Description

The invention relates to a catalyst which is suitable for selectively converting hydrocarbons in a hydrotreatment process. More particularly, the invention relates to catalysts suitable for hydrodesulphurising and/or hydrodenitrogenising hydrocarbons while simultaneously cracking them.

It is known that to enhance the cracking activity such catalysts may contain an alumina-silica-alumina carrier built up from alumina and amorphous silica-alumina, on which there have been provided hydrogenation metals, e.g., molybdenum, nickel, and/or cobalt. Such catalysts are described in US Patent Specification No. 4 238 316, which discloses catalysts containing 10-60 wt.% of alumina derived from boehmite or a mixture of boehmite and amorphous hydrous alumina and 40-90 wt.% of amorphous silica-alumina. In addition such catalysts may contain a small quantity of hydrogenation metals, e.g., tungsten, molybdenum, and nickel. This patent specification advises against the use of boron in such a quantity as might affect the catalytic conversion.

Alumina-silica-alumina-containing catalysts also can be employed to improve selectivity in hydrocarbon hydrotreatment processes. Such is described in US Patent Specification No. 4 062 809, which discloses the preparation of catalysts by mixing an alumina matrix with a silica-alumina cogel and adding thereto such hydrogenation metals as molybdenum, tungsten, nickel, and cobalt. Said catalysts display a high selectivity in particular when converting heavy oils into middle distillates.

The object of the catalysts according to the present invention is to achieve higher activity still both in the hydrotreatment and the hydrocracking process. In particular, it is envisaged to improve the conversion as well as the denitrogenation and the desulphurisation without the selectivity being reduced in the process. The invention is characterised in that, in addition to a carrier built up from alumina and silica-alumina, a Group VIB hydrogenation metal, and a Group VIII hydrogenation metal, the catalyst contains a catalytically active quantity of boron.

Employing a catalytically active quantity of boron generally means, a quantity of 1-20 wt.% of boron, calculated as the metal oxide on the catalyst's overall quantity by weight. However, these limits cannot be interpreted very strictly, since differences in catalyst composition, e.g., in the amount of alumina used, can lead to the utilisation of different, also appropriate quantities of boron. Preferably, the catalyst composition will contain 2-10 wt.% of boron, more particularly 4-8 wt.%, calculated on the catalyst's overall quantity by weight.

The boron-containing compound used in preparing the invention catalyst may be, e.g., H_3BO_3, B_2O_3 or organic boron compounds such as $B(OC_2H_5)_3$. It is preferred to use H_3BO_3. The compounds may be used either in the solid form or in solution.

If the carrier material is prepared by mixing alumina and silica-alumina according to one of the processes described hereinafter, the catalyst will display a high activity. The carrier material may be built up from a mixture of alumina and amorphous silica-alumina, but also from a mixture of alumina and silica-coated alumina. Whenever reference is made to silica-alumina in the description of the present invention, either silica-coated alumina or amorphous silica-alumina is meant.

For use in the catalyst according to the present invention it is preferred to employ mixtures of alumina and amorphous silica-alumina. Generally, suitable amorphous silica-alumina will contain 10-90 wt.% of silica, more particularly 20-90 wt.%. Preferably, use is made of amorphous silica-alumina containing 60-90 wt.% of silica.

If a carrier material of alumina and silica-coated alumina is employed, it is preferred for the silica-coated alumina to contain 10-20 wt.% of silica.

The catalyst according to the invention contains about 5-60 wt.% of silica, calculated on the whole catalyst. Preferably, the catalyst will contain 10-50 wt.% of silica, more particularly 10-40 wt.%.

To attain satisfactory hydrotreatment activity it is preferred to provide such a quantity of a Group VIB metal and a Group VIII metal as will give a prepared catalyst containing in the range of 2 to 40 wt.% of the Group VI B metal and in the range of 0,5 to 10 wt.% of the Group VIII metal, both calculated as the metal oxides.

The Group VIB metal provided advantageously is molybdenum and/or tungsten, with notably an amount in the range of 5 to 30 wt.%, more particularly in the range of 5 to 20 wt.%, being likely to give favourable results.

Eligible Group VIII metals include in particular nickel, cobalt or a combination thereof. The prepared catalyst preferably will contain 1-10 wt.% of such a metal or a combination of such metals, more particularly 2-8 wt.%.

Highly favourable results are obtained when the catalyst contains 5-20 wt.% of molybdenum and 2-6 wt.% of nickel and/or cobalt, the amounts being calculated on the weight of the prepared catalyst.

Suitable catalysts according to the invention will generally have a pore volume in the range of 0,3 to 1,0 ml/g, preferably in the range of 0,35 to 0,80 ml/g, as determined by mercury porosimetry. The catalyst's surface area will generally be in the range of 100 to 400 m^2/g, preferably in the range of 150 to 350 m^2/g, as determined by the BET nitrogen adsorption procedure. The median pore diameter to be selected will vary, depending on the feed to be treated, and generally is in the range of 3 to 30 nm (30 to 300 Å), preferably in the range of 5 to 15 nm (50 to 150 Å), as determined by mercury porosimetry.

The catalyst according to the present invention may be prepared employing conventional methods for preparing catalysts.

It was found that favourable results are obtained if prior to the introduction of the Group VIII hydrogenation metal a calcination step is carried out. If use is made of several Group VIII metals, the most favourable result is always obtained when calcination takes place prior to the introduction of the entire quantity of Group VIII hydrogenation metals. Highly favourable results are obtained if boron or a boron-containing compound is provided ahead of the Group VIII hydroge-nation component and at least one calcination step is carried out between the boron being added and the addition of the Group VIII metal. The calcination referred to may form the sole calcination step or, alternatively, be the first or last step or some intermediate step in a series of calcination steps.

Calcining may be carried out either in air or in nitrogen, with, generally, temperatures in the range of 400 • to 1000 • C being maintained for 0,5 to 16 hours. It is preferred to calcine in air.

It is possible to provide the boron either in the dry form by mixing or in solution by means of impregnation. Further suitable ways of adding the boron component are co-extrusion with (a portion of) the carrier material or co-impregnation with a solution containing a Group VIB metal component.

A very suitable way of providing the hydrogenation metals can be by means of impregnation with an appropriate metal-containing solution. Examples of suitable (water) soluble Group VIB compounds include molybdic acid, ammonium dimolybdate, and ammonium heptamolybdate. Also MoO_3 was found to be very suitable, notably in the case of the molybdenum being provided by means of copelletisation and/or co-extrusion.

As suitable water-soluble Group VIII metal compounds may be mentioned salts derived from strong acids, such as chlorides, nitrates, and sulphates, and salts derived from weak acids, such as acetates and carbonates. Also eligible are the metal hydroxides in question. Preference is given to nitrates and carbonates. Examples of such water-soluble compounds include $Ni(NO_3)_2$, $Co(NO_3)_3$, $Ni(CO_3)_2$, $Co(CO_3)_3$, and $Co_2(CO_3)_3$, with $Ni(NO_3)_2$ and $Co(NO_3)_2$ being preferred.

In actual practice the carrier material will be subjected to a calcination step before impregnation is proceeded with. In the case of multiple impregnation the catalyst may be dried between times and, optionally, calcined.

Alternatively, one or more of the hydrogenation metal compounds may be added to all or a portion of the not yet shaped carrier material in the dry form. A further alternative consists in the intimate mixture of one or more appropriate metal compounds with the carrier material during the shaping step. Procedures that can be used to this end are copelletisation and co-extrusion. Preferably, calcining will always take place prior to the introduction of the Group VIII metal. More particularly, in the above processes there will be a calcination step between the boron being added and the addition of the Group VIII metal.

The carrier material can be prepared, int. al., as disclosed in US 4 062 809. In general, the preparation of a suitable carrier material will comprise mixing alumina with amorphous silica-alumina in the dry or the hydrous form. Thus, e.g., it is possible to mix hydrated alumina, boehmite or pseudoboehmite with a homogeneous silica-alumina cogel, or to mix the alumina hydrogel with a graft copolymer of silica and alumina and then extrude the homogenised mixture. The resulting carrier material is built up from silica and alumina, with a portion of the alumina that is present having silica incorporated into the lattice.

The preparation of the alumina may be as in US Patent Specification No. 4 154 812, which describes the preparation of a hydrated alumina by precipitating one or more aluminium salts, and then heating the alumina to dry the material.

As suitable materials for the preparation of alumina may be mentioned boehmite, pseudoboehmite, and pseudoalumina. The preferred starting material for alumina is pseudoboehmite.

A suitable procedure for preparing the amorphous silica-alumina is disclosed, int. al., in US 3 210 294. A different method of preparation which is also suitable is given, int. al., in US 4 238 316. It is preferred to prepare amorphous silica-alumina by means of coprecipitation of soluble silica and alumina compounds.

A different carrier material which is also suitable can be prepared by mixing alumina with a silica-coated alumina. For a description of the preparation of such a silica-coated carrier material reference is made to EP-A 0160 475.

The sequence in which the catalyst components are to be added is subject to wide variation. Thus, the boron-containing compound may be mixed with precursor carrier material, e.g., boehmite. Alternatively, it is possible to mix said compound with the carrier material either before or during the shaping process. The boron-containing compound may be added to, say, a silica-alumina slurry and/or an alumina slurry, or be provided by means of co-extrusion. In each of these cases the carrier material may have been mixed with a Group VIB metal component or not. Depending on the catalyst's field of application, it may well be advisable to carry out an intermediate shaping step.
According to another catalyst preparation method which is also suitable, the carrier is shaped, dried, and/or calcined prior to the addition of a boron-containing compound.

It is preferred to provide the hydrogenation metals as follows: first, the Group VIB metal is co-extruded with the carrier material; the product is shaped, and calcined, whereupon the shaped material is impregnated with the Group VIII metal. In such a preparative process boron is preferably added prior to the calcination.

It has been found that very favourable hydrotreatment and cracking processes for vacuum gas oil feeds can be carried out using a catalyst prepared by mixing the Group VIB metal oxide in the dry form with the alumina in the dry form, mixing the resulting mixture with a boron-containing compound, and then adding a suitable amount of water-containing amorphous silica-alumina. In such a process the boron-containing compound may be added either in the dry form or in aqueous solution. The envisaged catalyst is finally obtained by adding the Group VIII metal by means of impregnation after shaping and calcining, and then calcining again.
A suitable alternative consists in the boron compound being added to the hydrated alumina gel during or after its precipitation, followed by further processing as described above.

A highly suitable procedure for preparing the catalyst carrier was found to comprise mixing an alumina precursor, such as boehmite, with silica-alumina, MoO_3, and H_3BO_3, all in the powdered form, followed by the addition of a nitric acid solution and homogenising to form an extrudable paste. Such a preparative process can very readily be followed by the shaping, drying, and calcining of the material, after which, say, nickel is added to the resulting carrier by means of impregnation. Finally, the catalyst composition, having been dried or not, can be calcined.

The present catalyst is highly suitable for hydrotreating vacuum gas oil, displaying unexpected activity on all fronts: not only its desulphurisation activity, but also its denitrogenation and cracking activity are found to be highly satisfactory if use is made of the now developed catalyst. Notably, the catalyst is found to display increased activity if it is used for the hydrotreatment of vacuum gas oil to form middle distillate oil.
By vacuum gas oils are meant in particular those oils boiling in the range of 200° to 580°C. The term middle distillate refers to oils boiling in the range of 175° to 390°C.

Typical hydrotreatment process conditions include temperatures between 300° and 450°C, hydrogen pressures between 25 and 200 bar, H_2:oil ratios between 150 and 1500 Nl/l, and space velocities (hr^{-1}) between 0,1 and 5.

The invention will be illustrated with reference to the following examples.

Example 1

Preparation of catalyst A according to the invention

A boron acid-containing solution was prepared by dissolving 167,5 g of H_3BO_3 in 30 ml of a 65%-nitric acid solution and 2260 ml of water at a temperature of 60°C.
Meanwhile, 914 g of alumina (LOI = 24,4%) were mixed with 203,5 g of molybdenum oxide powder. To this whole were added the aqueous solution of boric acid and 1013 g of amorphous silica-alumina (LOI = 30,5%). The resulting mixture was shaped to form cylindrical extrudates of 1,5 mm in diameter and, after drying at 120°C for 20 hours, the extrudates were calcined in an air atmosphere at 600°C for one hour.
The calcined extrudates were then impregnated with an aqueous solution of nickel nitrate; the product was dried and subsequently calcined at 600°C for one hour. The resulting catalyst contained 4,8 wt.% of boron oxide, 11,2 wt.% of molybdenum oxide, 3,9 wt.% of nickel oxide, and 33,4 wt.% of silica, the remainder of the catalyst being made up of alumina.
The surface area of the obtained catalyst A was found to be 301 m^2/g, the pore volume, as determined by mercury porosimetry, was 0,58 ml/g. The average pore diameter was determined to be 7,2 nm (72 Å), the pore volume of pores having a diameter greater than 3,6 nm (36 Å) being 0,54 ml/g and that of pores with a diameter greater than 20,0 nm (200 Å) being 0,027 ml/g.

Example 2

Testing

Catalyst A of Example 1 was tested in an isothermal pilot unit containing 100 ml of catalyst diluted with 100 ml of inert SiC chips (46 mesh) of the trademark Carborundum. This dilution was used to reduce backmixing. (A. de Bruyn, 6th International Congress on Catalysis, London (1976), p. 951.)
Prior to its introduction into the reactor the catalyst was dried at 350 °C for one hour. The weight of 100 ml of catalyst after being dried at this temperature was 66 g.
The catalyst was presulphided in the reactor with gas oil enriched with dimethyldisulphide according to generally accepted presulphiding procedures.

The feedstock used was Kuwait vacuum gas oil analysing as follows:

sulphur	2,9 wt.%
nitrogen	900-1000 ppm
density (50 °C)	0,900 kg/l
5% BP (ASTM-1160)	384 °C
50% BP (ASTM-1160)	451 °C
95% BP (ASTM-1160)	545 °C

The testing conditions were as follows:

feeding rate (ml/hr)	50
H_2 pressure (bar)	50
H_2 oil ratio (Nm^3/m^3)	320
temperature (°C) test I	390
temperature (°C) test II	407

The following results were obtained from two tests:

	Test I (390 °C)		Test II(407 °C)	
% desulphurisation	99	99	99	99
% denitrogenation	89	91	87	91
% conversion to C24-minus	38	36	52	52
% selectivity to C11-C24	81	81	78	76

The conversion to C24-minus is defined as:

$X = (D-B)/(1-B)$,

wherein

D = fraction of C24-minus in product
B = fraction of C24-minus in feed
C24-minus = hydrocarbons having a boiling point below that of n-C24 paraffin (= 392 °C), determined by means of gas chromatography (ASTM D-2887).

The selectivity to C11-C24 is defined as:

$[100.(X-Y)]/X$,

wherein

X = C24-minus conversion
Y = C11-minus conversion,

with C11-minus and the C11-minus conversion being determined in a manner analogous to that of the C24-minus and C24-minus conversion determinations, respectively.

Comparative Example 3

Preparation of comparative catalyst B

1050 g of alumina (LOI = 30,5%) were mixed with 200 g of molybdenum oxide powder. To this whole were added 936 g of amorphous silica-alumina (LOI = 15%). The resulting mixture was shaped to form cylindrical extrudates of 1,5 mm in diameter and, after drying at 120 °C for 20 hours, the extrudates were calcined in an air atmosphere at 600 °C for one hour.

The calcined extrudates next were impregnated with an aqueous solution of nickel nitrate; the product was dried and subsequently calcined at 600 °C for one hour. The resulting catalyst contained 4,0 wt.% of nickel oxide, 11,5 wt.% of molybdenum oxide, 33,6 wt.% of silica, and for the remainder was made up of alumina.

The surface area of the obtained comparative catalyst B was found to be 314 m^2/g and the pore volume, as determined by mercury porosimetry, was 0,59 ml/g. The average pore diameter was determined to be 7,8 nm (78 Å), the pore volume of pores having a diameter greater than 3,6 nm (36 Å) being 0,53 ml/g and that of pores with a diameter greater than 20,0 nm (200 Å) being 0,057 ml/g.

Testing

Comparative catalyst B was tested under conditions identical with those given in Example 2. The following results were obtained from two tests:

	Test I (390 °C)		Test II (407 °C)	
% desulphurisation	98	98	98	98
% denitrogenation	76	80	81	81
% conversion to C24-minus	30	34	47	50
% selectivity to C11-C24	82	78	78	76

The above Examples show that, in addition to increased conversion, catalyst A according to the invention surprisingly provides improved denitrogenation and improved desulphurisation in comparison with comparative catalyst B. Also unexpected is the very high selectivity to middle distillates (C11-C24). Although middle distillate selectivity is known to decrease as conversion increases, it was found that when use is made of the catalyst according to the invention, there is obtained, with increased conversion, at least the same selectivity.

The next Examples show that similar advantages are obtained when using catalysts according to the invention which contain cobalt instead of nickel as the Group VIII metal component.

Example 4

Preparation of catalyst C according to the invention

A boron acid-containing solution was prepared by dissolving 904 g of H_3BO_3 in a mixture of 641 g of a 65%-nitric acid solution and 14 000 ml of water at temperature of 70 °C.

Meanwhile, 9080 g of aluminium oxide hydroxide (boehmite; LOI = 25,7%) were mixed with 2170 g of molybdenum oxide powder. To this mixture there were added the aqueous boron acid-containing solution, 10 050 g of amorphous silica-alumina (LOI = 17,9%), and 3800 ml of water. The resulting mixture was shaped to cylindrical extrudates of 1,5 mm in diameter and, after drying at 120 °C for 20 hours, the extrudates were calcined in an air atmosphere at 550 °C for one hour.

470 g of the so obtained extrudates were impregnated with an aqueous solution of cobalt nitrate; the product was dried and subsequently calcined at 530 °C for one hour. The resulting catalyst C contained 4,74 wt.% of boron oxide, 3,18 wt.% of cobalt oxide, 11,2 wt.% of molybdenum oxide, and 33,3 wt.% of silica, the remainder of the catalyst being made up of alumina.

The surface area of catalyst C was 264 m^2/g, the pore volume, as determined by N_2 desorption (77 K), was 0,54 ml/g. The average pore diameter, as determined by mercury penetration, was 8,7 nm (87 Å), the pore volume of pores having a diameter greater than 3,6 nm (36 Å) being 0,54 ml/g and that of pores having a diameter greater than 20,0 nm (200 Å) being 0,049 ml/g.

Example 5

Preparation of catalyst D according to the invention

A boron acid-containing solution was prepared by dissolving 2739 g of H_3BO_3 in a mixture of 2314 g of a 65%-nitric acid solution and 15 000 ml of water at a temperature of 70 °C.
Meanwhile, 9400 g of aluminium oxide hydroxide (boehmite; LOI = 26,0%) were mixed with 2274 g of molybdenum oxide powder. To this mixture there were added the aqueous boron acid-containing solution and 10 020 g of amorphous silica-alumina (LOI = 15,2%). The resulting mixture was shaped to cylindrical extrudates of 1,5 mm in diameter and, after drying at 120 °C for 20 hours, the extrudates were calcined in an air atmosphere at 600 °C for one hour.
1725 g of the so obtained extrudates were impregnated with an aqueous solution of cobalt nitrate; the product was dried and subsequently calcined at 530 °C for one hour. The resulting catalyst D contained 7,2 wt.% of boron oxide, 3,2 wt.% of cobalt oxide, 11,3 wt.% of molybdenum oxide, and 32,1 wt.% of silica, the remainder of the catalyst being made up of alumina.
The surface area of catalyst D was 243 m^2/g, the pore volume, as determined by N_2 desorption (77 K), was 0,47 ml/g. The average pore diameter, as determined by mercury penetration, was 7,6 nm (76 Å), the pore volume of pores having a diameter greater than 3,6 nm (36 Å) being 0,43 ml/g and that of pores having a diameter greater than 20,0 nm (200 Å) being 0,033 ml/g.

Example 6

Catalysts C and D from Examples 4 and 5, respectively, were tested under conditions identical with those given in Example 2. The following results were obtained.

	Catalyst C		Catalyst D	
Temperature (°C)	390	407	390	407
% desulphurisation	99	99	99	99
% denitrogenation	88	85	88	84
% conversion to C24-minus	39	53	37	49
% selectivity to C11-C24	80	76	80	77

Comparative Example 7

Preparation of comparative catalyst E

Comparative catalyst E was prepared in the same manner as described in comparative Example 3, except that in the impregnation solution employed the nickel nitrate was replaced by an equivalent amount of cobalt nitrate.
The catalyst's surface area was 314 m^2/g and the pore volume, as determined by mercury penetration, 0,59 ml/g; the average pore diameter was 7,8 nm (78 Å), the pore volume of pores having a diameter greater than 3,6 nm (36 Å) being 0,53 ml/g, and that of pores having a diameter greater than 20,0 nm (200 Å) being 0,06 ml/g.

Testing

Comparative catalyst E was tested under conditions identical with those given in Example 2. The results are listed below.

Temperature (°C)	390	407
% desulphurisation	98	98
% denitrogenation	72	79
% conversion to C24-minus	31	49
% selectivity to C11-C24	80	77

Claims

1. A catalyst composition containing a carrier material built up from alumina and silica-alumina, a Group VIB metal component, and a Group VIII metal component, characterised in that the catalyst contains 1-20 wt.% of boron.

2. A catalyst according to claim 1, characterised in that the carrier material is built up from alumina and amorphous silica-alumina containing in the range of 60 to 90 wt.% of silica.

3. A catalyst according to claim 2, characterised in that it contains 5-20 wt.% of Mo, 2-6 wt.% of Ni and/or Co, 1-20 wt.% of B, calculated as the metal oxides, 10-40 wt.% of silica, and for the remainder alumina.

4. A catalyst according to any one of the preceding claims, characterised in that the active surface area of the catalyst is in the range of 150 to 350 m^2/g, and the average pore diameter is in the range of 5 to 15 nm (50 to 150 Å).

5. Use of a catalyst according to any one of the preceding claims 1 to 4 for converting vacuum gas oil feeds to middle distillates.

Patentansprüche

1. Katalysator-Zusammensetzung enthaltend ein Trägermaterial, das aus Aluminiumoxid, Siliciumdioxid-Aluminiumoxid aufbebaut ist, einer Metallkomponente der Gruppe VIB und einer Metallkomponente der Gruppe VIII, dadurch gekennzeichnet, dass der Katalysator 1- 20 Gew.% Bor enthält.

2. Katalysator nach Anspruch 1, dadurch gekennzeichnet dass das Trägermaterial aufgebaut ist aus Aluminiumoxid und amorphem Siliciumdioxid-Aluminiumoxid enthaltend Siliciumdioxid im Bereich von 60 bis 90 Gew.% Siliciumdioxid.

3. Katalysator nach Anspruch 2, dadurch gekennzeichnet, dass er 5 - 20 Gew.% Mo, 2 - 6 Gew.% Ni und/oder Co, 1 - 20 Gew.% B, berechnet als Metalloxide, 10 - 40 Gew.% Siliciumdioxid und als Rest Aluminiumoxid enthält.

4. Katalysator nach einem der vorangehenden Ansprüche 1 - 3, dadurch gekennzeichnet, dass die aktive Oberfläche des Katalysators im Bereich von 150 bis 350 m^2/g und der mittlere Porendurchmesser im Bereich von 5 bis 15 nm (50 bis 150 Å) liegt.

5. Verwendung eines Katalysators nach einem der vorangehenden Ansprüche 1 bis 4 zur Konvertierung von Vakuum-Gasölspeisungen in Mittelbereichsdestillate.

Revendications

1. Une composition catalytique renfermant un matériau support constitué d'alumine et de silice-alumine, d'un dérivé de métal du groupe VIB, et d'un dérivé de métal du groupe VIII, caractérisée en ce que le catalyseur contient 1 à 20% en poids de bore.

2. Catalyseur selon la revendication 1, caractérisé en ce que le matériau support est constitué d'alumine et de silice-alumine amorphe contenant de l'ordre de 60 à 90% en poids de silice.

3. Catalyseur selon la revendication 2, caractérisé en ce qu'il renferme 5 à 20% en poids de Mo, 2 à 6% en poids de Ni et/ou de Co, 1 à 20% en poids de B, exprimés par rapport aux oxydes de métal, 10 à 40% de silice, et le reste d'alumine.

4. Catalyseur selon l'une quelconque des revendications 1 à 3, caractérisé en ce que l'aire superficielle spécifique du catalyseur est comprise entre 150 et 350 m^2/g et le diamètre de pore moyen est de l'ordre de 5 à 15 nanomètres (50 à 150 Angstroms).

* C L M S *

5. Utilisation d'un catalyseur selon l'une quelconque des revendications 1 à 4, pour transformer les charges de gazole sous vide en distillats moyens.