Catalyst Carrier and Catalyst Composition, Processes for their Preparation and their Use

The present invention concerns a catalyst carrier suitable for a hydrocracking catalyst, a catalyst composition incorporating said carrier, the preparation of both carrier and catalyst composition and the use of the catalyst composition as a hydrocracking catalyst.

Processes that comprise treating crude oil and other petroleum feedstocks with hydrogen in the presence of a catalyst are well known. One such process is hydrocracking, in which heavy distillate hydrocarbons are converted under hydrogen pressure into products of lower molecular weight in the presence of a catalyst. Hydrocracking is used in the oil industry to prepare a wide range of materials, ranging from C3/C4 production to luboil manufacture.

Hydrocracking may be operated as either a single or two-stage process. Two-stage hydrocracking involves a first stage, which is predominantly a hydrotreatment stage wherein impurities and unsaturated compounds are hydrogenated in the presence of a first catalyst having a high hydrogenation function, and a second-stage where most of the cracking occurs in the presence of a second catalyst having a strong cracking function. In single-stage hydrocracking, the treatment and cracking steps occur in one reactor and may be performed using a single catalyst. The catalysts employed in hydrocracking are generally made from a carrier material on which there are deposited catalytically active metals such as nickel, molybdenum, tungsten, palladium etc.

The higher the activity of a hydrocracking catalyst the more efficient a conversion will be. In particular, a

more active catalyst can be operated at a lower temperature than a less active catalyst to achieve the same degree of conversion. This is advantageous as a lower operating temperature prolongs catalyst life and decreases operating costs. Accordingly, there is always a need for improving catalyst activity. There is also a continuing need to increase selectivity of catalytic action, particularly to increase the yield of middle distillate fractions and to reduce the production of light (C_1-C_4) gaseous materials.

Prior proposals to improve selectivity and activity have mainly concentrated on proposing new active materials, such as modified Y zeolites or silica-alumina materials, or new formulations comprising several active ingredients to provide a combined activity and selectivity improvement. Prior art proposals include US 2002/0160911; WO 00/12213, and WO 2004/047988.

The present invention provides a shaped catalyst carrier which comprises at least one inorganic refractory oxide, which carrier has a monomodal pore size distribution wherein at least 50% of the total pore volume is present in pores having a diameter in the range of from 4 to 50 nm and wherein the pore volume present in said pores is at least 0.4 ml/g, all as measured by mercury intrusion porosimetry.

The inorganic refractory oxide material may be any conventional oxide material suitable for hydroconversion processes. These are suitably selected from alumina, silica, silica-alumina or a mixture of two or more thereof. However it is also possible to use zirconia, clays, aluminium phosphate, magnesia, titania, silica-zirconia and silica-boria, though these are not often used in the art. The oxide material maybe amorphous or crystalline, or a mixture of two or more such materials.

Crystalline aluminosilicates are suitably zeolitic materials; faujasite zeolites, such as zeolite Y materials are very suitable.

Preferred refractory oxides are those having a hydrocracking capability, and may be selected from amorphous silica-alumina and ultrastable zeolite Y oxidic materials.

The term "amorphous" indicates a lack of crystal structure, as defined by X-ray diffraction, in the carrier material, although some short range ordering may be present. Amorphous silica-alumina suitable for use in preparing the catalyst carrier is available commercially. Conventional homogeneous amorphous silica alumina materials can be used, as can the heterogeneous dispersions of finely divided silica alumina in an alumina matrix, as described in US Patent Specifications Nos. 4,097,365 and 4,419,271. Alternatively, the silica-alumina may be prepared by a co-gelation process or a grafting process, as are well known in the art. The amorphous silica-alumina preferably contains silica in an amount in the range of from 25 to 95 % by weight as calculated on the carrier alone (i.e. based on total carrier). More preferably the amount of silica in the carrier is greater than 35 % wt, and most preferably at least 40 % wt. A very suitable amorphous silica-alumina product for use in preparing the catalyst carrier of the invention comprises 45% by weight silica and 55% by weight alumina and is commercially available (ex. Criterion Catalysts and Technologies, USA).

Preferred zeolitic Y materials are an ultrastable zeolite Y (USY) or a very ultrastable zeolite Y (VUSY) of unit cell size (a_o) less than 2.440 nm (24.40 Ångstroms), in particular less than 2.435 nm (24.35 Ångstroms) and a silica to alumina ratio of from 4 or more, for example

from 4 to 100. Suitable zeolite Y materials are known, for example, from European Patent Specifications Nos. 247 678 and 247 679, and WO 2004/047988.

Whilst USY and VUSY Y zeolites are the preferred form of cracking component used in the present invention, other Y zeolite forms are also suitable for use, for example the known ultrahydrophobic Y zeolites.

Preferred VUSY zeolite of EP-A-247 678 or EP-A-247 679 is characterised by a unit cell size below 2.445 nm (24.45 Ångstroms) or 2.435 nm (24.35 Ångstroms), a water adsorption capacity (at 25 °C and a p/p_o value of 0.2) of at least 8 %w of the zeolite and a pore volume of at least 0.25 ml/g wherein between 10% and 60% of the total pore volume is made up of pores having a diameter of at least 8 nm.

Most preferred are the low unit cell size, high surface area zeolite Y materials described in WO 2004/047988. Such materials can be described as a zeolite of the faujasite structure having a unit cell size in the range of from 24.10 to 24.40 Å, a bulk silica to alumina ratio (SAR) above 12, and a surface area of at least 850 m^2/g as measured by the BET method and ATSM D 4365-95 with nitrogen adsorption at a p/po value of 0.03. Said materials are prepared by a process which comprises

a) providing a starting zeolite of the faujasite structure having a silica to alumina ratio of from 4.5 to 6.5 and an alkali level of less than 1.5%wt;

b) hydrothermally treating said starting zeolite at a temperature in the range of from 600 to 850 °C, preferably 600 to 700°C more preferably 620 to 680°C and especially 630 to 670°C, and at a partial pressure of, preferably externally supplied, steam in the range of from 0.2 to 1 atmosphere for a time effective to produce a intermediate zeolite having

a unit cell size of from 24.30 to 24.45 Å, being suitably in the range of from 0.5 to 5 hours, more suitably 1 to 3 hours;

c) contacting the intermediate zeolite with an acidified solution comprising an acid and optionally an ammonium salt under conditions effective to produce a high surface area zeolite having a unit cell size in the range of from 24.10 to 24.40 Å, a molar silica to alumina ratio of greater than 12 and a surface area of greater than 850 m^2/g, thereby producing the high surface area zeolite; and

d) recovering said high surface area zeolite.

Especially preferred high surface area materials have one or more of the following features:

unit cell size in the range of from 24.14 to 24.38, preferably from 24.24, more preferably from 24.30, to 24.38, preferably to 24.36, especially to 24.35 Å, and maybe for example in the range of from 24.14 to 24.33 Å;

a SAR in the range of from 20 to 100, preferably from 20 to 80, especially to 50;

surface area of at least 875, preferably at least 890, for example at least 910 m^2/g;

a micropore volume,as determined by nitrogen porosimetry using the t-plot method, also known as the t-method, using nitrogen as the adsorbate as described by Lippens, Linsen and de Boer, Journal of Catalysis, 3-32,(1964), of greater than 0.28 ml/g, suitably greater than 0.30 ml/g. Generally micropore volume will be less than 0.40 ml/g, suitably less than 0.35 ml/g. Herein micropores are pores having a diameter of less than 2 nm.

Mercury intrusion porosimetry is a standard technique to determine particularly mesoporosity and

macroporosity of a refractory oxide or other solid porous materials since it can determine pore volume distributions of 4 nm and above. Mesopores herein are pores having a diameter in the range of from 4 to 50 nm; macropores herein are pores having a diameter above 50 nm. It is the aim of the present invention to maximise the mesoporosity and minimise the macroporosity of the carrier, and at least to increase the number of mesopores without increasing the number of macropores in the carriers.

The shaped carrier of the invention has a monomodal distribution. This means that in a conventional pore size distribution (PSD) graph which shows dD plotted against dV/dD there is a single peak, suitably a single sharp peak, which in the case of the carrier of the invention lies in the mesopore range: pores of diameter in the range of from 4 to 50 nm. Herein D indicates pore diameter and V indicates pore volume. It is possible in carriers of the invention that a rounded or bell shaped curve could also exist in the macropore range of such a PSD graph; this is not a peak within the meaning of the present text.

Preferably the mesopore pore volume is at least 0.45 ml/g, preferably at least 0.5 ml/g. Preferably the mesopore pore volume is at most 0.8 m/g, more preferably at most 0.7 ml/g. The nature of the inorganic refractory oxide can influence the most preferred mesopore pore volumes for the shaped carrier of the invention. Where the refractory oxide is wholly or predominantly amorphous in nature, for example an alumina, silica or amorphous silica-alumina material, then the mesopore pore volume is most suitably in the range of from 0.5 to 0.8 ml/g, preferably 0.6 to 0.75 ml/g, and more preferably 0.65 to 0.70 ml/g. Where the refractory oxide material comprises or contains a crystalline material, for example an

aluminosilicate zeolite, particularly a zeolite Y material, then the mesopore pore volume is most suitably in the range of from 0.4 to 0.6 ml/g, preferably 0.45 to 0.6 ml/g, more preferably 0.5 to 0.6 ml/g.

Preferably the proportion of the pore volume that is in the mesopores is at least 60 % and at most 90%. Again the nature of the refractory oxide material can influence the most preferred proportions. Where the refractory oxide material is wholly or predominantly an amorphous material, as above, then most suitably the proportion of the pore volume in the mesopores is in the range of from 75 to 90%, preferably 80 to 90%, and more preferably 85 to 90%. Where the refractory oxide material comprises or contains a crystalline material, as above, then most suitably the proportion of the pore volume in the mesopores is in the range of from 50 to 75%, preferably from 60 to 75%.

The effect of this high mesopore pore volume is that the compacted bulk density (CBD) of the catalyst carrier becomes greatly reduced. Reduction of the CBD can generally be desirable since it means that a reduced amount of expensive catalyst is required. There are various ways to reduce compacted bulk density, but other means do not result in an increased activity or middle distillate selectivity. By the use of a catalyst carrier of the invention the CBD of the final catalyst is lowered allowing a more economical catalyst refill for the refiner, but also surprisingly the activity of the catalyst is increased alongside an increased middle distillate selectivity and aromatics hydrogenation. This is particularly seen with the preferred zeolitic materials for use in the catalysts of the present invention: the high surface area zeolite Y materials described herein.

A further advantage of the catalyst carrier of the invention is that this increased activity of the final catalyst is maintained over time, and thus the stability of the catalyst is greatly enhanced. This is particularly seen with catalyst carriers made wholly or predominantly, for example from 95 to 100 wt%, of amorphous refractory oxide materials.

A yet further advantage of the shaped catalyst carrier of the invention is that the carrier when in extrudate form exhibits an increased strength and attrition resistance, and thus enables a longer catalyst lifetime in use.

The CBD of the carrier of the invention is suitably in the range of from 0.35 to 0.50 g/ml, preferably 0.35 to 0.45 g/ml, more preferably 0.38 to 0.43 g/ml.

In forming a catalyst carrier of the present invention, the refractory oxide material(s) may be usefully mixed with an amorphous binder component. The amorphous binder component may be any other refractory inorganic oxide or mixture of oxides conventional for such compositions. Generally this is an oxidic material not having a cracking capability and may be selected from, for example, alumina, silica, or a mixture thereof, alumina being preferred, but may also be a silica-alumina material, containing in the range of from 5 to 95%w silica, most suitably amorphous silica alumina materials hereinbefore mentioned. However again it is also possible to use zirconia, clays, aluminium phosphate, magnesia, titania, silica-zirconia and silica-boria, though these are not often used in the art. The amount of binder is generally in the range of from 0 to 70 wt% and is suitably less than 50 wt%, and may be less than 30 wt%. However where a zeolite is present in the carrier, the amount of zeolite in the catalyst support when binder is also present may be up to 90 % by weight, but is

preferably in the range of from 2, more preferably 10, especially 20, to 80 % by weight, based on the total catalyst support, with the balance being binder.

It is possible, and may be preferred in certain cases, for the catalyst carrier, and thus the catalyst composition, of the present invention, also to include a second cracking component. This is preferably a second zeolite. Most preferably a second zeolite is selected from zeolite beta, zeolite ZSM-5, or a zeolite Y of different unit cell size. Where a second zeolite Y is used, preferably it has a unit cell size greater than 24.40 A. A second cracking component may be present in an amount up to 20 parts by weight, based on total zeolite plus binder, but preferably is present in an amount in the range of from 0.5 to 10 parts by weight.

It should be noted that amorphous silica alumina may act both as a second cracking component and as a binder. As a cracking component it is most usefully employed in high operating temperature processes; as a binder it has been found useful in protecting a zeolite from loss of crystallinity, and therefore from deactivation, in use in any process that water and/or fluoride is present or generated.

The shaped carrier may be prepared by any conventional way of compressing the refractory oxides into a shaped form. It is a routine measure to check the mesporosity of the resulting materials once prepared. Compression may be via pelletization, extrusion or other compression means common in the art. We have found that the mesoporous shaped carrier of the present invention may be prepared more consistently if the oxides are prepared from a mix having a selected LOI (loss on ignition). Additional consistency of material is obtained if the mix has a selected pH range.

The present invention provides a process for the preparation of the shaped catalyst carrier of the invention, which comprises shaping a mix comprising said at least one refractory oxide wherein the mix has an LOI in the range of from 55 to 65%.

Herein loss on ignition (LOI) for a material is the relative amount of lost mass upon heating the material, ie the water content. Unless otherwise specified herein, this is determined herein by heating the material to 540°C under the following procedure: a sample is mixed well to prevent any inhomogeneity. The weighed sample is transferred into a weighed and precalcined crucible. The crucible is place to a preheated oven at 540°C for a minimum time of 15 minutes, but typically for 1 hour. The crucible containing the dried sample is weighed again, and the LOI is determined according to the formula:

$$LOI\% = (w - w_{calc})/w * 100\%$$

where w is the original weight of the sample, w_{calc} is the weight of the calcined sample after heating in the oven, both corrected with the weight of the crucible.

The mix may be formed of the refractory oxide materials and additional components, eg binder, with an aqueous liquid, most suitably water. The oxidic and binder materials are usually used in powder or crystal form. Shaping is most suitably and preferably by extrusion.

Conventionally extrusion mixes have an LOI determined by the need to combine particulate materials into a form which can be forced as a combined homogeneous entity through an extrusion die wherein the shear forces and generated heat cause fusion of the component materials into a shaped product which will maintain its integrity over time and in use, ie maintain mechanical strength. An extrusion mix is conventionally formed as a

dough-like material through kneading or mulling with the addition of water. The water will penetrate the pores of the materials as well as the interstices between materials. The LOI of an extrusion mix is therefore different depending on the nature (porosity) of the materials and size of the particles, and is often in the range of from 50 to 70%. The process of the present invention generally requires a higher water content for the mix than would normally or conventionally be applied for the materials utilised. Thus if a mix would normally require a 54% LOI, then a higher LOI, eg 58%, will increase the mesoporosity of the carrier.

The LOI is most suitably at least 56%, very suitably at least 57%, preferably at least 58%, more preferably at least 59%, especially at least or just in excess of 60%. Since LOI can be assessed to a high accuracy, 'in excess' includes for example 60.01%. Most preferably the LOI is in the range of from 60, or just in excess of 60, to 75%, particularly for carriers in which the refractory oxide is wholly or predominantly amorphous silica alumina.

Preferably the extrusion mix has an acidic pH, i.e. a pH of 7.0 or less. Most preferably the pH is in the range of from 3.5, suitably 4.0, to 7.0; more preferably 4.0 to 5.0, especially 4.2 to 4.7.

A suitable combination of LOI and pH conditions are an LOI of from 58, very suitably 60 or just in excess of 60, to 75%, and a pH in the range of from 3.5, preferably 4.0, to 5.0.

Any convenient mono-basic acid may be used to adjust the pH for the acidic solution; examples are nitric acid and acetic acid. During extrusion, conventionally extrusion aids may be utilized; usual extrusion aids include Superfloc, obtainable from Nalco.

Extrusion may be effected using any conventional, commercially available extruder. In particular, a screw-

type extruding machine may be used to force the mixture through orifices in a die plate to yield carrier extrudates of the required form, e.g. cylindrical or trilobed. The strands formed on extrusion may then be cut to the appropriate length.

The form of the carrier extrudates can also affect the activity of the final catalyst as is known in the art. The form is very suitably a conventional TRILOBE, twisted trilobe, or quadrilobe form (Trilobe is a trade mark). The form may usefully be a shaped trilobe as described in International patent publication WO 03/013725. Thus it may usefully be an elongate, shaped particle comprising three protrusions each extending from and attached to a central position aligned along the central longitudinal axis of the particle, the cross-section of the particle occupying the area encompassed by the outer edges of six outer circles around a central circle minus the area occupied by three alternating outer circles, wherein each of the six outer circles is touching two neighbouring outer circles and wherein three alternating outer circles are equidistant to the central circle, have the same diameter, and may be attached to the central circle. The three alternating outer circles preferably have a diameter in the range of from 0.74 to 1.3 times the diameter of the central circle, and more preferably have the same diameter as the central circle. Such particles most usefully have a length to diameter (L/D) ratio of at least 2, preferably in the range of from 2 to 5, and a length in the range of from 1 to 25 mm.

If desired, the carrier extrudates may be dried, e.g. at a temperature of from 100 to 300°C for a period of from 30 minutes to 3 hours, prior to calcination.

Calcination is conveniently carried out in air at a

temperature in the range of from 300 to 850°C, preferably from 400 to 825°C, for a period of from 30 minutes to 4 hours.

Specifically for the preparation of the shaped carrier when the oxide is an amorphous material, especially an amorphous silica alumina, any of the general carrier preparation techniques known in the art may be utilised, with the LOI and pH conditions adapted as above. A preferred method for the preparation of such a carrier comprises mulling a mixture of the amorphous silica-alumina and a suitable liquid, extruding the mixture and drying and heating the resulting extrudates, at a temperature in the range of from 400 to 850 °C, as for example described in WO-9410263 but is preferably from 650°C to 850°C, more preferably 700°C to 825°C, especially 750°C to 810°C. The extrudates may have any suitable form known in the art, for example cylindrical, hollow cylindrical, multilobed or twisted multilobed. A preferred shape for the catalyst particles is multilobed, for example trilobed. Typically, the extrudates have a nominal diameter of from 0.5 to 5 mm, preferably from 1 to 3 mm. After extrusion, the extrudates are dried. Drying may be performed at an elevated temperature, preferably up to 300 °C, more preferably up to 200 °C. The period for drying is typically up to 5 hours, preferably in the range of from 30 minutes to 3 hours. Preferably, the extrudates are then calcined after drying at very high temperature, as above, typically for a period of up to 5 hours, preferably in the range of from 30 minutes to 4 hours.

The present invention further provides a catalyst composition which comprises a carrier of the present invention, and at least one hydrogenation metal component selected from Group VIb and Group VIII.

At least one hydrogenation metal component is incorporated into the catalyst of the invention. This addition may occur at any stage during catalyst preparation, using techniques conventional in the art. For example, the hydrogenation component can be added to the oxide, or a mixture of oxide and binder, through co-mulling. However preferably the hydrogenation component is added to the formed extrudates either before or after optional calcining, using conventional impregnation techniques, eg as one or more aqueous impregnating solutions of Group VIB and/or Group VIII metal salts. If the impregnation occurs after calcination of the formed extrudates, then a further drying and optional calcination procedure is usefully employed.

Herein reference is made to the Periodic Table of Elements which appears on the inside cover of the CRC Handbook of Chemistry and Physics ('The Rubber Handbook'), 66th edition and using the CAS version notation.

Suitably the hydrogenation component is selected from nickel, cobalt, molybdenum, tungsten, platinum and palladium.

Examples of hydrogenation components that may thus suitably be used include Group VIB (e.g. molybdenum and tungsten) and Group VIII metals (e.g. cobalt, nickel, iridium, platinum and palladium), their oxides and sulphides. The catalyst composition will preferably contain at least two hydrogenation components, e.g. a molybdenum and/or tungsten component in combination with a cobalt and/or nickel component. Particularly preferred combinations are nickel/tungsten and nickel/molybdenum. Very advantageous results are obtained when these metal combinations are used in the sulphide form.

The present catalyst composition may contain up to 50 parts by weight of hydrogenation component, calculated

as metal per 100 parts by weight (dry weight) of total catalyst composition. For example, the catalyst composition may contain from 2 to 40, more preferably from 5 to 30 and especially from 10 to 20, parts by weight of Group VIB metal(s) and/or from 0.05 to 10, more preferably from 0.5 to 8 and advantageously from 1 to 6, parts by weight of Group VIII metal(s), calculated as metal per 100 parts by weight (dry weight) of total catalyst composition.

Particularly where the oxide is amorphous and especially amorphous silica alumina, the amount of Group VIII metal and Group VIB metal in the catalyst may vary depending on the metal type and the intended purpose of the catalyst, however, the amount of Group VIII metal will preferably be in the range of from 0.5 to 10 % wt, whilst the amount of Group VIB metal will preferably be in the range of from 3 to 30 % wt, measured as the metal, based on total weight of catalyst. A preferred catalyst according to the present invention, comprises nickel in an amount in the range of from 1 to 6 % wt, more preferably 3 to 5 % wt; and molybdenum in an amount in the range of from 6 to 18 %wt, preferably 10 to 15 % wt, or tungsten in an amount in the range of from 10 to 25 %wt, preferably 15 to 22 % wt.

As previously noted the Group VIII and Group VIB metals may be deposited on the carrier using any of the suitable methods known in the art, for example by ion exchange, competitive ion exchange or impregnation. Conveniently, the metals may be deposited by impregnating the carrier with an impregnation solution comprising appropriate metal-containing compounds, and optionally a chelating agent such as ethylene glycols, ethylene diamine, tartaric acid, malonic acid, citric acid, malic acid, nitriloacetic acid or ethylenediaminetetraacetic acid(EDTA). After impregnation, the catalyst is

preferably dried at a temperature of up to 200 °C, then heated or calcined at a temperature in the range of from 200 to 600 °C.

It has been found that the mesoporous carrier of the present invention permits a higher metals incorporation with a greater metal accessibility as well as a lower CBD for the resulting catalyst. This in turn permits a higher hydrogenation activity such that not only is an increased aromatics hydrogenation obtained but also desulphurisation can be given. This means that to achieve current low sulphur requirements for fuels, it would not be necessary to apply a further treatment with a desulphurisation catalyst.

In addition to the carrier of the invention possessing a uniquely low compacted bulk density (CBD), the catalyst composition of the invention has a CBD of at most 0.70, preferably at most 0.68, ml/g. The CBD is generally at least 0.55 ml/g; suitably at least 0.6 ml/g, and preferably at least 0.62 ml/g. Generally a catalyst composition based on an amorphous silica alumina carrier, especially one essentially free of aluminosilicate zeolite, suitably has a CBD in the range of from 0.60 to 0.65 ml/g.

For most preferred formulations containing amorphous silica-alumina or zeolite Y oxidic materials it is thus preferred that the Group VIb metal is tungsten present in an amount in the range of from 20 to 27 wt%, most preferably 21 to 27 wt%, especially 21 wt%, calculated as the trioxide and based on total weight of catalyst, and that the Group VIII metal is nickel present in an amount in the range of from 4 to 6 wt%, preferably 5 to 6 wt%, especially 5 wt%, calculated as the oxide and based on total weight of catalyst.

It can be difficult to impregnate such a high amount of metals using conventional impregnation solutions. We

have found particularly that the use of an organic compound having at least two moieties selected from carboxyl, carbonyl and hydroxyl, but especially from carboxyl groups, assists in the impregnation.

The present invention therefore provides a process for the preparation of a catalyst composition of the invention, which comprises drying or calcining a carrier of the present invention, if necessary or desired, and depositing at least one hydrogenation metal selected from Group VIb and Group VIII in the appropriate amount, wherein the deposition is effected by an impregnation solution containing an organic compound having at least two moieties selected from carboxyl, carbonyl, and hydroxyl groups. Following deposition the composition is suitably dried at elevated temperature, or by aging at room temperature until drying is effected. Most suitably drying occurs at a temperature in the range of from 100 to 200°C, eg 120°C. Calcination is preferably carried out, eg at a temperature in the range of from 200 to 500°C, but is optional.

The process preferably utilises an organic compound which is an organic acid selected from citric acid, tartaric acid, oxalic acid, malonic acid and malic acid.

Where the inorganic refractory oxide material of the carrier is an amorphous material, and particularly an amorphous alumina or the more preferred amorphous silica alumina, and is essentially free of zeolitic material, then the catalyst composition may further usefully contain one or more promoter elements.

Promoters to enhance the performance of catalysts based on amorphous carrier materials are known and described in the art. Thus silicon promotion is disclosed for amorphous catalyst compositions for a variety of uses in WO 95/11753, US-A-5,507,940, EP-A-533,451, and EP-A-586,196. Other promoters are also

known particularly for use in amorphous-based hydrocracking catalysts, for example in US-A-2002/0160911 and US-B-6,251,261 the use of boron and phosphorus is disclosed in addition to silicon as a promoter.

Thus the catalyst composition of the invention when utilising a shaped carrier of the invention consisting essentially of an amorphous inorganic refractory oxide material may contain in the range of from 0 to 20 wt%, preferably 0.1 to 15 wt%, and more preferably 0.1 to 10 wt% of a promoter element selected from silicon, boron and phosphorus, preferably silicon and boron, especially silicon. Where the promoter is silicon and the oxide comprises a silica material, then the amount of promoter silicon is additional to the amount of silicon present in the silica oxide material. Preferably the oxide is silica-alumina and the promoter is selected from silicon and boron; most preferably the promoter is silicon.

Many silicon sources can be used. Thus, it is possible to use ethyl orthosilicate $Si(OEt)_4$, siloxanes, polysiloxanes, silicones, silicone emulsions, halide silicates such as ammonium fluorosilicate $(NH_4)_2SiF_6$ or sodium fluorosilicate Na_2SiF_6. The silicomolybdic acid and its salts, and the silicotungstic acid and its salts can also be used advantageously. The silicon may also be added by, for example, impregnation of ethyl silicate in solution in a water/alcohol mixture. The silicon can be added by, for example, impregnation of a silicon compound of silicone type or silicic acid that is suspended in water.

The boron source may be boric acid, preferably orthoboric acid H_3BO_3, ammonium biborate or ammonium pentaborate, boron oxide, or boric esters. Boron can be introduced, for example, in the form of a mixture of boric acid, oxidized water and a basic organic compound

that contains nitrogen, such as ammonia, primary and secondary amines, cyclic amines, the compounds of the pyridine family and quinolines, and the compounds of the pyrrole family. Boron may be introduced by, for example, a solution of boric acid in a water/alcohol mixture.

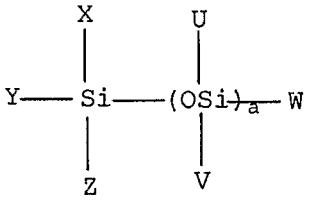
Suitable phosphorus sources are orthophosphoric acid H_3PO_4, and its salts and esters, such as the ammonium phosphates. The phosphorus can, for example, be introduced in the form of a mixture of phosphoric acid and a basic organic compound that contains nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the pyridine family and quinoliines and compounds of the pyrrole family.

We have found that the increase in catalyst activity that results from treating the hydrocracking catalyst with a liquid silicon-containing compound is confined to catalysts based on a predominantly amorphous silica-alumina carrier, and is not achieved when using an aluminosilicate zeolite carrier. Indeed, it has been found that the presence of aluminosilicate zeolite material in the amorphous silica-alumina carrier reduces the advantageous properties imparted by the promoter. Accordingly where the catalyst of the invention contains a promoter element then the carrier has to be essentially free of aluminosilicate zeolite, i.e. the amount of aluminosilicate zeolite in the carrier is less than 1 % wt, based on total carrier, more preferably less than 0.5 % wt and even more preferably less than 0.1 % wt. Most preferably, the carrier contains no aluminosilicate zeolite.

A promoted hydrocracking catalyst employed in the process of the present invention preferably comprises at least 0.5 % wt of silicon based on total weight of catalyst, which silicon has been incorporated in the

catalyst by treating the amorphous silica-alumina carrier with a liquid silicon-containing compound. For the avoidance of doubt, the amount of silicon incorporated by treatment with the liquid silicon-containing compound is additional to the silicon in the amorphous silica-alumina carrier. The additional silicon may be incorporated by treating the carrier with a liquid-silicon containing compound either before or after the metal components have been deposited on the carrier, however, in a preferred embodiment of the present invention the carrier is treated with the liquid silicon-containing compound after the metal components have been deposited on the carrier.

The liquid silicon-containing compound may be any silicon-containing compound that may act as a source of silicon and which may be applied to the carrier in liquid form. Preferably, the liquid silicon-containing compound is of general formula:-

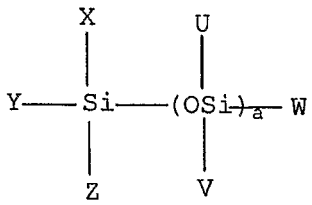


(I)

wherein U, V, W, X, Y, and Z can each individually and independently represent -R, -OR, -Cl, -Br, $-SiH_3$, -COOR, $-SiH_nCl_m$, R being either hydrogen, or an alkyl, cycloalkyl, aromatic, alkyl aromatic, alkylcycloalkyl radical having from 1 to 30 carbon atoms, "n" and "m" being whole numbers in the range of from 1 to 3 and "a" being a whole number in the range of from 0 to 1000. Preferably "a" is no more than 100, more preferably no more than 80, as liquids wherein "a" is greater than 100 have a high viscosity and are thus inconvenient to apply to the carrier.

In a particularly preferred embodiment, the liquid

silicon-containing compound is of general formula



(II)

wherein U, V, W, X, Y, and Z can each individually and independently represent -R or -OR, R being either hydrogen, or an alkyl, cycloalkyl, alkylcycloalkyl radical having from 1 to 30 carbon atoms and "a" being a whole number in the range of from 0 to 60.

Examples of liquid silicon-containing compounds that may advantageously be employed in the present invention include alkyl orthosilicates such as ethyl orthosilicate ($Si(OEt)_4$), methyltriethyl siloxane ($Si(OEt)_3Me$), and silicone oils such as polydimethylsiloxane.

A convenient means of treating the carrier with the liquid silicon-containing compound comprises adding the liquid to the carrier and subsequently heating the silicon-liquid treated carrier at elevated temperature, typically in the range of from 100 to 400 °C. In order to facilitate the treatment, the liquid silicon-containing compound may optionally be dissolved in a suitable organic solvent such as a lower alkane, however, in some circumstances, for example when preparing a large quantity of catalyst, the liquid silicon-containing compound may be applied neat. As will be understood by those skilled in the art, the amount of liquid silicon-containing compound applied to the carrier may vary depending on the particular silicon-containing compound employed, however, it is preferably such that the amount of silicon deposited on the carrier, as determined by elemental analysis, is at least 1 % wt, based on total catalyst. More preferably the amount of silicon is in the range of from 1 to 10 % wt,

even more preferably 1 to 5 % wt, based on total catalyst.

In a preferred embodiment of the present invention, the promoted hydrocracking catalyst is prepared by a process which comprises impregnating an amorphous silica-alumina carrier with a Group VIII metal and a Group VIB metal, heating the impregnated carrier at a temperature in the range of from 150 to 500 °C, treating the impregnated carrier with a liquid silicon-containing compound, and then heating the silicon-liquid treated catalyst at a temperature in the range of from 100 to 300 °C.

When preparing the hydrocracking catalyst in accordance with the above preferred embodiment, the activity of the catalyst may be optimised by varying the temperature at which the catalyst is heated. In this regard, very good results have been achieved when the heating temperature following metal impregnation is in the range of from 150 to 250 °C, and the heating temperature following silicon-compound treatment is in the range of from 150 to 250 °C.

In the process of the present invention, all hydrocracking catalysts of the invention, whether promoted or not, are preferably sulphided prior to use. The catalyst may conveniently be sulphided by any of the techniques known in the art, such a ex-situ or in-situ sulphidation. For example, sulphidation may be performed by contacting the catalyst with a sulphur-containing gas, such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide or a mixture of hydrogen and a mercaptan, such as butylmercaptan. Alternatively, sulphidation may be carried out by contacting the catalyst with hydrogen and a sulphur-containing hydrocarbon oil, such as sulphur-containing kerosene or gas oil. The sulphur may also be introduced into the

hydrocarbon oil by the addition of a suitable sulphur-containing compound, for example dimethyldisulphide or tert-nonylpolysulphide.

The present invention also provides a process for converting a hydrocarbonaceous feedstock into lower boiling materials which comprises contacting the feedstock with hydrogen at elevated temperature and elevated pressure in the presence of a catalyst composition according to the present invention. Such a process is commonly termed hydrocracking.

Examples of such processes comprise single-stage hydrocracking, two-stage hydrocracking, and series-flow hydrocracking. Definitions of these processes can be found in pages 602 and 603 of Chapter 15 (entitled "Hydrocarbon processing with zeolites") of "Introduction to zeolite science and practice" edited by van Bekkum, Flanigen, Jansen; published by Elsevier, 1991.

It has been found that particularly with catalysts containing carriers comprising the preferred amorphous silica alumina and/or zeolitic materials of the present case and the high metals contents mentioned above, the catalyst formed can also exhibit good hydrodesulpurisation of the remaining sulphur in a conventional hydrocracking feedstock. Furthermore the presence of nitrogen contaminants in the feedstock does not hinder or deactivate the catalysts of the invention.

It will be appreciated that the hydroconversion processes of the present invention can be carried out in any reaction vessel usual in the art. Thus the process may be performed in a fixed bed or moving bed reactor. Also the catalyst of the invention may be used in conjunction with any suitable co-catalyst or other materials usual in the art. Thus for example the catalyst of the invention may be used in stacked bed formation with one or more other catalysts useful in

hydroprocessing, for example with a catalyst containing a different zeolite, with a catalyst containing a faujasite zeolite of different unit cell size, with a catalyst utilizing an amorphous carrier, and so on. Various stacked bed combinations have been proposed in the lierature: WO-99/32582; EP-A-310,164; EP-A-310,165; and EP-A-428,224 may, for example, be mentioned. As noted above, with preferred catalyst compositions of the present invention additional post-treatment with a hydrotreating catalyst to remove residual sulphur may not be necessary.

The hydrocarbonaceous feedstocks useful in the present process can vary within a wide boiling range. They include atmospheric gas oils; coker gas oils; vacuum gas oils; deasphalted oils; fractions, eg gas oils and waxes, obtained from a Fischer-Tropsch synthesis process, long and short residues, catalytically cracked cycle oils, thermally or catalytically cracked gas oils, and syncrudes, optionally originating from tar sand, shale oils, residue upgrading processes and biomass. Combinations of various hydrocarbon oils may also be employed. The feedstock will generally comprise hydrocarbons having an initial boiling point of at least 330°C. The boiling range will generally be from about 330 to 650°C, with preference being given to feedstocks having a boiling range of from about 340 to 620°C. The feedstock may have a nitrogen content of up to 5000 ppmw (parts per million by weight) and a sulphur content of up to 6 %w. Typically, nitrogen contents are in the range from 250 to 2000 ppmw and sulphur contents are in the range from 0.2 to 5 %w. It is possible and may sometimes be desirable to subject part or all of the feedstock to a pre-treatment, for example, hydrodenitrogenation, hydrodesulphurisation (HDS) or hydrodemetallisation,

methods for which are known in the art.

The process of the invention may conveniently be carried out at a reaction temperature in the range of from 250 to 500°C, preferably in the range of from 300 to 450°C.

The present process is preferably carried out at a total pressure (at the reactor inlet) in the range of from 3 x 10^6 to 3 x 10^7 Pa, more preferably from 4 x 10^6 to 2.5 x 10^7 Pa and even more preferably from 8 x 10^6 to 2 x 10^7 Pa. Where a hydrocracking process is carried out at a low pressure of, for example 4 x 10^6 to 1.2 x 10^7 Pa, this may be termed 'mild hydrocracking'.

The hydrogen partial pressure (at the reactor inlet) is preferably in the range from 3 x 10^6 to 2.9 x 10^7 Pa, more preferably from 4 x 10^6 to 2.4 x 10^7 Pa and still more preferably from 8 x 10^6 to 1.9 x 10^7 Pa.

A space velocity in the range from 0.1 to 10 kg feedstock per litre catalyst per hour ($kg.l^{-1}.h^{-1}$) is conveniently used. Preferably the space velocity is in the range from 0.1 to 10, particularly from 0.2 to 8, and preferably from 0.5 to 5 $kg.l^{-1}.h^{-1}$.

The ratio of hydrogen gas to feedstock (total gas rate or the gas/feed ratio) used in the present process will generally be in the range from 100 to 5000 Nl/kg, but is preferably in the range from 200 to 3000 Nl/kg, more preferably 250 to 2000 Nl/Kg.

The hydrocracking process of the present invention may be used to particularly advantageous effect in single-stage hydrocracking, wherein it gives a good efficiency of conversion even on exposure to feedstocks comprising nitrogen and sulphur-containing contaminants.

One application of single-stage hydrocracking is the production of middle distillate fractions. Middle

distillate fractions are liquid fractions having a boiling point in the range of from 150 to 370 °C, and include products such as kerosene (150 to 250 °C) and gas oil (250 to 370 °C). There is a growing demand for middle distillate products, and as such there is always a need for hydrocracking processes that show a strong selectivity for middle distillates with minimum formation of gaseous (C_1-C_4) material, i.e. processes whose products contain low amounts of gaseous material and high amounts of middle distillate. In this regard, the hydrocracking process of the present invention has proven to be extremely selective at converting heavy distillate feedstocks, such as heavy gas oils or deasphalted oils to middle distillate fractions.

Accordingly, a preferred embodiment of the present invention provides for the single-stage conversion of a heavy gas oil or a deasphalted oil to a middle distillate fraction.

The present invention will now be illustrated by the following Examples.

Examples

By the following general procedure catalyst carriers and catalysts were prepared using different amounts of zeolite and inorganic refractory oxide in each catalyst formulation as noted below.

General procedure:

A catalyst carrier was prepared by mixing a zeolite with refractory inorganic oxide in the proportions required. Water and acid were added in order to achieve the specified LOI and pH and the mixture mulled in a mix-muller until an extrudable mix was obtained. The mixture was then extruded, together with an extrusion aid (Superfloc), into extrudates having, in cross-section, a tri-lobe shape. The extrudates were dried statically for

2 hours at 120°C and then calcined for 2 hours at 535°C. The catalyst particles so-obtained were cut to be of regular length with a diameter of either 1.5 mm or 2.5 mm, measured from the top to the bottom of a nominal triangle formed by the tri-lobe.

The metal hydrogenation components of nickel and tungsten were then incorporated by impregnation of the pellets with an homogenized aqueous solution of nickel nitrate and ammonium metatungstate. Citric acid or malic acid was incorporated into certain of the impregnation solutions as noted. The impregnated extrudates were dried at ambient conditions in hot circulating air for 1 hour and then at 120°C for 2 hours and finally calcined at 500°C for 2 hours.

Activity testing

The hydrocracking performance of the catalysts was assessed in a number of second stage series-flow simulation tests. The testing was carried out in once-through microflow equipment which had been loaded with a top catalyst bed comprising 1 ml C-424 catalyst (commercially available from Criterion Catalysts & Technologies USA) diluted with 1 ml of 0.1 mm SiC particles and a bottom catalyst bed comprising 10 ml of the test catalyst diluted with 10 ml of 0.1 mm SiC particles. Both catalyst beds were presulphided prior to testing.

Each test involved the sequential contact of a hydrocarbonaceous feedstock (a heavy gas oil) with the top catalyst bed and then the bottom catalyst bed in a once-through operation under the following process conditions: a space velocity of 1.5 kg heavy gas oil per litre catalyst per hour ($kg.l^{-1}.h^{-1}$), a hydrogen gas/heavy gas oil ratio of 1440 Nl/kg, a hydrogen sulphide partial pressure of 5.6×10^5 Pa (5.6 bar) and a

total pressure of 14 x 10^6 Pa (140 bar).

A standard heavy gas oil test feed was used having the following properties:

Carbon content	:	86.64 %w
Hydrogen content	:	13.36 %w
Sulphur (S) content	:	122 ppmw
Nitrogen (N) content	:	12 ppmw
Added n-Decylamine	:	12.3 g/kg (equivalent to 1100 ppmw N)
Total nitrogen (N) content	:	1112 ppmw
Density (15/4 °C)	:	0.8805 g/ml
Density (70/4 °C)	:	0.8463 g/ml
Molar weight	:	433 g
Initial boiling point	:	355 °C
50 %w boiling point	:	425 °C
Final boiling point	:	606 °C
Fraction boiling below 370 °C	:	2.57 %wt
Fraction boiling above 540 °C	:	10.0 %wt

Hydrocracking performance was assessed at conversion levels between 40 and 90 %wt net conversion of feed components boiling above 370°C. To compare activity, the obtained results, expressed as the temperature required to obtain 65 %wt net conversion of feed components boiling above 370°C, are shown in the Tables below.

Hydrodesulphurisation (HDS) activity was assessed using the same test feed and under the same conditions as above but without using hydrogen sulphide addition.

Loss on ignition (LOI) was assessed by the method hereinbefore described. Compacted bulk density was assessed following the method of ASTM D 4180-03 except that a tamper is placed on the top of the test sample within a 250 ml graduated cylinder placed firmly on a

vibrating table, and the sample is assessed without predrying and a correction for dry weight is made separately according to the formula

CBD = measured CBD x $\frac{100-LOI}{100}$.

Here LOI is determined by the same method described herein but with heating to 485°C.

Total pore volume and mesopore volume were determined by mercury intrusion porosimetry following ASTM D4284-03.

In carriers C to K the same high surface area USY zeolite Y was used and is a very ultrastable zeolite Y having a unit cell size of 24.32Å, a molar silica to alumina ratio of 29, a BET surface area of 893 m^2/g, and a micropore volume of 0.298 ml/g, prepared as described in WO 2004/047988. Herein, unit cell size is determined by X-ray diffraction using ASTM D 3942-80; SAR is bulk or overall SAR and is determined by chemical analysis; BET surface area is determined by the BET method of Brunauer, Emmett and Teller, J.Am. Chm. Soc., 60, 309 (1938), and ASTM D4365-95 using a single point assessment from nitrogen adsorption at a p/po value of 0.03; micropore voume is assessed by the t-plot method using nitrogen as adsorbate as described by Lippens, Linsen and de Boer, Journal of Catalysis, 3-34 (1964).

The carriers used have the following compositions. All percentages are percentages by weight, basis total carrier. Unless otherwise stated, the amorphous silica alumina is Al-Si:55-45%w and the alumina is wide pore alumina, both available from Criterion Catalysts and Technologies, USA (CC&T).

Carrier A has 10% USY zeolite Y of SAR 10; 22.5 % alumina; 62.5 % amorphous silica alumina

Carrier B has 10% USY zeolite of SAR 10; and 90% amorphous silica alumina

Carrier C has 48% high surface area USY zeolite Y; 8% alumina; 44% amorphous silica alumina

Carrier D has 50% high surface area USY zeolite Y; 8% alumina; 42% amorphous silica alumina

Carrier E has 45% high surface area USY zeolite Y; 9% alumina; 46% amorphous silica alumina

Carrier F has 45% high surface area USY zeolite Y; 9% alumina; 46%amorphous silica alumina

Carrier G has 35% high surface area USY zeolite Y; 34% silica alumina (containing 6% silica, available from CC&T); 31% wide pore alumina available from CCIC

Carriers H to K have 35% high surface area USY zeolite Y; 10% alumina; 55% amorphous silica alumina.

The catalysts used have the following metal loadings given as %w basis total catalyst weight.

Catalysts 1,2 and 14 have 5 wt% nickel and 21wt% tungsten

Catalysts 3, 4, 7, and 13 have 3.3 wt% nickel and 16 wt% tungsten

Catalysts 5, 6, 8 to 11 have 4 wt% nickel and 17 wt% tungsten

Catalyst 12 has 2 wt% nickel and 6.5 wt% tungsten.

In the Tables below TL indicates trilobe; TX indicates a shaped trilobe of the type described in WO 03/013725.

Carrier	Shape	LOI extrusion mix	Acidity extrusion mix	CBD	Hg total pore volume (PV)	Hg meso pore volume	% PV in mesopores
		%w	pH	g/ml	ml/g	ml/g	
A	1.6 mm			0.52	0.66		
B	1.6 mm			0.44	0.917		
C	2.5 mm	54.80	3.4	0.52	0.516	0.368	71.31
D	2.5 mm	59.60	3.6	0.40	0.740	0.520	70.27
E	2.5 mm	56.80	3.7	0.43	0.696	0.490	70.40
F	2.5 mm	56.80	3.7	0.38	0.696	0.487	69.97
G	2.5 mm	60.40	5.8	0.42	0.864	0.459	53.12
H	2.5 mm	61.20	7.0	0.39	0.862	0.491	56.96
I	2.5 mm	61.60	4.2	0.42	0.782	0.558	71.35
J	2.5 mm	61.00	4.7	0.40	0.839	0.579	69.01
K	2.5 mm	58.60	4.4	0.42	0.778	0.576	74.04

Effect of carrier CBD/pore volume

Catalyst	Carrier	Carrier CBD g/ml	Carrier Hg pore volume ml/g	T 65%w 370 °C+ °C	C1-C4 %w	C5-150 °C %w	150-370 °C %w	Mono arom. %wof	Di-arom. %wof	Tri+-arom. %wof
1	A	0.52	0.66	398	2.8	27.4	69.8	47	81	75
2	B	0.44	0.92	399	2.3	27.7	70.1	44	80	75
3	C	0.52	0.52	374	4.7	36.8	58.4	28	71	64
4	D	0.40	0.74	371	4.1	34.5	61.4	44	85	78

In catalysts 1 and 2, a reduction solely in CBD brings little activity or selectivity advantage. The reduced CBD and increased mesopore volume shown by catalyst 4 of the invention however displays a higher activity, selectivity and hydrogenation compared with catalyst 3.

Effect of shape and surface area/metal load

Catalyst	Carrier	Shape	Carrier CBD	Carrier Hg surface Area	Ni	W	T 65%w 370+	C1-C4	C5-150 °C	150-370 °C	Mono arom.	Di- arom.	Tri+- arom.
		mm	g/ml	m2/g	%w	%w	°C	%w	%w	%w	%wof	%wof	%wof
5	E	TL 2.5	0.43	257	4	17	377	4.8	35.2	60.0	37	82	76
6	F	TX 2.5	0.38	257	4	17	376	4.5	33.5	62.0	38	81	74
7[2]	F	TX 2.5	0.38	257	3.3	14	375	3.2	33.8	63.0	38	82	78

Effect of mesopore volume

Catalyst	Carrier	Carrier CBD	Carrier Hg pore volume	Hg mesopore volume	T 65%w 370+	C1-C4	C5-150 °C	150-370 °C	Mono arom.	Di- arom.	Tri+- arom.
		g/ml	ml/g	ml/g	°C	%w	%w	%w	%wof	%wof	%wof
8[2]	G	0.42	0.86	0.46	381	4.4	34.3	61.3	37	81	70
9[2]	H	0.39	0.86	0.49	380	4.3	33.8	61.9	39	82	76
10[2]	I	0.42	0.78	0.56	380	4.0	34.1	61.9	43	85	75
11[1]	J	0.40	0.84	0.58	377	3.3	33.6	63.1	42	83	77

Effect of metals content

Catalyst	Carrier	Ni	W	T 65%w 370+	C1-C4	C5-150 °C	150-370 °C	Mono arom.	Di-arom.	Tri+- arom.	HDS
		%w	%w	°C	%w	%w	%w	%wof	%wof	%wof	%wof
12[1]	K	2	6.5	382	3.8	35	61.0	44	81	72	76
13[1]	K	3.3	16.2	380	3.3	33	63.2	71	91	83	92
14[1]	K	5	21	378	3.5	31	65.4	77	94	87	93

[1] impregnation solution contains citric acid
[2] impregnation solution contains malic acid
%wof indicates percent weight removed basis original amount in feed.

C L A I M S

1. Shaped catalyst carrier which comprises at least one inorganic refractory oxide, which carrier has a monomodal pore size distribution wherein at least 50 % of the total pore volume is present in pores having a diameter in the range of from 4 to 50 nm and wherein the pore volume present in said pores is at least 0.4 ml/g, all as measured by mercury intrusion porosimetry.

2. Catalyst carrier as claimed in claim 1, wherein the pore volume present in pores of diameter from 4 to 50 nm is at least 0.5 ml/g, preferably in the range of from 0.5 to 0.8 ml/g.

3. Catalyst carrier as claimed in claim 1 or claim 2, wherein at least 60 %, preferably in the range of from 60 to 90 %, of the total pore volume is present in pores having a diameter in the range of from 4 to 50 nm

4. Catalyst carrier as claimed in any one of claims 1 to 3, which comprises an amorphous silica-alumina material or a crystalline aluminosilicate faujasite material.

5. Catalyst carrier as claimed in any one of claims 1 to 4, wherein the compacted bulk density is in the range of from 0.35 to 0.50 g/ml.

6. Process for the preparation of a catalyst carrier as claimed in any one of claims 1 to 5, which comprises shaping a mix comprising said at least one refractory oxide wherein the mix has an LOI in the range of from 55 to 75%.

7. Process as claimed in claim 6, wherein the shaping is by extrusion.

8. Process as claimed in claim 7, wherein the mix is an extrusion mix which has a pH in the range of from 3.5 to 7.0.

9. Process as claimed in any one of claims 6 to 8, wherein the LOI is in the range of from 58% to 75%, preferably 60 to 65%, and the pH is in the range of from 3.5 to 5.0, preferably 4.0 to 5.0.

10. Process as claimed in claim 8 or claim 9, wherein acid is added to the extrusion mix to adjust the pH, which acid is selected from acetic acid and nitric acid.

11. Carrier obtainable by a process as claimed in any one of claims 6 to 10.

12. Catalyst composition which comprises a carrier as claimed in any one of claims 1 to 5, and 11; at least one hydrogenation metal component selected from Group VIb and Group VIII metals; and optionally, where the carrier is essentially free of aluminosilicate zeolite, at least one promoter element selected from silicon and boron.

13. Catalyst composition as claimed in claim 12, wherein the Group VIb metal is tungsten present in an amount in the range of from 20 to 27 wt%, preferably 21 wt%, calculated as the trioxide and based on total weight of catalyst, and the Group VIII metal is nickel present in an amount in the range of from 4 to 6 wt%, preferably 5 wt%, calculated as the oxide and based on total weight of catalyst.

14. Process for the preparation of a catalyst composition as claimed in claim 12 or claim 13, which comprises optionally calcining a carrier as claimed in any one of claims 1 to 5 and 11, and depositing at least one hydrogenation metal selected from Group VIb and Group VIII in the appropriate amount, wherein the deposition is effected by an impregnation solution containing an organic compound having at least two moieties selected from carboxyl, carbonyl, and hydroxyl.

15. Process as claimed in claim 14, wherein the organic compound is an organic acid selected from citric acid, tartaric acid, oxalic acid, malonic acid and malic acid.

16. Catalyst composition obtainable by the process as claimed in claim 14 or claim 15.

17. Hydrocracking process which comprises contacting a hydrocarbonaceous feed with a catalyst composition as claimed in any one of claims 12, 13 and 16 at elevated temperature and pressure.

18. Use of a catalyst composition as claimed in any one of claims 12, 13 and 16 as a combined hydrocracking plus desulphurisation catalyst for a hydrocarbonaceous feedstock.