Description

The present invention relates to hydrocarbon conversion processes and catalysts which can be used in such processes. The present invention also relates to compositions of matter suitable as catalyst or catalyst base in hydroprocessing.

Of the many hydroconversion processes known in the art, hydrocracking is becoming increasingly important since it offers product flexibility together with product quality. As it is also possible to subject rather heavy feedstocks to hydrocracking it will be clear that much attention has been devoted to the development of hydrocracking catalysts.

Modern hydrocracking catalysts are generally based on zeolitic materials which may have been adapted by techniques like ammonium-ion exchange and various forms of calcination in order to improve the performance of the hydrocracking catalysts based on such zeolites.

One of the zeolites which is considered to be a good starting material for the manufacture of hydrocracking catalysts is the well-known synthetic zeolite Y as described in US-A-3,130,007. A number of modifications has been reported for this material which include, inter alia, ultrastable Y (US-A-3,536,605) and ultrahydrophobic Y (GB-A-2,014,970). In general, it can be said that the modifications cause a reduction in the unit cell size depending on the treatment carried out.

The ultrahydrophobic Y zeolites as described in GB-A-2,014,970 are also referred to in EP-B-28,938 and EP-B-70,824 as suitable components for hydrocracking catalysts. From said publications it appears that such zeolites have an intrinsically low water adsorption capacity. Water adsorption capacities below 5% (EP-B-28,938), respectively 8% (EP-B-70,824) by weight of zeolite are considered to be the maximum levels acceptable and it is confirmed experimentally in EP-B-28,938 that a water adsorption capacity of 8.5% by weight on zeolite causes a drastic decrease in selectivity.

In EP-A-162,733 zeolite Y components for hydrocracking catalysts are described which must possess a rather stringent pore diameter distribution which in essence means that at least 80% of the total pore volume is made up of pores having a diameter of less than 2 nm, and preferably at least 85% of the total pore volume is made up of pores having a diameter of less than 2 nm.

In GB-B-2,114,594 a process for the production of middle distillates is disclosed wherein use is made of catalysts comprising so-called expanded pore faujasitic zeolites. The pore expansion referred to in said patent specification has been obtained by firstly steaming the faujasitic zeolite at a temperature of at least 538 °C, in particular at a temperature above 760 °C, followed by contacting the steamed faujasitic zeolite with an acid, preferably an acid having a pH less than 2. It should be noted that the degree of crystallinity retained in the expanded pore zeolite dramatically decreases at increasing amounts of acid used (see Fig. 3 of GB-B-2,114,594). Since the SiO@/Al@O# molar ratio substantially increases linearly with the amounts of acid used (see Fig. 2) it appears that the crystallinity of the faujasitic zeolites treated according to the process described in GB-B-2,114,594 intrinsically decreases at increasing SiO@/Al@O# molar ratios.

It has now been found that the use of certain modified Y zeolites as components in hydrocracking catalysts gives an unexpected high selectivity to the desired product(s) combined with a significantly lower gas make than experienced thus far with catalysts based on Y-zeolite. Moreover, it was found that the quality of the product(s) was improved despite a lower hydrogen consumption. These improvements are even more remarkable since they can be achieved with catalysts showing a higher activity than thus far achievable with Y type zeolites.

The present invention thus relates to compositions of matter suitable as a catalyst (base) in hydroprocessing comprising a crystalline aluminosilicate zeolite and a binder wherein the crystalline aluminosilicate comprises a modified Y zeolite having a unit cell size below 2.435 nm, a degree of crystallinity which is at least retained at increasing SiO@/Al@O# molar ratios, a water adsorption capacity (at 25 °C and a p/p_o value of 0.2) of at least 8% by weight of modified 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.

Preference is given to compositions of matter wherein between 10% and 40% of the total pore volume of the modified Y zeolite is made up of pores having a diameter of at least 8 nm. The pore diameter distribution is determined by the method described by E.P. Barrett, G. Joyner and P.P. Halenda (J. Am. Chem. Soc.73,373 (1951)) and is based on the numerical analysis of the nitrogen desorption isotherm. It should be noted that inter-crystalline voids are excluded in the determination of the percentage of the total pore volume made up in pores having a diameter of at least 8 nm when said percentage is between 10% and 40%.

It has been found that very good results in terms of performance and activity can be obtained when modified Y zeolites are used having a water adsorption capacity of at least 10% by weight on zeolite, in particular between 10% and 15% by weight of zeolite. The water adsorption capacity of the modified Y zeolites present in the compositions of matter and/or the catalysts according to the present invention is measured at 25 °C and a p/p_o value of 0.2. In order to determine the water adsorption capacity the modified Y zeolite is evacuated at elevated temperature, suitably 400 °C, and subsequently subjected at 25 °C to a water pressure corresponding to a p/p_o value of 0.2 (ratio of the partial water pressure in the apparatus and the saturation pressure of water at 25 °C).

The unit cell size of the modified Y zeolites present in the compositions of matter is below 2.435 nm (as determined by ASTM-D-3492, the zeolite being present in its NH$+-form). It should be noted that the unit cell size is but one of the parameters which determine the suitability of modified Y zeolites. It has been found that also the water adsop-

tion capacity and the pore diameter distribution as well as the crystallinity have to be taken into account in order to be able to obtain marked improvements in performance as referred to hereinbefore.

As regards crystallinity it should be noted that the modified Y zeolites according to the present invention should at least retain their crystallinity (relative to a certain standard, e.g. Na-Y) when comparing crystallinity as a function of increasing SiO@/Al@O# molar ratio. Generally, the crystallinity will slightly improve when comparing modified Y zeolites with increasing SiO@/Al@O# molar ratios.

The compositions of matter according to the present invention suitably comprise 5-90% by weight of modified Y zeolite and 10-95% by weight of binder. Preferably the compositions of matter comprise rather high amounts of modified Y zeolite: 50-85% by weight of modified Y zeolite and 15-50% by weight of binder being particularly preferred.

The binder(s) present in the composition(s) of matter suitably comprise inorganic oxides or mixtures of inorganic oxides. Both amorphous and crystalline binders can be applied. Examples of suitable binders comprise silica, alumina, silica-alumina, clays, zirconia, silica-zirconia and silica-boria. Preference is given to the use of alumina as binder.

Depending on the desired unit cell size the SiO@/Al@O# molar ratio of the modified Y zeolite will have to be adjusted. There are many techniques described in the art which can be applied to adjust the unit cell size accordingly. It has been found that modified Y zeolites having a SiO@/Al@O# molar ratio between 4 and 25 can be suitably applied as the zeolitic component of the compositions of matter according to the present invention. Preference is given to modified Y zeolites having a molar SiO@/Al@O# ratio between 8 and 15.

The present invention further relates to catalyst compositions comprising besides a binder and a modified Y zeolite as defined hereinbefore at least one hydrogenation component of a Group VI metal and/or at least one hydrogenation component of a Group VIII metal. Suitably, the catalyst compositions according to the present invention comprise one or more components of nickel and/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium.

The amount(s) of hydrogenation component(s) in the catalyst compositions suitably range between 0.05 and 10% by weight of Group VIII metal component(s) and between 2 and 40% by weight of Group VI metal component(s), calculated as metal(s) per 100 parts by weight of total catalyst. The hydrogenation components in the catalyst compositions may be in the oxidic and/or the sulphidic form. If a combination of at least a Group VI and a Group VIII metal component is present as (mixed) oxides, it will be subjected to a sulphiding treatment prior to proper use in hydrocracking.

The present invention also relates to a process for converting hydrocarbon oils into products of lower average molecular weight and lower average boiling point wherein a hydrocarbon oil is contacted at elevated temperature and pressure in the presence of hydrogen with a catalyst comprising a modified Y zeolite having a unit cell size below 2.435 nm, a water adsorption capacity (at 25 °C and a p/p_o value of 0.2) of at least 8% by weight of modified 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, a binder and at least one hydrogenation component of a Group VI metal and/or at least one hydrogenation component of a Group VIII metal.

Preferably, the hydroconversion process is carried out by using catalysts comprising a modified Y zeolite wherein between 10% and 40% of the total pore volume (excluding inter-crystalline voids) is made up of pores having a diameter of at least 8 nm. Good results have been obtained using modified Y zeolites in the catalyst compositions wherein the water adsorption capacity is at least 10% by weight of modified zeolite, and in particular between 10% and 15% by weight of modified zeolite.

Suitably, the process according to the present invention is carried out using a catalyst composition comprising 5-90% by weight of modified Y zeolite and 10-95% by weight of binder, and preferably 50-85% by weight of modified Y zeolite and 15-50% by weight of binder. Suitable binders comprise inorganic oxides or mixtures of inorganic oxides. Examples of binders comprise silica, alumina, silica-alumina, clay, silica-zirconia and silica-boria. Preference is given to the use of alumina as binder.

Modified Y zeolites having a SiO@/Al@O# molar ratio between 4 and 25 and in particular between 8 and 15 can be suitably applied as the zeolitic components in the catalyst compositions to be used in the hydroconversion process according to the present invention.

Preferably, the process according to the present invention is carried out by using catalysts comprising, in addition to the zeolitic component and the binder, one or more components of nickel and/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium. In particular, use is made of hydrogenation components comprising between 0.05 and 10% by weight of nickel and between 2 and 40% by weight of tungsten, calculated as metals per 100 parts by weight of total catalyst. Preferably the hydrogenation components are used in sulphided form.

Hydroconversion process configurations in accordance with the present invention are those wherein a substantial reduction in average molecular weight and boiling point can be accomplished by contacting the feed with a catalyst composition comprising a modified Y zeolite as described hereinbefore and a binder.

Examples of such processes comprise single-stage hydrocracking, two-stage hydrocracking, series-flow hydrocracking as well as mild hydrocracking.

It will be appreciated that the hydroconversion processes in accordance with the present invention can also be carried out suitably in bunker-type operations, i.e. by using reactor vessels allowing for

periodical or intermittent catalyst removal and replenishment. Use can be made of the various bunker-techniques described in the art.

Feedstocks which can be suitably applied in the process according to the present invention comprise gas oils, vacuum gas oils, deasphalted oils, long residues, catalytically cracked cycle oils, coker gas oils and other thermally cracked gas oils and syncrudes, optionally originating from tar sands, shale oils, residue upgrading processes or biomass. Combinations of various feedstocks can also be applied.

It may be desirable to subject part or all of the feedstock to one or more (hydro)treatment steps prior to its use in the hydrocarbon conversion process according to the present invention. It is often found convenient to subject the feedstock to a (partial) hydrotreatment. When rather heavy feedstocks are to be processed it will be advantageous to subject such feedstocks to a (hydro) demetallization treatment.

Suitable process conditions to be applied comprise temperatures in the range of from 250 °C to 500 °C, pressures up to 300 bar and space velocities between 0.1 and 10 kg feed per litre of catalyst per hour (kg/l.h). Gas/feed ratios between 100 and 5000 Nl/kg feed can suitably be used.

Preferably, the hydroconversion process according to the present invention is carried out at a temperature between 300 °C and 450 °C, a pressure between 25 and 200 bar and a space velocity between 0.2 and 5 kg feed per litre of catalyst per hour. Preferably, gas/feed ratios between 250 and 2000 are applied.

The catalysts to be used in the hydrocarbon conversion process according to the present invention, and in particular in the hydrocracking process appear to be very flexible as they are capable of producing product fractions with rather narrow boiling point ranges because of their inherent property of limited overcracking. Therefore, they can be used advantageously in various modes of operation dependent on the desired product slate.

It is thus possible to use as feed a hydrocarbon oil fraction having a boiling point range slightly above the boiling point range of the product to be obtained in the process. However, substantially higher boiling feeds can also be used conveniently to produce materials of similar product boiling point range. For instance, a vacuum gas oil appears to be an excellent feedstock to produce middle distillates using the catalysts in accordance with the present invention but also naphtha can be produced in high yields. By adjusting, for instance, the operating temperature and/or the recycle cut-point (when operating in recycle mode) either middle distillate or naphtha will become the main product whilst retaining high selectivity with respect to the desired product.

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

Example I

a) Preparation of modified Y zeolite/binder composition.

A commercially available ammonium-ultra stable zeolite Y having a unit cell size of 2.457 nm, a sodium oxide content of 0.12 %wt and a SiO@/Al@O# molar ratio of about 6 was subjected to an ion-exchange treatment with 0.2 M aluminium sulphate for one hour under reflux-conditions. Thereafter, the material thus treated was subjected to a calcination in the presence of steam for a period of one hour at 700 °C. The calcined material obtained had a unit cell size of 2.430 nm and a SiO@/Al@O# molar ratio of 6.85.

The material obtained was then subjected to an ion-exchange treatment with 0.66 M aluminium sulphate for one hour under reflux conditions followed by a treatment with 1M ammonium nitrate under the same conditions. This treatment was repeated once. The modified Y-zeolite obtained had a unit cell size of 2.433 nm and a SiO@/Al@O# molar ratio of 9.85. 466 g of modified Y zeolite having a unit cell size of 2.433 nm, a SiO@/Al@O# molar ratio of 9.85, a water adsorption capacity (at 25 °C and a p/p_o value of 0.2) of 11.3% by weight, a nitrogen pore volume of 0.40 ml/g wherein 18% of the total pore volume is made up of pores having a diameter > 8 nm and a loss of ignition (550 °C) of 14.1% by weight is mixed with 135 g hydrated aluminium oxide (boehmite, ex Condea) with a loss of ignition of 25.8% by weight. Subsequently a solution of 5 g of acetic acid and 302.6 g of water was added to the powdery mixture. After mulling the mixture obtained it was extruded in a Bonnot extruder provided with a die plate producing 1.5 mm extrudates. The extrudates obtained were dried for 2 hours at 120 °C and finally calcined for 2 hours at 500 °C. The extrudates obtained had a water pore volume of 0.66 ml/g.

b) Preparation of catalyst composition.

50 g of the extrudates as prepared according to the procedure described in Example I a were dried at 450 °C for 1 hour prior to impregnation with 33 ml of a solution which is made up of 25 g of a solution prepared by blending 214.3 g of a nickel nitrate solution (14% by weight of Ni), 150 g of water and 137 g of ammonium meta tungstate (69.5% by weight of W), and 8 g of water. The impregnated extrudates were homogenized for 1 hour using a rolling device. Finally the metal-containing extrudates were dried for 2 hours at 120 °C and calcined at 500 °C for 1 hour. The catalyst obtained contained 2.6% by weight of nickel and 8.2% by weight of tungsten. The ready catalyst contained 77.5% by weight of modified Y zeolite and 22.5% by weight of binder (based on total amount of zeolite and binder on a dry basis).

c) Hydrocracking experiments.

The catalyst as described in Example I b was subjected to a hydrocracking performance test involving a low sulphur, low nitrogen vacuum gas oil having the following properties:

C (%wt)	86.2
H (%wt)	13.8
d (70/4)	0.826
viscosity (100°C)	4.87 cS (ASTM-D-445)
viscosity (60°C)	12.43 cS (ASTM-D-445)
RCT (%wt)	0.05 (ASTM-D-542)
I.B.P.	205°C
10/20	332/370
30/40	392/410
50/60	428/448
70/80	467/492
90	525
F.B.P.	598

The catalyst was firstly subjected to a presulphiding treatment by slowly heating in a 10% v H@S/H@-atmosphere to a temperature of 370 °C. The catalyst was tested in a 1:1 dilution with 0.2 mm SiC particles under the following operating conditions: WHSV 1.1 kg.l^{-1}h^{-1} H@S partial pressure 1.4 bar, total pressure 130 bar and a gas/feed ratio of 1,000 Nlkg^{-1} The experiment was carried out in once-through operation.
When operating the hydrocracking in a kerosene mode of operation, the catalyst performance is expressed at 70% by weight conversion of 300 °C+ boiling point material in the feed after allowing the catalyst to stabilize.
The following results were obtained:
Temperature required (70% conv. of 300 °C+): 318 °C
Distribution of 300 °C– product (in % by weight)

C_1–C_4	7
C_5–130°C	46
130°C–300°C	47

The chemical hydrogen consumption amounted to 1.2% by weight.

Example II

The hydrocracking experiment as described in Example I c was repeated in the naphtha mode of operation, i.e. the catalyst as described in Example I b was subjected to the presulphiding, the feedstock and operating conditions as described in Example I c but in this case the performance is expressed at 70% by weight conversion of 180 °C+ boiling point material in the feed.
The following results were obtained:
Temperature required (70% conv. of 180 °C+): 321 °C
Distribution of 180 °C– product (in % by weight):

C_1–C_4	11
C_5–65°C	21
65°C–180°C	68

The chemical hydrogen consumption amounted to 1.3% by weight.

Comparative Example

A commercially available ultra-stable Y zeolite having a unit cell size of 2.456 nm, a water adsorption capacity of 24% by weight (at 25 °C and a p/p_o value of 0.2) and a nitrogen pore volume of 0.38 ml/g wherein 8% of the total pore volume is made up of pores having a diameter of > 8 nm was treated with hydrated aluminium oxide and a solution of nickel nitrate and ammonium metatungstate so as to obtain a catalyst containing 2.6% by weight of nickel and 8.2% by weight of tungsten.
The comparative catalyst was subjected to a presulphiding treatment as described in Example Ic and subjected to the same feed. When operating in kerosene mode (i.e. expressing catalyst performance at 70% by weight conversion of 300 °C+ boiling point material in the feed) after allowing the catalyst to stabilize, the following results were obtained:
Temperature requirement (70% conve. of 300 °C+): 325 °C
Distribution of 300 °C– product (in % by weight):

C_1–C_4	13
C_5–130°C	57
130°C–300°C	30

The chemical hydrogen consumption amounted to 1.5% by weight.
The comparative catalyst was also subjected to an experiment as described in Example II, i.e. in the naphtha mode of operation. The following results were obtained:
Temperature requirement: 325 °C
Distribution of 180 °C– product (in % by weight):

C_1–C_4	16
C_5–65°C	26
65°C–180°C	58

The chemical hydrogen consumption amounted to 1.5% by weight. It will be clear that the catalysts in accordance with the present invention are more active and selective than catalysts based on known ultra-stable Y zeolites. Also the chemical hydrogen consumption is slightly reduced.

Claims

1. Composition of matter suitable as a catalyst (base) in hydroprocessing comprising a crystalline

C (%wt)	86.2
H (%wt)	13.8
d (70/4)	0.826
viscosity (100°C)	4.87 cS (ASTM-D-445)
viscosity (60°C)	12.43 cS (ASTM-D-445)
RCT (%wt)	0.05 (ASTM-D-542)
I.B.P.	205°C
10/20	332/370
30/40	392/410
50/60	428/448
70/80	467/492
90	525
F.B.P.	598

The catalyst was firstly subjected to a presulphiding treatment by slowly heating in a 10% v H@S/H@ atmosphere to a temperature of 370 °C. The catalyst was tested in a 1:1 dilution with 0.2 mm SiC particles under the following operating conditions: WHSV 1.1 kg.l−1h−1 H@S partial pressure 1.4 bar, total pressure 130 bar and a gas/feed ratio of 1,000 Nlkg−1 The experiment was carried out in once-through operation.
When operating the hydrocracking in a kerosene mode of operation, the catalyst performance is expressed at 70% by weight conversion of 300 °C+ boiling point material in the feed after allowing the catalyst to stabilize.
The following results were obtained:
Temperature required (70% conv. of 300 °C+): 318 °C
Distribution of 300 °C− product (in % by weight)

C_1–C_4	7
C_5–130°C	46
130°C–300°C	47

The chemical hydrogen consumption amounted to 1.2% by weight.

Example II

The hydrocracking experiment as described in Example I c was repeated in the naphtha mode of operation, i.e. the catalyst as described in Example I b was subjected to the presulphiding, the feedstock and operating conditions as described in Example I c but in this case the performance is expressed at 70% by weight conversion of 180 °C+ boiling point material in the feed.
The following results were obtained:
Temperature required (70% conv. of 180 °C+): 321 °C
Distribution of 180 °C− product (in % by weight):

C_1–C_4	11
C_5–65°C	21
65°C–180°C	68

The chemical hydrogen consumption amounted to 1.3% by weight.

Comparative Example

A commercially available ultra-stable Y zeolite having a unit cell size of 2.456 nm, a water adsorption capacity of 24% by weight (at 25 °C and a p/p_o value of 0.2) and a nitrogen pore volume of 0.38 ml/g wherein 8% of the total pore volume is made up of pores having a diameter of > 8 nm was treated with hydrated aluminium oxide and a solution of nickel nitrate and ammonium metatungstate so as to obtain a catalyst containing 2.6% by weight of nickel and 8.2% by weight of tungsten.
The comparative catalyst was subjected to a presulphiding treatment as described in Example Ic and subjected to the same feed. When operating in kerosene mode (i.e. expressing catalyst performance at 70% by weight conversion of 300 °C+ boiling point material in the feed) after allowing the catalyst to stabilize, the following results were obtained:
Temperature requirement (70% conve. of 300 °C+): 325 °C
Distribution of 300 °C− product (in % by weight):

C_1–C_4	13
C_5–130°C	57
130°C–300°C	30

The chemical hydrogen consumption amounted to 1.5% by weight.
The comparative catalyst was also subjected to an experiment as described in Example II, i.e. in the naphtha mode of operation. The following results were obtained:
Temperature requirement: 325 °C
Distribution of 180 °C− product (in % by weight):

C_1–C_4	16
C_5–65°C	26
65°C–180°C	58

The chemical hydrogen consumption amounted to 1.5% by weight. It will be clear that the catalysts in accordance with the present invention are more active and selective than catalysts based on known ultra-stable Y zeolites. Also the chemical hydrogen consumption is slightly reduced.

Claims

1. Composition of matter suitable as a catalyst (base) in hydroprocessing comprising a crystalline

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aluminosilicate zeolite and a binder wherein the crystalline aluminosilicate comprises a modified Y zeolite having a unit cell size below 2.435 nm, a degree of crystallinity which is at least retained at increasing SiO@/Al@O# molar ratios, a water adsorption capacity (at 25 °C and a p/p_o value of 0.2) of at least 8% by weight of modified 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.

2. Composition according to claim 1, wherein between 10% and 40% of the total pore volume of the modified zeolite is made up of pores having a diameter of at least 8 nm.

3. Composition according to claim 1 or 2, wherein the modified zeolite Y has a water adsorption capacity of at least 10% by weight of modified zeolite.

4. Composition according to claim 3, wherein the modified zeolite has a water adsorption capacity between 10% and 15% by weight of modified zeolite.

5. Composition according to any one of claims 1-4, wherein the composition comprises 5-90% by weight of modified Y zeolite and 10-95% by weight of binder.

6. Composition according to claim 5, wherein the composition comprises 50-85% by weight of modified zeolite Y and 15-50% by weight of binder.

7. Composition according to any one of claims 1-6, wherein the binder comprises an inorganic oxide or mixture of inorganic oxides.

8. Composition according to claim 7, wherein the binder comprises silica, alumina, silica-alumina, silica-zirconia or silica-boria.

9. Composition according to any one of claims 1-8, wherein the modified Y zeolite has a SiO@/Al@O# molar ratio of from 4 to 25.

10. Composition according to claim 9, wherein the modified Y zeolite has a SiO@/Al@O# molar ratio of from 8 to 15.

11. Catalyst composition comprising a binder, a modified Y zeolite according to any one of claims 1–10 and at least one hydrogenation component of a Group VI metal and/or at least one hydrogenation component of a Group VIII metal.

12. Catalyst composition according to claim 11, wherein the hydrogenation component comprises one or more components of nickel and/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium.

13. Catalyst composition according to claim 12, wherein the hydrogenation component comprises between 0.5 and 10% by weight of nickel and between 2 and 40% by weight of tungsten, calculated as metals per 100 parts by weight of binder.

14. Catalyst composition according to any one of claims 11–13, wherein the hydrogenation component(s) is (are) present in sulphided form.

15. A process for converting hydrocarbon oils into products of lower average molecular weight and lower average boiling point comprising contacting a hydrocarbon oil at elevated temperature and pressure in the presence of hydrogen with a catalyst composition as defined in any one of claims 11 to 14.

16. A process accordong to claim 15, which is carried out at a temperature in the range of from 250°C to 500°C, a pressure up to 300 bar and a space velocity between 0.1 and 10 kg feed per litre of catalyst per hour.

17. A process according to claim 16, which is carried out at a temperature between 300°C and 450°C, a pressure between 25 and 200 bar and a space velocity between 0.2 and 5 kg feed per litre catalyst per hour.

Patentansprüche

1. Als ein Katalysator (Basis) in Hydrierverfahren geeignete Zusammensetzung, umfassend einen kristallinen Alumosilikat-Zeolith und ein Bindemittel, in welcher das kristalline Alumosilikat einen modifizierten Y-Zeolith umfaßt, welcher eine Elementarzelle mit einer Größe unterhalb 2,435 nm, einen Kristallinitätsgrad, der mit ansteigenden Molverhältnissen von SiO@:Al@O# mindestens beibehalten wird, eine Wasseradsorptionskapazität (bei 25°C und einem p/p_o-Wert von 0,2) von mindestens 8 Gewichtsprozent, bezogen auf den modifizierten Zeolith, und ein Porenvolumen von mindestens 0,25 ml/g aufweist, wobei zwischen 10 und 60 Prozent des Gesamtporenvolumens von Poren mit einem Durchmesser von mindestens 8 nm gebildet werden.

2. Zusammensetzung gemäß Anspruch 1, in welcher zwischen 10 und 40 Prozent des Gesamtporenvolumens von Poren mit einem Durchmesser von mindestens 8 nm gebildet werden.

3. Zusammensetzung gemäß Anspruch 1 oder 2, in welcher der modifizierte Zeolith Y eine Wasseradsorptionskapazität von mindestens 10 Gewichtsprozent, bezogen auf den modifizierten Zeolith, aufweist.

4. Zusammensetzung gemäß Anspruch 3, in welcher der modifizierte Zeolith eine Wasseradsorptionskapazität zwischen 10 und 15 Gewichtsprozent, bezogen auf den modifizierten Zeolith, aufweist.

5. Zusammensetzung gemäß irgendeinem der Ansprüche 1 bis 4, wobei die Zusammensetzungen 5 bis 90 Gewichtsprozent modifizierten Y-Zeolith und 10 bis 95 Gewichtsprozent Bindemittel enthält.

6. Zusammensetzung gemäß Anspruch 5, in welcher die Zusammensetzung 50 bis 85 Gewichtsprozent modifizierten Zeolith Y und 15 bis 50 Gewichtsprozent Bindemittel enthält.

7. Zusammensetzung gemäß irgendeinem der Ansprüche 1 bis 6, in welcher das Bindemittel ein anorganisches Oxid oder eine Mischung aus anorganischen Oxiden umfaßt.

8. Zusammensetzung gemäß Anspruch 7, in welcher das Bindemittel Siliciumdioxid, Aluminiumoxid, Siliciumdioxid-Aluminiumoxid, Siliciumdioxid-Zirkonoxid oder Siliciumdioxid-Boroxid umfaßt.

9. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 8, in welcher der modifizierte Y-Zeolith ein Molverhältnis SiO@:Al@O# von 4 bis 25 aufweist.

10. Zusammensetzung nach Anspruch 9, in welcher der modifizierte Y-Zeolith ein Molverhältnis SiO@:Al@O# von 8 bis 15 aufweist.

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11. Katalysatorzusammensetzung, umfassend ein Bindemittel, einen modifizierten Y-Zeolith gemäß irgendeinem der Ansprüche 1 bis 10 und mindestens eine hydrieraktive Komponente in Form eines Metalles der Gruppe VI und/oder mindestens eine hydrieraktive Komponente in Form eines Metalles der Gruppe VIII.

12. Katalysatorzusammensetzung gemäß Anspruch 11, in welcher die hydrieraktive Komponente ein oder mehrere Komponenten von Nickel und/oder Kobalt und eine oder mehrere Komponenten von Molybdän und/oder Wolfram oder eine oder mehrere Komponenten von Platin und/oder Palladium umfaßt.

13. Katalysatorzusammensetzung gemäß Anspruch 12, in welcher die hydrieraktive Komponente zwischen 0,5 und 10 Gewichtsprozent Nickel und zwischen 2 und 40 Gewichtsprozent Wolfram, berechnet als Metalle je 100 Gewichtsteile Bindemittel, umfaßt.

14. Katalysatorzusammensetzung gemäß irgendeinem der Ansprüche 11 bis 13, in welcher die hydrieraktive Komponente(n) in sulfidierter Form vorliegt (vorliegen).

15. Ein Verfahren zur Umwandlung von Kohlenwasserstoffölen in Produkte mit niedrigerem Durchschnittsmolekulargewicht und niedrigerem Durchschnittssiedepunkt, umfassend das Kontaktieren eines Kohlenwasserstofföls bei erhöhter Temperatur und erhöhtem Druck in Anwesenheit von Wasserstoff mit einer Katalysatorzusammensetzung wie in irgendeinem der Ansprüche 11 bis 14 definiert.

16. Ein Verfahren gemäß Anspruch 15, welches bei einer Temperatur im Bereich von 250 bis 500°C, einem Druck bis zu 300 bar und einer Raumgeschwindigkeit zwischen 0,1 und 10 kg Zuspeisung je Liter Katalysator je Stunde durchgeführt wird.

17. Ein Verfahren gemäß Anspruch 16, welches bei einer Temperatur zwischen 300 und 450°C, einem Druck zwischen 25 und 200 bar und einer Raumgeschwindigkeit zwischen 0,2 und 5 kg Zuspeisung je Liter Katalysator je Stunde durchgeführt wird.

Revendications

1. Composition de matière appropriée comme catalyseur (base) dans un hydrotraitement, comportant une zéolite cristalline en aluminosilicate et un liant, dans laquelle l'aluminosilicate cristallin comprend une zéolite modifiée Y présentant une taille unitaire des cellules inférieure à 2,435 nm, un degré de cristallinité qui est au moins conservé pour des rapports molaires SiO@/Al@O# accrus, une capacité d'adsorption de l'eau (à 25°C et pour une valeur p/p) de 0,2) d'au moins 8% en poids de la zéolite modifiée et un volume des pores d'au moins 0,25 ml/g dans lequel entre 10% et 60% du volume total des pores est constitué de pores présentant un diamètre d'au moins 8 nm.

2. Composition selon la revendication 1, dans laquelle entre 10% et 40% du volume total des pores de la zéolite modifiée est constitué de pores présentant un diamètre d'au moins 8 nm.

3. Composition selon la revendication 1 ou 2, dans laquelle la zéolite modifiée Y présente une capacité d'adsorption de l'eau d'au moins 10% en poids de la zéolite modifiée.

4. Composition selon la revendication 3, dans laquelle la zéolite modifiée présente une capacité d'adsorption d'eau entre 10% et 15% en poids de la zéolite modifiée.

5. Composition selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la composition comprend 5 à 90% en poids de zéolite modifiée Y et 10 à 95% en poids de liant.

6. Composition selon la revendication 5, dans laquelle la composition comprend 50 à 85% en poids de zéolite modifiée Y et 15 à 50% en poids de liant.

7. Composition selon l'une quelconque des revendications 1 à 6, dans laquelle le liant comprend un oxyde inorganique ou un mélange d'oxydes inorganiques.

8. Composition selon la revendication 7, dans laquelle le liant comprend de la silice, de l'alumine, de la silice-alumine, de la silice-zircone ou de la silice-borite.

9. Composition selon l'une quelconque des revendications 1 à 8, dans laquelle la zéolite modifiée Y présente un rapport molaire SiO@/Al@O# de 4 à 25.

10. Composition selon la revendication 9, dans laquelle la zéolite modifiée Y présente un rapport molaire SiO@/Al@O# de 8 à 15.

11. Composition catalytique comportant un liant, un zéolite modifiée Y selon l'une quelconque des revendications 1 à 10 et au moins un composant d'hydrogénation d'un métal du groupe IV et/ou au moins un composant d'hydrogénation d'un métal du groupe VIII.

12. Composition catalytique selon la revendication 11, dans laquelle le composant d'hydrogénation comprend un ou plus d'un composant du nickel et/ou du cobalt ou un ou plus d'un composant du molybdène et/ou du tungstène ou un ou plus d'un composant du platine et/ou du palladium.

13. Composition catalytique selon la revendication 12, caractérisée en ce que le composant d'hydrogénation comprend entre 0,5 et 10% en poids de nickel et entre 2 et 40% en poids de tungstène, calculé comme métaux par 100 parties en poids de liant.

14. Composition catalytique selon l'une quelconque des revendications 11 à 13, dans laquelle le (les) composant(s) d'hydrogénation est (sont) présents sous forme sulfurée.

15. Un procédé pour convertir des huiles d'hydrocarbures en produits de poids moléculaire moyen inférieur et de point d'ébullition moyen inférieur, consistant à mettre en contact une huile d'hydrocarbure à température élevée et à pression élevée en présence d'hydrogène avec une composition catalytique telle que définie dans l'une quelconque des revendications 11 à 14.

16. Un procédé selon la revendication 15, qui est réalisé à une température dans la plage de 250°C à 500°C, sous une pression allant jusqu'à 300 bars et avec une vitesse spatiale entre 0,1 et 10 kg de charge par litre de catalyseur et par heure.

17. Un procédé selon la revendication 16, qui est réalisé à une température entre 300°C et 450°C,

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(15)

sous une pression entre 25 et 200 bars et une vitesse spatiale entre 0,2 et 5 kg de charge par litre de catalyseur et par heure.

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