.

11. The process of claim 1 wherein said oil stock is a crude oil comprising a total nickel and vanadium content of between about ½ ppm and about 75 ppm.

12. The process of claim 11 wherein the temperature is from about 675°F to about 800°F, the pressure is from about 1,800 psig to about 3,000 psig and the liquid hourly space velocity is from about 0.25 to about 1.

13. The process of claim 1 wherein said cobalt and molybdenum impregnated on said spinel are in the form of oxides.

14. The process of claim 13 wherein said cobalt oxide comprises from about 1 to about 5 weight percent of said cobalt-molybdenum impregnated magnesium aluminate spinel and said molybdenum oxide comprises from about 8 to about 20 weight percent of said cobalt-molybdenum impregnated magnesium aluminate spinel.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,867,282

DATED : February 18, 1975

INVENTOR(S) : Ronald H. Fischer, Julius Ciric, Thaddeus E. Whyte, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 15	"hydrometalation" should be --hydrodemetalation--.
Column 2, line 41	"hydrogen" should be --hydrocarbon--.
Column 3, line 32	"whens aid" should be -- when said--
Table 1, second part thereof, Column 5	"090.38" should be --0.38-- and raised to the "LHSV" line.

Signed and Sealed this

twenty-first Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks