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(54) Process for the demetallation of residual oils

(57) Process for the demetallation of petroleum crude oil by contacting the oil together with hydrogen with a catalyst having at least one metal or compound thereof of Group VIII and/or Group VI of the Periodic Table as its active material supported on a carrier comprising a zeolite with a SiO_2/Al_2O_3 ratio of at least 5 and a unit cell size of between 24.30 and 24.60.

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Description

The present invention relates to demetallation of petroleum crude oil, and, more particular, to the removal of metals in the oil by contact with a catalyst having Ni, Mo and/or CoMo supported on a zeolitic carrier.

Petroleum crudes are known to contain metals such as Ni, V, Fe, Co, etc. in ppm levels. To a large extent, these components are associated with the heaviest parts of the resid, i.e. the part of the resid with the highest boiling points. This means that these components are concentrated in the bottom fractions often designated atm. or vacuum residuum.

The presence of metallic compounds is generally undesirable as they are poisonous to many subsequent upgrading steps usually used to convert or treat the atm. or vacuum residuum in refineries, e.g. fuel oil desulphurisation, resid hydrocracking or resid FCC.

Heavy oil fractions containing metal compounds are predominantly those with an atmospheric boiling point above 350°C. The heavy oil fractions will typically contain 50-500 ppm of mainly Ni and V. Those trace metals are normally removed in a fixed bed catalytic process, where the residual oil comes into contact with a demetallation catalyst at high temperature, typically at 300-450°C at a high H_2 pressure, such as 20-200 bars and at a space velocity in the range of 0.25-4 h^{-1}. When the oil comes into contact with the demetallation catalyst, the metals presented in the feedstock will react and accumulate on the catalyst surface.

In order to be able to efficiently treat residual oils, it is important that metallic compounds are removed from the oil. Conventional demetallation catalysts consist of Ni and Mo or CoMo supported on alumina. It has now been found that metals are removed from petroleum crude oil with a high efficiency in a demetallation process, when employing a demetallation catalyst supported on a carrier comprising zeolitic material.

Accordingly, this invention provides a process for the demetallation of petroleum crude oil by contacting the oil together with hydrogen with a catalyst having at least one metal or compound thereof of Group VIII and/or Group VI of the Periodic Table as active material supported on a carrier, wherein the carrier comprises a zeolite with a SiO_2/Al_2O_3 ratio of at least 5 and a unit cell size of between 24.30 and 24.60. Preferred metals for use in the process are Ni, Mo, CoMo or mixtures thereof.

It is furthermore preferred to composite the carrier material of the catalyst of 30-70% by weight with the above zeolitic material and 30-70% by weight with alumina.

The catalyst may be prepared by any method being conventional in the art and including impregnation of the calcined carrier with an aqueous solution of salts of the active metal or metals, drying the impregnated carrier and finally calcinating the carrier to obtain the active catalyst.

In operating the inventive process, the catalyst is arranged as fixed bed in a demetallation reactor and crude oil feedstock passed together with hydrogen in a ratio of typically 200-2000 Nl/l through the catalyst bed. During demetallation, the bed temperature is maintained at elevated temperature and pressure of usually 350-450°C and 120-170 atm.

By passage through the catalyst bed, the metal content in the feedstock is reduced to few ppm.

Example 1

A catalyst support was prepared by mixing 70 g of dried CBV 500 HY Zeolite (available from P.Q. Zeolites), having a unit cell size of 24.53 and a SiO_2/Al_2O_3 = 5.4 with a gel obtained by adding 29 g of Catapal (Vista Corporation) to 1.8 g of 65% HNO_3 and 78 g of water. The components were thoroughly mixed in a Z-kneader with 11 g Catapal until a pasta was formed. The pasta was then extruded into 1/32" extrudates. After extrusion, the wet extrudates were dried at room temperature for 16 hours. The dried extrudates were then calcined at 550°C for 2 hours in a laboratory furnace.

The calcined carrier was impregnated by pore volume filling with an impregnation solution containing 18.3 g of $Co(NO_3)_2 \cdot 6H_2O$, 15 g of ammonium dimolybdate and distilled water up to 82 ml. After impregnation, the catalyst was dried at room temperature for 16 hrs. The dried and impregnated catalyst was finally calcined at 500°C for 2 hours. The catalyst thus prepared is designated A.

Example 2

Using a similar procedure to that of Example 1, a catalyst carrier was prepared by mixing 30 g of dried HY Zeolite CBV 500 with 62 g of Versal 300 alumina and 126 g of alumina gel. The catalyst carrier was dried, calcined, impregnated and decomposed at the same conditions as described under Example 1. The catalyst thus prepared is designated B.

Example 3

Using the procedure of Example 2, a catalyst was prepared where the CBV 500 zeolitic component was exchanged for a CBV 600 (available from P.Q. Zeolites) with a unit cell size of 24.34 Å and a SiO_2/Al_2O_3 = 5.4. The catalyst thus prepared is designated C.

Example 4

As comparison catalyst in the evaluation of the catalysts prepared in Examples 1-3, commercial Al_2O_3 based catalysts were used. These catalysts are commercially available from Haldor Topsøe A/S under the trade name TK-711/TK-751 and TK-771.

The ability of removing metals from a residual oil was tested in a fixed bed pilot plant. For the test, a residual oil of Middle East origin was used. The properties of the feedstock used in the test are listed in Table 1.

Table 1

Feedstock Properties	
SG	0.9513
Sulphur, wt%	2.964
Nitrogen, ppm	1850
Ni + V, ppm	38
CCR, wt%	8.15
Asph., wt%	2.0
C, wt%	11.60
H, wt%	84.8
GC Dist.	
IBP-190°C,wt%	2.1
IBP-343°C,wt%	7.3
IBP-440°C,wt%	27.6
IBP-565°C,wt%	60.6

The conditions used in the test are listed in Table 2. As apparent from Table 2, the tests were conducted at different temperatures ranging from 385°C to 405°C. Each temperature level was maintained for one week in order to reach a stable activity level for the catalyst.

Table 2

Process Conditions	
LHSV	0.26^{h-1}
H_2/oil	500
Pressure	150 atm.
Temp.	385/400/405/385°C

The catalysts of Examples 1-3 were tested in a fixed bed with a small protective layer of commercial demetallation catalysts, in order to control the amounts of metals that will deposit on the catalyst of the invention. The catalyst bed lay-out used in the test is summarized in Table 3.

Table 3

Catalyst Bed Lay-Out				
Vol.-%[1)]	Loading 1	Loading 2	Loading 3	Loading 4
10	TK-711 1/32"C			
25	TK-751 1/32"C			
60	Catalyst A	Catalyst B	Catalyst C	Comparative Cat. TK-771

[1)] Vol% of total loading.

Fig. 1-3 show the catalyst activity of catalyst loadings 1-3 in comparison with the conventional Al_2O_3 based system.

Fig. 1-3 are Arrhenius plots giving the first order rate constants for demetallation. The first order rate constant is calculated according to equation 1 as follows:

$$k_1 = LHSV \cdot \ln \frac{MeF}{MeP} \qquad (1)$$

where:

k_1: is the first order rate constant for demetallation, h^{-1}

LHSV: is the space velocity

$$\frac{Feed\ flow\ rate\ (ml/h)}{Catalyst\ vol.\ (ml)}$$

MeF,MeP: feed and product metal content in ppm

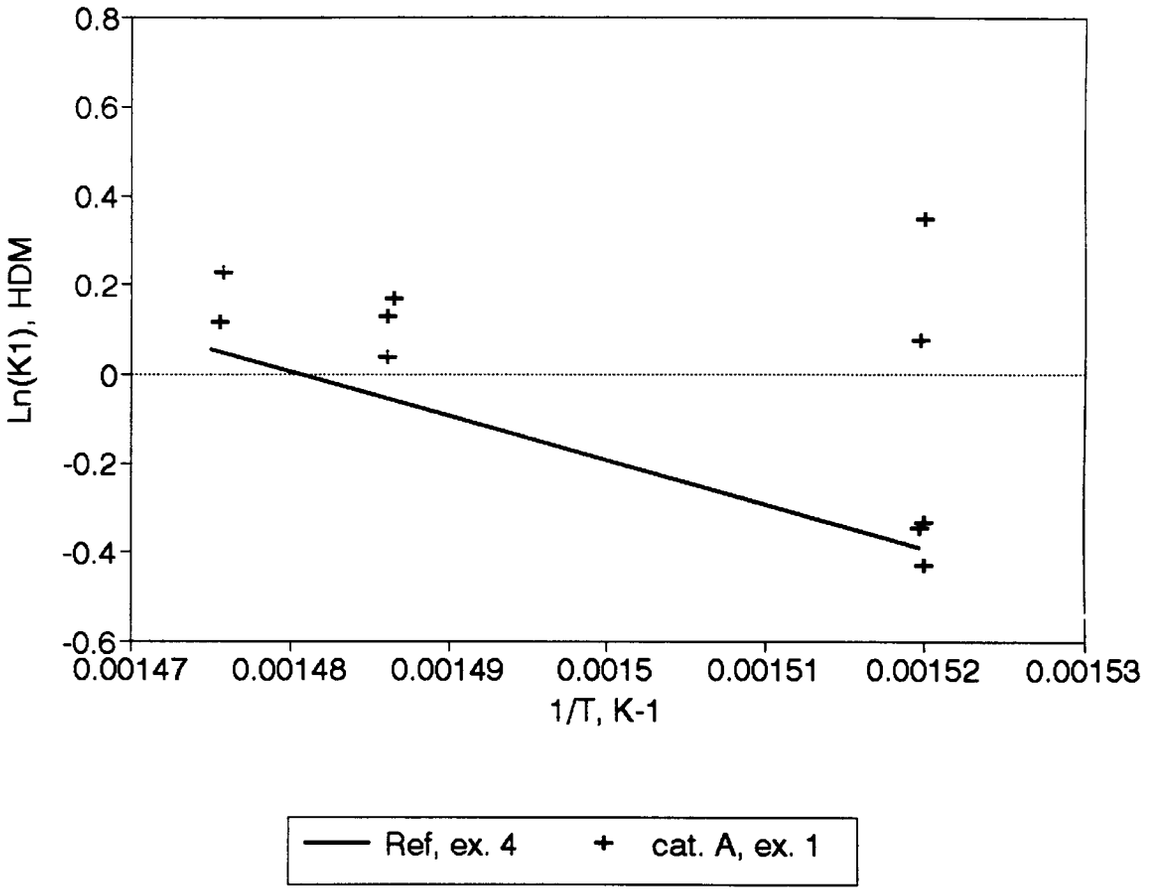
In Fig. 1-3, the activity obtained on a conventional catalyst system is given as solid lines. Each of the catalysts of this invention shows an improved activity for demetallation as apparent from the data in Fig. 1-3. The level of improvement in relation to known catalysts are in the order of 20-40%, which for the test conditions and feeds tested results in a substantially completely demetallized hydrocarbon product.

Claims

1. Process for the demetallation of petroleum crude oil by contacting the oil together with hydrogen with a catalyst having at least one metal or compound thereof of Group VIII and/or Group VI of the Periodic Table as active material supported on a carrier, wherein the carrier comprises a zeolite with a SiO_2/Al_2O_3 ratio of at least 5 and a unit cell size of between 24.30 and 24.60.

2. The process of claim 1, wherein the carrier consists of 30-70% by weight of the zeolite and 30-70% by weight of alumina.

3. The process of claim 1, wherein the Group VIII metal comprises Ni and the Group VI metal comprises Mo, and/or Co.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-0.4
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FIG. 1

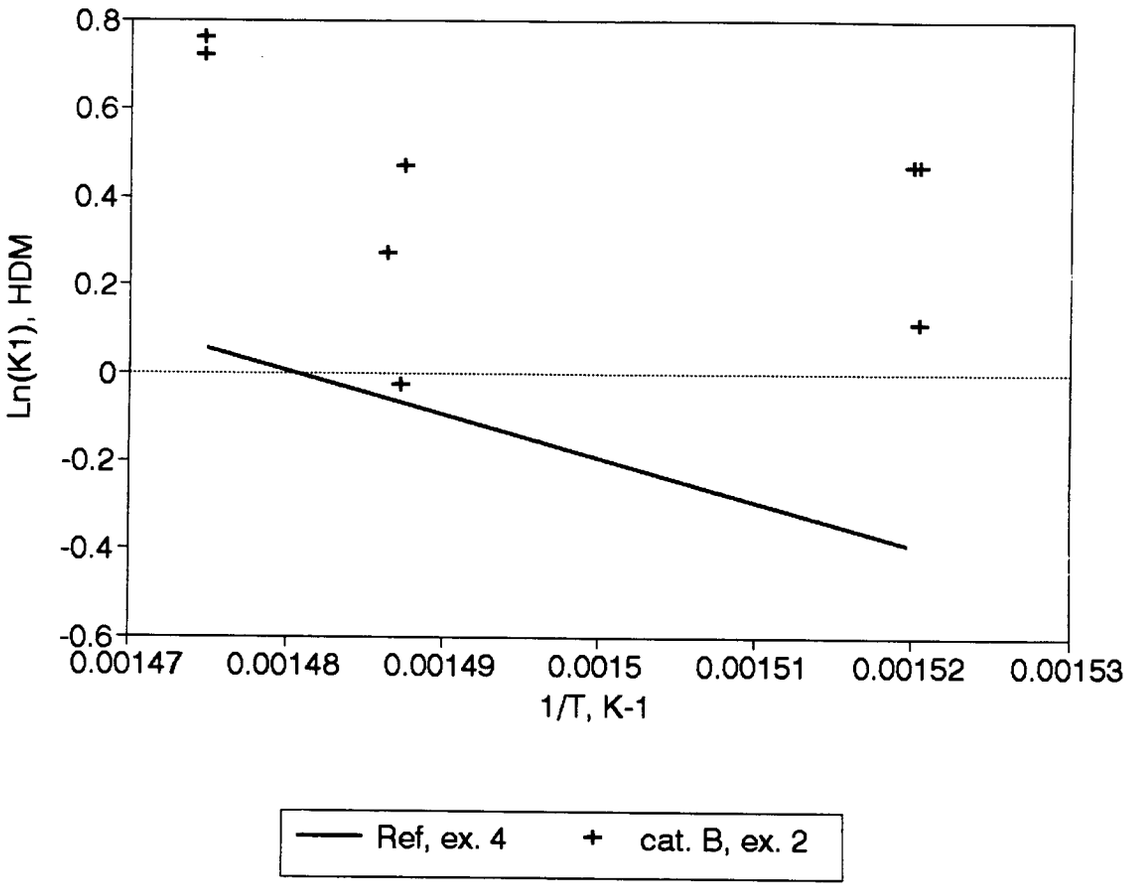
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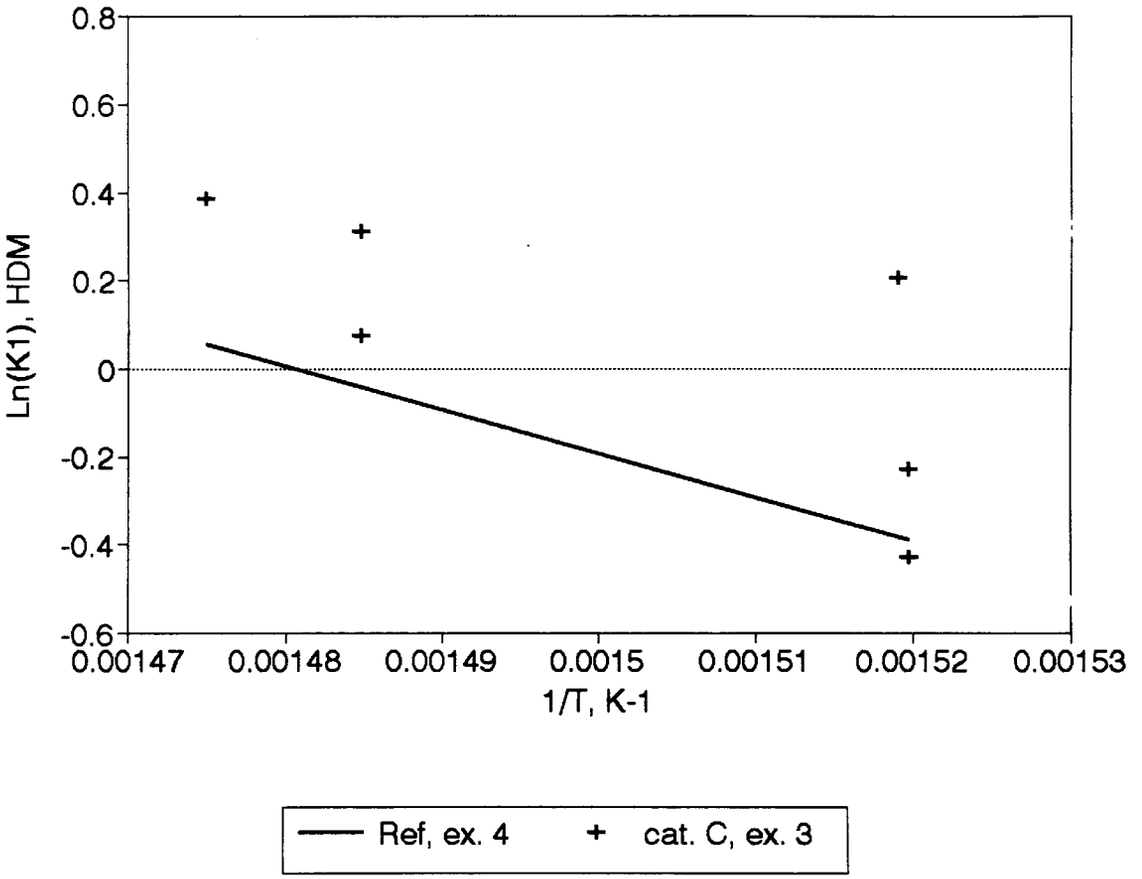
FIG. 2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0.00153
1/T, K-1
Ref, ex. 4
cat. C, ex. 3

FIG. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 96 10 1974

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 216 938 (CATALYSTS AND CHEMICALS) * page 1, line 15 - line 33; claims 1-8; examples 1-5 *	1-3	C10G45/12
X	US-A-4 554 263 (CATALYSTS AND CHEMICALS) * the whole document *	1-3	
A	EP-A-0 449 144 (COSMO OIL AND PETROLEUM ENERGY CENTER) * the whole document *	1-3	
A	EP-A-0 109 064 (GRACE)		
A	WO-A-93 02158 (MOBIL OIL)		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 May 1996	Michiels, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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