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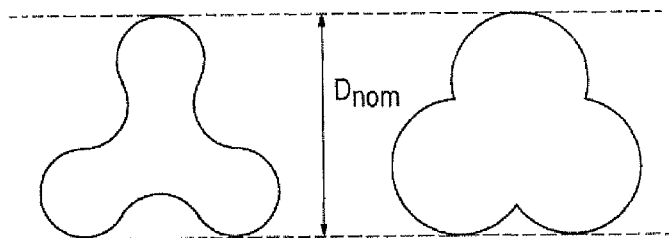
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(54) **Title:** PROCESS FOR THE HYDRO-DEMETALLIZATION OF HYDROCARBON FEEDSTOCKS

Fig.1



(57) **Abstract:** A process for the catalytic hydro-demetalization of a hydrocarbon feedstock over a fixed bed of hydro- demetal- lization catalyst particles, the process comprising contacting the heavy hydrocarbon oil and hydrogen at elevated temperature and elevated pressure with the catalyst particles in the fixed bed, the catalyst particles being extruded catalyst particles of one or more catalytically active metals on a porous carrier, the extruded particles comprising three protrusions each extending from and at- tached to a central position, wherein the central position is aligned along the longitudinal axis of the particle, the cross-section of the particle occupying the space encompassed by the outer edges of six circles around a central circle, each of the six circles touching two neighbouring circles whilst three alternating circles are equidistant to the central circle and may be attached to the central circle, minus the space occupied by the three remaining outer circles and including the six interstitial regions.

PROCESS FOR THE HYDRO-DEMETALLIZATION OF HYDROCARBON
FEEDSTOCKS

The present invention relates to a process for the conversion of hydrocarbon feedstocks. More specifically, the present invention relates to a process for the catalytic hydro-demetalization of hydrocarbon feedstocks in a fixed bed of catalyst particles, the process comprising feeding the feedstock and hydrogen over the fixed bed containing extruded catalyst particles at elevated temperature and pressure.

Hydrocarbon feedstocks, for instance heavy oils or residual oil as obtained in the distillation of crude oils at atmospheric or reduced pressure, usually contain smaller or larger amounts of metal compounds, in particular vanadium and nickel compounds, although also iron, zinc and copper compounds may be present. Depending on the source of the crude oil, the total amounts of metal compounds may be up till 1000 ppmw, occasionally even more. If such residual oils are applied as a feed for catalytic cracking processes or catalytic hydroprocesses or catalytic hydrocracking processes, a large part of the metals will be deposited on the catalyst particles. As a result of the increasing concentration of in particular nickel and vanadium on the active sites of the cracking catalyst particles, a rapid deactivation of the cracking catalyst occurs. In order to avoid a too rapid deactivation of the cracking catalyst it has therefore been proposed that the metal compounds should be removed at least partly from the feed before contacting with the cracking catalyst.

It is well known, e.g. from British patent specifications Nos. 1,438,645; 1,560,590 and 1,560,599, that removal of metals and metal compounds from a hydrocarbon oil feed can be achieved by contacting this feed at elevated temperature and pressure in the presence of hydrogen with a suitable demetallisation catalyst. Such demetallization catalysts are known. They usually consist of oxidic carriers such as alumina, silica or silica alumina, on which one or more metals or metal compounds having hydrogenation activity are optionally deposited. Metals from Groups VIB and VIII of the Periodic Table of Elements are widely known to be suitable for this purpose. Examples of suitable demetallisation catalysts are disclosed in inter alia U.S. Patents Nos. 3,891,541 and 3,876,523, British patent specifications Nos. 1,438,645; 1,560,590 and 1,560,599, Dutch patent specification No. 7901734, German patent specification No. 2638498 and British patent specifications Nos. 1,548,722 and 1,522,629.

Metals and metal compounds from the feedstock, such as vanadium and vanadium compounds, nickel and nickel compounds and iron and iron compounds, deposit inside the catalyst particles, often in their metallic form. The feed characteristics determine the diffusion resistance of hetero-atomic metal (vanadium and nickel) compounds inside the catalyst particles. As the results of diffusion limitation, the profile of the deposited metals, such as vanadium and nickel, over the catalyst particle cross section has a high gradient with much higher vanadium and nickel content in the particle outer area compared to the particle inner area. With increasing time on stream, the diffusion limitation becomes more and more serious as more metal is deposited in the particle

outer area, which blocks the reactants entering into the inner particle pores. Both the hydro-demetalization reaction rate and catalyst particle metal uptaking capacity are reduced due to the diffusion limitation.

5 Furthermore, the pressure drop for a fixed bed residue hydroprocessing reactor is high. With increasing time on stream of the catalyst, the pressure drop can be built up as a result of metal deposition, fouling and coking.

10 From the viewpoint of reducing mass transfer inside the catalyst particle, catalyst with small particle size has to be used. However, from the viewpoint of preventing pressure drop building-up, large sized catalyst particles are favoured to create sufficient high bed voidage in order to cope with increasing pressure drop due to
15 coking, metal deposition and fouling. Optimizing the catalyst shape may be the only solution to simultaneously achieve the above two objectives through shortening reactant diffusing distance inside catalyst particle and reducing the catalyst particle packing density. It will
20 be clear that a more open reactor bed will result in less catalyst being present per unit reactor volume.

In the past a tremendous amount of work has been devoted to the development of particles, in particular catalytically active particles, for many different
25 processes. There has also been a considerable effort to try to understand the advantages and sometimes disadvantages of effects of shape when deviating from conventional shapes such as pellets, rods, spheres and cylinders for use in catalytic as well as non-catalytic
30 duties.

Examples of well-known catalyst particle shapes are rings, cloverleaves, dumbbells, C-shaped particles and polylobal shaped particles. Many commercial catalysts are

available in TL (Trilobe) or QL (Quadrulobe) form. They serve as alternatives to the conventional cylindrical shape and often provide advantages because of their increased surface-to-volume ratio which enables the exposure of more catalytic sites thus providing more active catalysts. It has now surprisingly been found that specifically shaped particles of the general "trilobal" shape offer unexpected and sizeable advantages compared with conventional "trilobal" particles, in the catalytic hydro-demetalization of a heavy hydrocarbon oil.

Thus, the present invention relates to a process for the catalytic hydro-demetalization of a hydrocarbon feedstock over a fixed bed of hydro-demetalization catalyst particles, the process comprising contacting the hydrocarbon feedstock and hydrogen at elevated temperature and elevated pressure with the catalyst particles in the fixed bed, the catalyst particles being extruded catalyst particles comprising one or more catalytically active metals on a porous carrier, the extruded particles comprising three protrusions each extending from and attached to a central position, wherein the central position is aligned along the longitudinal axis of the particle, the cross-section of the particle occupying the space encompassed by the outer edges of six circles around a central circle, each of the six circles touching two neighbouring circles whilst three alternating circles are equidistant to the central circle and may be attached to the central circle, minus the space occupied by the three remaining outer circles and including the six interstitial regions.

The shape of the catalyst extrudates is known from EP-A-1412085. The extrudates have a larger surface-to-volume ratio than corresponding conventional trilobal

extrudates of similar size. The extrudates suffer substantially less from pressure drop than such corresponding conventional trilobal extrudates. Moreover, the shape of the extrudates according to the present invention allows a certain degree of packing which would be detrimental with respect to pressure drop. We now surprisingly found that the shape of the extrudates of the present invention is very advantageous with respect to diffusion limitation when metals and metal compounds from the feedstock, deposit inside the catalyst extrudates due to the hydro-demetalization process. It was found that metals were more uniformly distributed inside the extrudates. This means that the extrudates according to the invention have a higher particle metal uptaking capacity compared to conventional extruded catalyst particles.

The hydro-demetalization process is different from the function of fouling beds or guard beds. The function of the fouling or guard beds is to filter small fines or particles to protect the down stream catalysts. These catalysts may be for example hydro-demetalization catalysts. If there are small particles in the feedstock, the downstream catalyst will be fouled and the catalytic activity will be reduced because of fouling outside the catalyst particles. When fouling takes place, pressure build-up is one of the problems. Normally, no catalytic reactions take place in the fouling bed or only at a very low level. During the residue hydro-demetalization process metal content in the feedstock is removed via catalytic conversion. The metals in the feed are not in a state of particles or fines, but components of the feed. These components are not filtered of by fouling beds or guard beds.

The invention will be described in more detail with reference to the figures.

Figure 1 shows a cross-sectional view of the most preferred extrudates TX (left), and of conventional trilobal TL extrudates(right), including definition of nominal diameter (Dnom).

Figure 2 shows rate constants for the hydro-desulfurization reaction versus the time on stream for TX-shaped and for TL shaped catalyst particles.

Figure 3 shows rate constants for vanadium removal versus the time on stream for TX-shaped and for TL shaped catalyst particles.

Figure 4 shows rate constants for nickel removal versus the time on stream for TX-shaped and for TL shaped catalyst particles.

In Figure 1 a cross-sectional view of the most preferred extrudates, and of conventional trilobal extrudates has been depicted. The surface of the cross-sectional shape of the most preferred extrudates (indicated by the solid line 1) can be described as defined in the main claim. It will be clear from the Figure (depicting the cross-section of the preferred particles) that in the concept of six circles of even size aligned around a central circle of the same size each outer circle borders its two neighboring circles and the central circle whilst subtraction of three alternating outer circles (dotted line 2) provides the remaining cross-section, built up from four circles (the central circle and the three remaining alternating outer circles) together with the six areas (3) formed by the inclusions of the central circle and six times two adjacent outer circles. The circumference of the preferred shaped particles according to the present

invention is such that it does not contain sharp corners, which can also be expressed as the derivative of the cross-section being continuous. The nominal diameter for the preferred particles is indicated as D_{nom} in

Figure 1.

It will be clear that minor deviations from the shape as defined are considered to be within the scope of the present invention. It is known to those skilled in the art to manufacture die-plates having one or more holes in the shape of the particles according to the present invention and which tolerances can be expected in practice when producing such die-plates.

The suitable material for the shaped catalyst particles should be processed in such a way that their intended shape is obtained. One example of a processing method is an extrusion process, wherein a shapeable dough, preferably comprising one or more sources for one or more of the catalytically active elements, and optionally one or more sources for one or more of the promoters and the finely divided refractory oxide or refractory oxide precursor is mulled together with a suitable solvent. The mulled mixture is then extruded through an orifice in a die-plate. The resulting extrudates are dried. If necessary, (additional) catalytic element sources and/or promoters may be applied to the extrudates by impregnation. Other processes which may be used are palletizing and pressure moulding.

The solvent for inclusion in the mixture may be any of the suitable solvents known in the art. Examples of suitable solvents include water; alcohols, such as methanol, ethanol and propanol; ketones, such as acetone; aldehydes, such as propanal; and aromatic solvents, such

as toluene. A most convenient and preferred solvent is water, optionally in combination with methanol.

The use of specific die-plates enables the formation of the intended shape of the catalyst particles. Die-plates are well known in the art and can be made from metal or polymer material, especially a thermoplastic material.

Preferred catalyst particles according to the present invention have a cross-section in which the three alternating circles (forming part of the outer circles) have diameters in the range between 0.74 and 1.3 times the diameter of the central circle, preferably between 0.87 and 1.15 times the diameter of the central circle.

More preferred catalyst particles according to the present invention are those having a cross-section in which the three alternating circles have the same diameter as the central circle. Suitably the distance between the three alternating circles and the central circle is the same. This distance is preferably less than half the diameter of the central circle, more preferably less than a quarter of the diameter of the central circle, with most preference given to particles having a cross-section in which the three alternating circles are attached to the central circle. Preferably the three alternating circles do not overlap with the central circle. In case of any overlap, the overlap of each alternating circle and the central circle will be less than 5% of the area of the central circle, preferably less than 2%, more preferably less than 1%.

It is possible to produce catalyst extrudates according to the present invention which also contain one or more holes along the length of the particles. For instance, the particles can contain one or more holes in

the area formed by the central cylinder (the central circle in the cross-section given in Figure 1) and/or one or more holes in one or more of the alternating cylinders (the alternating circles in the cross-section given in Figure 1). The presence of one or a number of holes causes an increase of the surface to volume ratio which in principle allows exposure of more catalytic sites and, in any case, more exposure to incoming charges which may work advantageously from a catalytic point of view. Since it becomes increasingly difficult to produce hollow particles as their size becomes smaller it is preferred to use massive particles (still having their micropores) when smaller sizes are desired for certain purposes.

It has been found that the voidage of the extrudates according to the present invention is well above 50% (voidance being defined as the volume fraction of the open space present in a bed of particles outside the particles present, i.e. the volume of the pores inside the particles are not included in the voidage). The catalyst used in the experiment to be described hereinafter had a voidage of typically 58% which is substantially above that of the comparative "trilobal" catalyst, the voidage of which amounted to just over 43%. The higher voidage of the extrudates according to the present invention is advantageous, because it gives extra space for the deposition of the metal and metal complexes to be deposited inside and on the outside of the catalyst. The voidage of a bed of catalyst particles according to the invention is suitably between 50 and 80%, preferably between 50 and 70%, more preferably between 55 and 65%.

The particles according to the present invention can be described as having a length/diameter ratio (L/D) of

at least 2. The diameter of the particles as depicted in Figure 1 (the preferred particles in accordance with the present invention) is defined as the distance between the tangent line that touches two protrusions and a line parallel to this tangent line, that touches the third protrusion. It is indicated as D nom in Figure 1. The particles according to the present invention can have a L/D in the range between 1 and 25. Preferably, the particles according to the present invention have a L/D in the range between 1.5 and 20, more preferably in the range between 2 and 10. For example, the particles used in the experiment to be described hereinafter had a L/D in the range of from 2.5 and 3.5.

The length of the particles in accordance with the present invention is suitably in the range between 1 and 25 mm, preferably in the range between 3 and 20 mm.

The extrudates of the present invention are formed of porous carrier which can be used in catalytic hydro-demetalization processes. Examples of suitable porous carriers are inorganic refractory oxides such as alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures of two or more of such materials. Preferably, titania, alumina, in particular gamma-alumina, silica, and various forms of silica-alumina are used as support material. The pore volume of the initial carrier is preferably in the range of from 0.4 and 1.2 ml/g of carrier, more preferably in the range of from 0.5 to 1.1 ml/g of carrier, even more preferably in the range of from 0.6 to 1.0 ml/g of carrier. The pore size distribution, pore volume, and average pore diameter can be obtained via mercury porosimetry following the proceedings of ASTM D-4284. The higher pore volume of the carrier according to the present invention is

advantageous, because it gives extra space for the deposition of the metal and metal complexes to be deposited inside the catalyst extrudate particles. The median pore diameter is preferably in the range of from 6 to 100 nm, more preferably from 10 to 50 nm, even more preferably from 12 to 30 nm. With this median pore diameter the strength of the extrudate particles is still sufficient, while also diffusion of metal or metal compounds to be deposited inside the pores can still take place. The BET surface area of the carrier is preferably in the range of from 50 to 500 m²/g, more preferably in the range of from 100 to 300 m²/g.

In the process of the invention, the appropriate amount(s) of one or more catalytically active metals and/or metal compounds will be present on the porous carrier. Those skilled in the art know which metal(s) and/or metal compound(s) to apply for specific applications and also to which extent and how to incorporate the chosen moieties on the particles envisaged. The catalytically active metal may be deposited on the carrier material by any suitable treatment, such as impregnation, mixing/kneading and mixing/extrusion. Shaping into extrudates may be done before or after deposition of the catalytically active metals and/or metal compounds. After deposition of the metal the loaded carrier is typically subjected to calcination. The effect of the calcination treatment is to remove crystal water, to decompose organic compounds and to convert inorganic compounds to their respective oxides. After calcination, the resulting catalyst may be activated by contacting the catalyst with hydrogen or a hydrogen-containing gas, typically at temperatures of about 200 to 500 °C. Other processes for the preparation

of hydro-demetalization catalysts comprise kneading/mulling, followed by extrusion, drying/calcination and activation.

For the catalytic hydro-demetalization process of the invention, preferably one or more metal(s) of Group VI and/or one or more non-noble metal(s) of Group VIII of the Periodic Table of the Elements are conveniently present as oxides and/or as metal. More preferably, the catalyst comprises one or more metals selected from Mo, Co, W, V or Ni. Even more preferably, the catalyst comprises the combination Co or Ni and Mo.

The total amount of metal on the support is preferably in the range from 1 to 30 wt%, based on the total weight of the catalyst, more preferably in the range from 1 to 20wt%, even more preferably in the range from 2 to 15 wt%.

The hydrocarbon feedstock that requires treatment in the form of a hydro-demetalization process before any further treatment can be a whole crude. However, since the high metal content of a crude oil tends to be concentrated in the higher boiling fractions, the present process is more suitably applied for instance for a residual oil as obtained in the distillation of crude oils at atmospheric or reduced pressure. Those feedstocks usually contain smaller or larger amounts of metal compounds, in particular vanadium and nickel compounds, although also iron, zinc and copper compounds may be present. Depending on the source of the crude oil, the total amounts of metal compounds may be up to 1000 ppmw, occasionally even more. Preferably, the hydrocarbon feedstock is a heavy oil fraction, preferably having a boiling range between 200 °C and 1000 °C, more preferably between 300 and 850 °C. More preferably, the

hydrocarbon feedstock is a heavy gas oil or a vacuum gas oil, a deasphalted oil, or a residual oil. Even more preferably, the hydrocarbon feedstock is a residual crude oil, having an initial boiling point of at least 300 °C.

5 Preferably, the heavy hydrocarbon feedstock comprises between 1 up to 40 wt% asphaltenes, especially between 2.5 up to 25 wt% asphaltenes. Preferably, the hydrocarbon feedstock contains in total more than 1 ppmw of one or more metals selected from Fe, Ni, V, Mo, As, Ca, Mg, Zn, and Sn, especially more than 50 ppmw of one or more metals selected from Fe, Ni, V, Mo, As, Ca, Mg, Zn, and Sn.

The hydrogen gas which is used during the hydro-demetalization process is preferably used at a gas rate in the range from 250 to 2000 Nm³ per m³ of heavy hydrocarbon oil feed, more preferably in the range from 350 to 1750 Nm³ per m³ of heavy hydrocarbon oil feed. The hydrogen purity may vary from about 60 to 100 percent. If the hydrogen is recycled, which is customary, it is desirable to provide for bleeding off a portion of the recycle gas and to add makeup hydrogen in order to maintain the hydrogen purity within the specified range.

The hydro-demetalization process according to the present invention is performed under the normal conditions known to the person skilled in the art. Preferably, the process is carried out at a temperature in the range from 250 to 500 °C, more preferably in the range from 300 to 450 °C. Preferably, the total pressure at which the process is carried out is at a pressure in the range from 5 to 200 bara, more preferably in the range from 30 to 180 bara. The hydrogen partial pressure is preferably in the range from 4 to 180 bara, more preferably in the range from 45 to 160 bara. The total

weight hourly space velocity (WHSV) in which the process is carried out is preferably in the range from 0.2 to 3.0, more preferably in the range from 0.3 to 2.5. This depends, amongst others, on the purity of the gas that is being used.

The invention will now be illustrated by means of the following non-limiting examples.

Experiments were carried out to monitor the hydro-demetallization process using commercially available catalyst particles (Criterion) made up of trilobe-shaped alumina extrudates comprising 4 wt% Mo based on the total weight of the catalyst (comparative example) and using catalyst particles having a shape as defined in claim 1 (working examples).

Example I Catalyst preparation

Trilobe-shaped catalyst particles were obtained from Criterion, being the Criterion hydro-demetallization catalyst RM-430 with 2.5 mm TX shape. The L/D ratio of these shaped catalyst particles was in the range from 2.5 to 3.5.

Catalyst particles according to the invention were prepared by mixing 4 kg of pseudo boehmite alumina powder (obtained from Criterion) with 4 kg water containing 65 g of 69.5% nitric acid. The mixture was kneaded for 40 minutes. The mixture was shaped using a Bonnot extruder equipped with the appropriate dieplate to obtain the desired shape according to claim 1. The resulting extrudates were dried and calcined. The extrudates were impregnated with a solution of phosphoric acid and molybdenum trioxide. The impregnated catalyst particles were dried and calcined.

Both catalyst particles contained 4 wt% Mo, based on the total weight of the catalyst, on the same carrier,

only the shape of the extrudates was different. The L/D ratio of these shaped catalyst particles was in the range from 2.5 to 3.5.

Example II Testing of the catalysts

5 Two hydro-demetallization tests were carried in parallel using the catalysts of Example I. The feed used was a residual oil as obtained from a Middle East crude. The relevant properties of the feed are given in Table 1.

Table 1 Feed properties

Density at 15°C,	g/ml	0.9675
Density at 70°C,	g/ml	0.9333
Kin. viscosity at 100 °C,	CSt	43.71
Carbon content,	%w	84.70
Hydrogen content,	%w	11.20
Sulphur content,	%w	3.520
Total nitrogen content,	Ppmw	2440
Nickel content,	Ppmw	22.5
Vanadium content,	Ppmw	68
Ramsbottom Carbon Test,	%w	10.4
C5-asphaltene content,	%w	8.7
Mono-aromatics content,	mmol/100 g	59.75
Di-aromatics content,	mmol/100 g	26.42
Tri-aromatics content,	mmol/100 g	23.47
Tetra ⁺ -aromatics content,	mmol/100 g	33.09
Penta ⁺ -aromatics content,	mmol/100 g	15.54
Hexa ⁺ -aromatics content,	mmol/100 g	8.28
Hepta ⁺ -aromatics content,	mmol/100 g	5.34
0.5 %w recovery (IBP),	°C	258
2 %w recovery,	°C	294
4 %w recovery,	°C	319

Table 1 Feed properties (cont'd)

6 %w recovery,	°C	336
8 %w recovery,	°C	349
10 %w recovery,	°C	361
20 %w recovery,	°C	406
30 %w recovery,	°C	442
40 %w recovery,	°C	477
50 %w recovery,	°C	516
60 %w recovery,	°C	558
70 %w recovery,	°C	605
<=370 °C in feed,	%w	11.80
>520 °C in feed,	%w	49.00

The feed was added to a trickle flow reactor, that was filled with catalyst. The feedstock weight hourly space velocity was 0.44 kg/(litre of catalyst.hr). The operating hydrogen partial pressure was 150 bar and the gas rate was 500 Nl/kg of feed. The reactor temperature was adjusted to achieve total metal contents in the liquid product to be lower than 25 ppmw. The tests for the 2.5 mm TX catalyst and 2.5 mm TL catalyst (comparative) lasted 2200 and 1650 hours, respectively. The liquid products were sampled periodically, weighted, and analyzed off-line. Spent catalyst samples were collected from the reactor at different height positions after the tests. The spent catalyst samples were extracted with toluene and pentane in Soxhlet extractors. The extracted samples were dried at temperature of 60 °C under vacuum condition before sent for analyses. The spent catalyst samples were analyzed for profile distributions of V, Ni and S using a scanning electron microscope (SEM) fitted with an X-ray detector, and metal contents with XRF Bead.

The volume based hydrodesulfurization and hydro-demetallization rate constants were calculated according to equation (1),

$$k = \frac{WHSV}{n-1} \left[\left(\frac{1}{c_{product}} \right)^{(n-1)} - \left(\frac{1}{c_{feedt}} \right)^{(n-1)} \right] \quad (1)$$

where k is rate constant, WHSV is weight hourly space velocity of feed, n is reaction order and c is concentration. The results are given in Figures 2, 3 and 4.

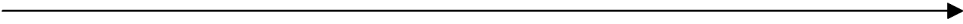
Figure 2 shows the hydrodesulfurisation activity for the TL-shaped catalyst particles (comparative catalyst) and the TX shaped catalyst particles. From this Figure it can be concluded that the hydrodesulfurization activity for both catalysts is about the same. Figure 3 shows the rate constant for vanadium removal of the TL-shaped catalyst particles (comparative catalyst) and the TX shaped catalyst particles. Figure 4 shows the rate constant for nickel removal of the TL-shaped catalyst particles (comparative catalyst) and the TX shaped catalyst particles. It can be concluded from this two Figures that the TX shaped catalyst particles have a higher hydro-demetallization activity in comparison with the TL shape catalyst.

To compare the depositional patterns of the metals in the used catalyst extrudate particles quantitatively, the profile index (PI) was determined. The PI is the ratio of the average metal concentration to the concentration at the maximum. A higher PI means (1) that the metal is deposited more uniformly inside the used catalyst particle, (2) that the catalyst particle has a higher metal uptaking capacity and (3) that less limitation of pore diffusion takes place during the

hydro-demetallization reactions. The PI depends on the on-stream hours for the same catalyst.

The spent catalysts analysis results are given in Table 2.

Table 2 results on spent catalyst analysis

From reactor top to bottom 						
Position sample	a	b	c	d	e	f
Vanadium on spent catalyst, %wt.						
2.5 mm TX	18.4	19.2	7.1	5.3	3.7	2.8
2.5 mm TL	17.0	8.5	5.8	4.2	3.1	2.5
Nickel on spent catalyst, %wt.						
2.5 mm TX	4.0	4.2	1.9	1.4	1.1	0.9
2.5 mm TL	3.5	2.0	1.5	1.1	0.9	0.8
Profile Index (PI) for vanadium on spent catalyst						
2.5 mm TX	0.33	0.35	0.41	0.43	0.47	0.53
2.5 mm TL	0.29	0.25	0.26	0.34	0.3	0.26
Profile Index (PI) for nickel on spent catalyst						
2.5 mm TX	0.36	0.35	0.41	0.43	0.47	0.55
2.5 mm TL	0.30	0.25	0.26	0.33	0.30	0.26

5 Since the on-stream hours for the TX shape catalyst particles (according to the invention) is longer than for the TL shape catalyst particles (comparative example), the metal uptaking content for TX shape catalyst is higher than the TL shape catalyst. However, the profile index (PI) for vanadium and nickel on the spent TX shape catalyst particles is higher even under higher vanadium and metal uptaking content when compared to the TL shape catalyst. It can be observed that for the TX shape catalyst particles (according to the invention) the

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profile index becomes higher when the metal uptaking content on the spent catalysts from reactor top position to bottom position decreases. This indicates that the lower profile index for the spent catalyst sample from the reactor top section was caused by metal uptake. When the metal content increased with on-stream hours, the diffusion path into the inner pores of particle was partially blocked and the reactant diffusion length increased. However, for the spent TL shape catalyst (comparative example), the profile index variation is minimal and the profile index keeps consistently low for all spent catalyst samples for different reactor height positions. This indicates that for the TL shaped catalyst particles, the serious diffusion limitation exists even for the fresh catalyst.

The compact bulk density of the two different shaped catalyst particles was measured. It was measured that the compact bulk density of the 2.5 mm TX shape is lower than that of the 2.5 mm TL shaped catalyst particles (according to the invention). The difference in weight for the same volume and shape reactor is 10%. It can thus be concluded that the reactor with 2.5 mm TX shape catalyst has a higher bed voidage than the one with 2.5 mm TL shape catalyst. This results in a lower pressure drop for the reactor loaded with 2.5 mm TX shaped catalyst particles as compared to the 2.5 mm TL shaped catalyst particles.

C L A I M S

1. A process for the catalytic hydro-demetalization of a hydrocarbon feedstock over a fixed bed of hydro-demetalization catalyst particles, the process comprising contacting the hydrocarbon feedstock and hydrogen at elevated temperature and elevated pressure with the catalyst particles in the fixed bed, the catalyst particles being extruded catalyst particles comprising one or more catalytically active metals on a porous carrier, the extruded particles comprising three protrusions each extending from and attached to a central position, wherein the central position is aligned along the longitudinal axis of the particle, the cross-section of the particle occupying the space encompassed by the outer edges of six circles around a central circle, each of the six circles touching two neighbouring circles whilst three alternating circles are equidistant to the central circle and may be attached to the central circle, minus the space occupied by the three remaining outer circles and including the six interstitial regions.

2. A process according to claim 1, in which the hydrocarbon feedstock is a heavy oil fraction, preferably having a boiling range between 200 °C and 1000 °C, more preferably between 300 and 850 °C, especially a heavy gas oil or a vacuum gas oil, a deasphalted oil, or a residual oil, especially a residual crude oil, having an initial boiling point of at least 300 °C.

3. A process according to claim 1 or 2, in which the hydrocarbon feedstock comprises between 1 up to 40 wt% asphaltenes, especially between 2.5 up to 25 wt%.

4. A process according to any of claims 1 to 3, in which the hydrocarbon feedstock contains in total more than 1 ppmw of one or more metals selected from Fe, Ni, V, Mo, As, Ca, Mg, Zn, and Sn, especially more than 50 ppmw of one or more metals selected from Fe, Ni, V, Mo, As, Ca, Mg, Zn, and Sn.

5. A process according to any of claims 1 to 4, in which the catalyst comprises one or more metals selected from Group VIII of the Periodic Table, especially Co or Ni, in combination with one or more metals from Group VIB of the Periodic Table, especially Mo or V.

6. A process according to claim 5, in which the catalyst comprises the combination Co or Ni and Mo.

7. A process according to any of claims 1 to 6, in which the catalyst comprises a porous refractory oxide as catalyst carrier, especially silica, alumina, silica/alumina, titania or mixtures thereof.

8. A process according to any of claims 1 to 7, in which the process is carried out at a temperature in the range from 250 to 500 °C, preferably in the range from 300 to 450 °C.

9. A process according to any of claims 1 to 8, in which the process is carried out at a pressure in the range from 5 to 200 bara, preferably in the range from 30 to 180 bara.

10. A process according to any of claims 1 to 9, in which the process is carried out at a hydrogen partial pressure in the range from 4 to 180 bara, preferably in the range from 45 to 160 bara.

11. A process according to any of claims 1 to 10, in which the process is carried out at a WHSV in the range from 0.2 to 3.0, preferably in the range from 0.3 to 2.5.

12. A process according to any of claims 1 to 11, in which the process is carried out at a gas rate in the range from 250 to 2000 Nm³ per m³ of hydrocarbon feedstock, preferably in the range from 350 to 1750 Nm³ per m³ of hydrocarbon feedstock.

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Fig.1

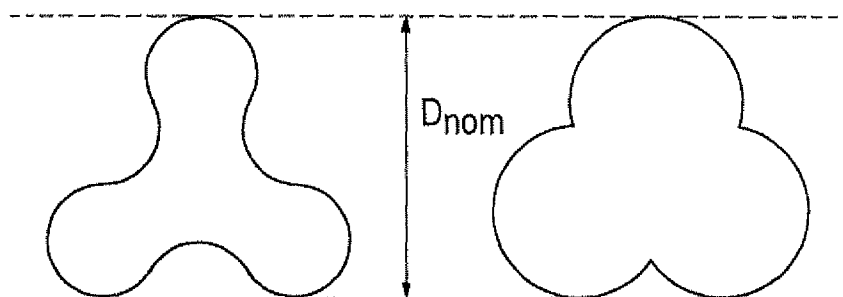


Fig.2

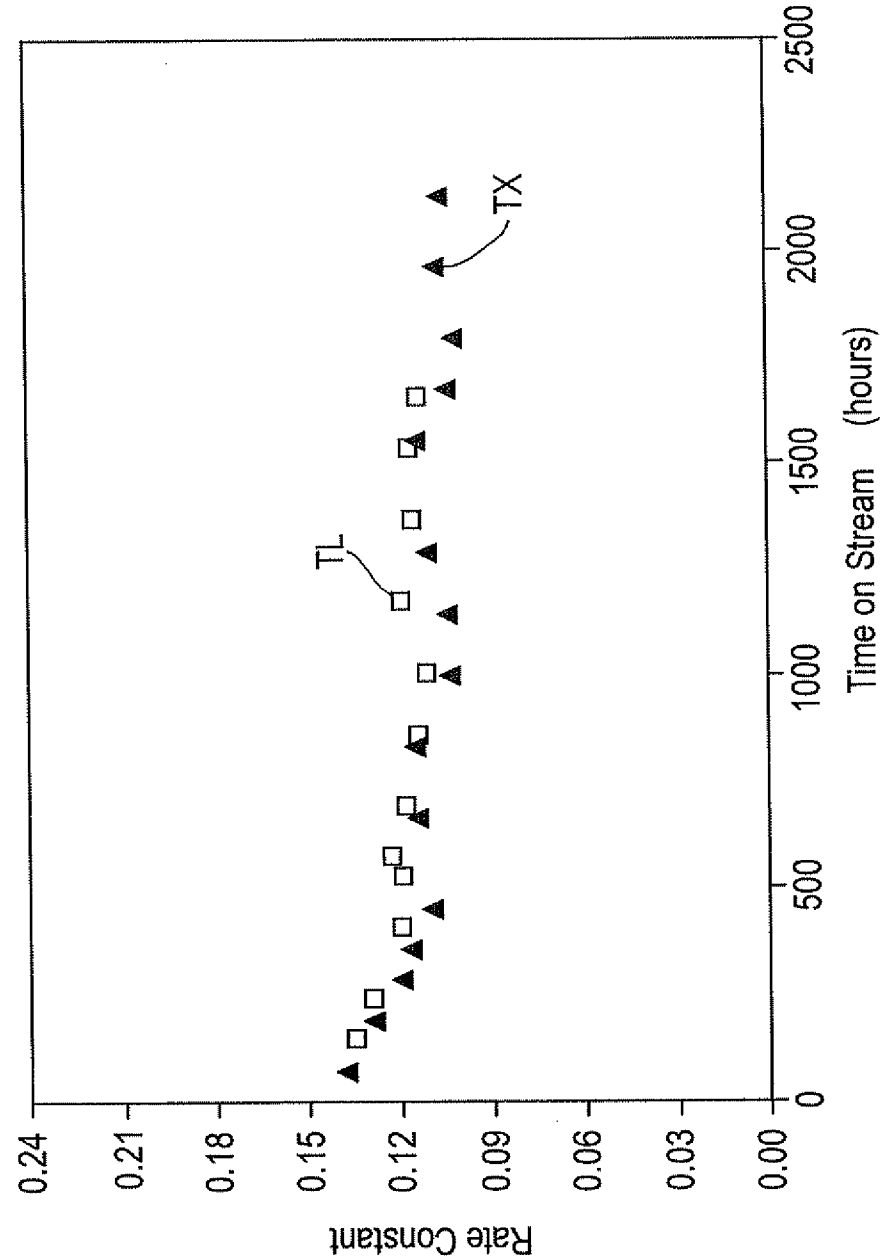


Fig.3

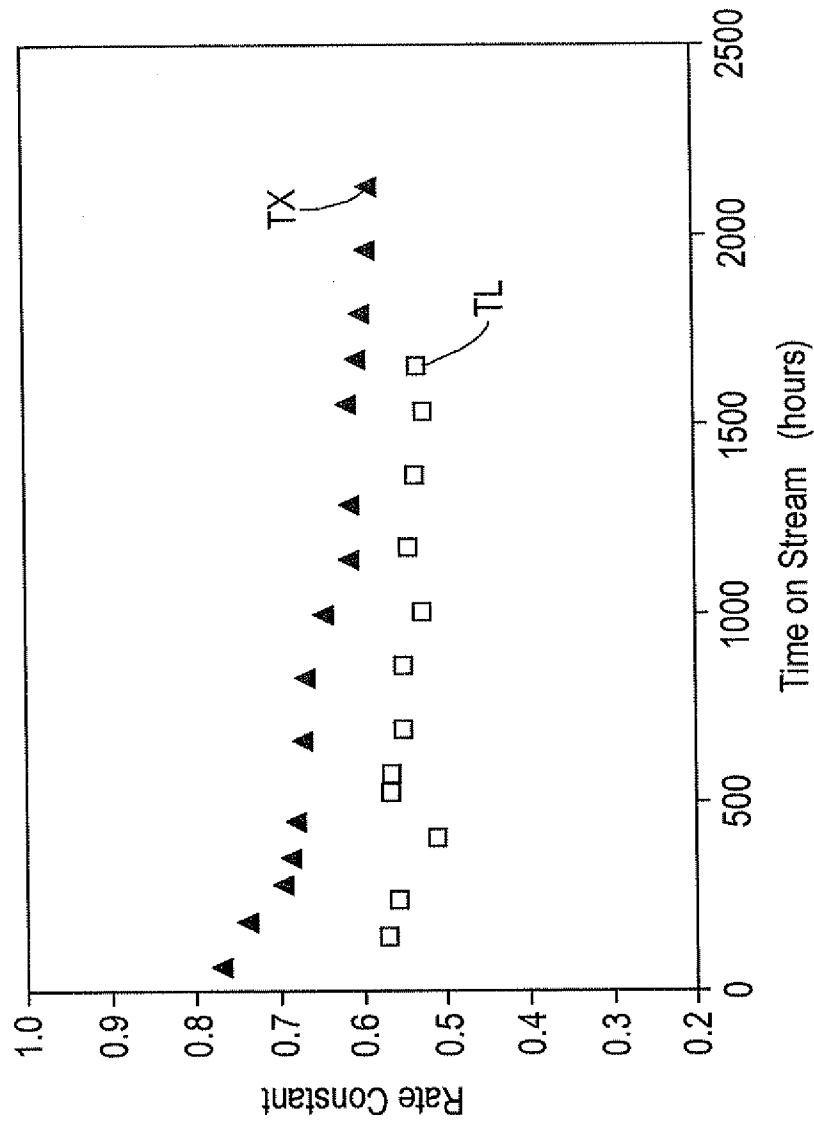
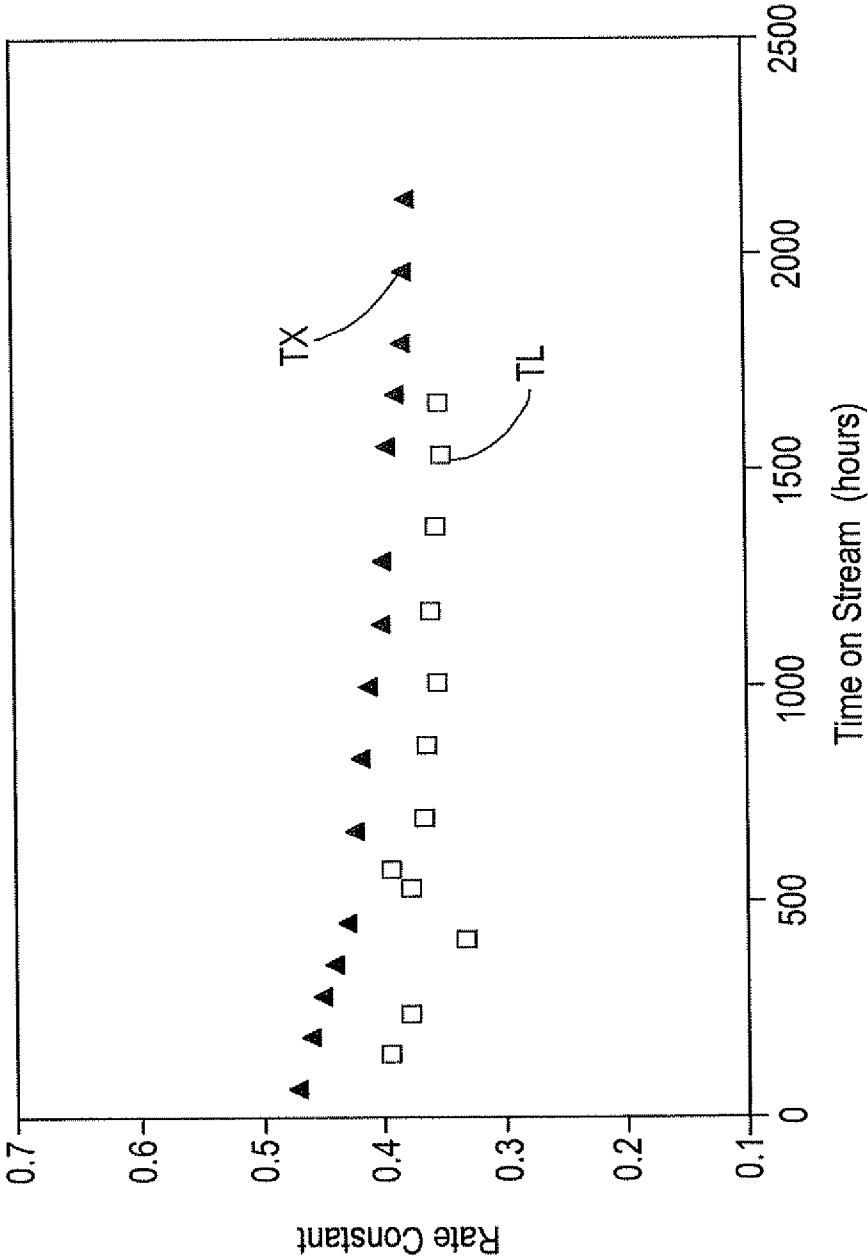


Fig.4



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/050560

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J35/02 C10G45/04 C10G45/06 C10G45/08
ADD.

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)
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 33 15 105 A1 (LEUNA WERKE VEB [DD]) 17 November 1983 (1983-11-17) page 4; figure 1	1-12
X	CN 100 363 106 C (CHINA PETROCHEMICAL CORP [CN]) 23 January 2008 (2008-01-23) page 1, paragraphs 1,2; figure 6	1-12
Y	US 4 394 303 A (GIBSON KIRK R) 19 July 1983 (1983-07-19) column 1, line 39 - line 65 column 2, line 9 - line 26 column 2, line 52 - line 55 column 3, line 33 - line 35 column 4, line 25 - line 36 column 6, line 34 - line 46 figure 1	1-12
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

7 May 2010

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2010/050560

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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