

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios.

It has now been found that the presence of certain modified Y zeolites together with an amorphous cracking component 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. Also substantial amounts of polynaphthenic compounds present in the feed to be processed, which compounds are notoriously difficult to process, if at all, can be conveniently converted in the process according to the present invention.

It has been found that the presence of amorphous cracking components has a significant impact on the conversion of polynaphthenic compounds. The expression "polynaphthenic compounds" as used herein should be understood as relating to polynaphthenic compounds which as measured by mass spectroscopy have four or more rings in their respective structures which are predominantly condensed. 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 thusfar achievable with Y type zeolites.

The present invention thus relates to 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 comprising a modified Y zeolite having a unit cell size below 2.445 nm, a degree of crystallinity which is at least retained at increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios, a water adsorption capacity (at 25 °C and a p/p_0 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, an amorphous cracking component, 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 catalysts are used 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 as well as conversion of unwanted polynaphthenic compounds 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 catalysts according to the present invention is measured at 25 °C and a p/p_0 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_0 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 catalyst compositions to be used in the process according to the present invention is below 2.445 nm (as determined by ASTM-D-3492, the zeolite being present in its NH_4^+ -form) and preferably below 2.440 nm, in particular below 2.435 nm. 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 adsorption 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. Generally, the crystallinity will slightly improve when comparing modified Y zeolites with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios.

The catalyst compositions to be used in the process according to the present invention suitably comprise 50-90% by weight of modified Y zeolite and amorphous cracking catalyst and 10-50% by weight of binder. Preferably the catalyst compositions comprise rather high amounts of modified Y zeolite: 60-85% by weight of modified Y zeolite and amorphous cracking component and 15-40% by weight of binder being particularly preferred.

The process according to the present invention is suitably carried out by using a catalyst wherein the amount of modified zeolite Y ranges between 5 and 95% of the combined amount of modified Y zeolite and amorphous cracking component. In particular, the process according to the present invention is carried out by using a catalyst wherein the amount of modified zeolite Y ranges between 10 and 75% of the combined amount of modified Y zeolite and amorphous cracking component.

Suitably, silica-based amorphous cracking components can be used in the process according to the present invention. Preference is given to the use of silica-alumina as amorphous cracking component. The amount of silica in silica-based cracking components suitably comprises 50-95% by weight. Also so-called X-ray amorphous zeolites (i.e. zeolites having crystallite sizes too small to be detected by standard X-ray techniques) can be suitably applied as cracking components in the process according to the present invention.

The binder(s) present in the catalyst compositions suitably comprise inorganic oxides. Both amor-

phous and crystalline binders can be applied. Examples of suitable binders comprise silica, alumina, clays and zirconia. Preference is given to the use of alumina as binder.

Depending on the desired unit cell size the $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio between 4 and 25 can be suitably applied as the zeolitic component of the catalyst composition according to the present invention. Preference is given to modified Y zeolites having a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between 8 and 15.

Suitably, the catalyst compositions to be used in the process 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.

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, an amorphous cracking component and a binder as described hereinbefore.

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 NI/kg feed can suitably be used.

It has been found that at least 10% by weight of polynaphthenic components (either already present in the starting material or accumulated therein via recycle operation) can be converted in addition under the prevailing reaction conditions at a gross conversion level of at least 40% by weight per pass.

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 also relates to catalyst compositions comprising a modified Y zeolite having a unit cell size below 2.445 nm, a degree of crystallinity which is at least retained at increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios, a water adsorption capacity (at 25 °C and a p/p₀ 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, an amorphous cracking component, 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, and wherein 50-90% by weight of the catalyst is made up of modified Y zeolite and amorphous cracking component and 10-50% by weight is made up of binder. Preference is given to catalyst compositions where-

in 60-85% by weight of the catalyst is made up of modified Y zeolite and amorphous cracking component and 15-40% by weight is made up of binder.

Preferably, the catalyst compositions comprise modified Y zeolites wherein between 10% and 40% of the total pore volume is made up of pores having a diameter of at least 8 nm. The catalyst compositions preferably comprise modified Y zeolites having a water adsorption capacity between 10% and 15% by weight of modified zeolite. Suitably, the modified Y zeolites have a unit cell size below 2.440 nm, in particular below 2.435 nm.

The amount of modified Y zeolite in the catalyst compositions in accordance with the present invention preferably ranges between 10% and 75% of the combined amount of modified Y zeolite(s) and amorphous cracking component. Silica-based cracking components are preferred. The modified Y zeolite in accordance with the present invention has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of from 4 to 25, in particular of from 8 to 15.

The catalyst compositions in accordance with the present invention preferably comprise 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.

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

Example I

a) Preparation of catalyst.

96.5 g of a modified Y zeolite having a unit cell size of 2.437 nm, a water adsorption capacity (at 25 °C and a p/p₀ value of 0.2) of 11.8 % by weight, a nitrogen pore volume of 0.28 ml/g wherein 21% of the total pore volume is made up of pores having a diameter of > 8 nm and a loss of ignition (550 °C) of 6.7% by weight is mixed with 625.8 g of amorphous silica-alumina (ex Akzo) with a loss on ignition of 18.5% by weight. To this powdery mixture were added a slurry of 500 g of water and 191 g of hydrated aluminium oxide (boehmite, ex Condea) having a loss of ignition of 22% by weight and 7.5 g of acetic acid. After mulling the mixture obtained it was extruded in a Bonnot extruder provided with a die plate producing 1.5 mm extrudates. The extrudates were dried at 120 °C for a 2 hours and finally calcined for 2 hours at 500 °C. The extrudates obtained had a water pore volume of 0.83 ml/g.

A nickel/tungsten solution was made up containing 107 g nickel nitrate solution (14% by weight of Ni), 76 g of water and 68 g of ammonium metatungstate (69.5% by weight of W). 25.2 g of the nickel/tungsten solution was diluted with water to 42 ml and used to impregnate 50 g of the extrudates described hereinbefore. Finally, the impregnated extrudates were dried at 120 °C for 4 hours and calcined at 500 °C for 1 hour. They contained 2.6% by weight of nickel and 8.2% by weight of tungsten. The ready catalyst contained 10.6% by weight of modified Y zeolite, 68.5% by weight of amorphous cracking component and 20.9% by weight of binder, on a dry basis.

b) Hydrocracking experiments.

The catalyst as described in Example Ia was subjected to a hydrocracking performance test involving a hydrotreated heavy vacuum gas oil having the following properties:

C (%wt)	86.1
H (%wt)	13.9
S (ppm)	400
N (ppm)	9
d (70/4)	0.8277
pour point (°C)	36 (ASTM D-97)
I.B.P. (°C)	205°
10% wt rec.	360
20% wt rec.	399
30% wt rec.	427
40% wt rec.	447
50% wt rec.	465
60% wt rec.	482
70% wt rec.	500
80% wt rec.	521
90% wt rec.	544
F.B.P.	>620

The catalyst was firstly subjected to a presulphiding treatment by slowly heating in a 10 %v H₂S/H₂-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 1.45 kg.l⁻¹.h⁻¹, H₂S partial pressure 1.2 bar, total pressure 118 bar and a gas/feed ratio of 1.500 NI kg⁻¹. The experiment was carried out in once-through operation. The catalyst performance is expressed at 50% by weight conversion of 320 °C⁺ boiling point material in the feed after allowing the catalyst to stabilize. The following results were obtained:

Temperature required (50% conv. of 320 °C⁺) : 351 °C.

Distribution of 320 °C⁻ product (in % by weight):

C ₁ -C ₄	6
C ₅ -140°C	40
140°C-320°C	54

The chemical hydrogen consumption amounted to 0.7% by weight on feed.

Example II

a) Preparation of catalyst.

295 g of a modified Y zeolite having a unit cell size of 2.437 nm, a water adsorption capacity (at 25 °C and a p/p₀ value of 0.2) of 11.8% by weight, a ni-

trogen pore volume of 0.28 ml/g wherein 21% of the total pore volume is made up of pores having a diameter of > 8 nm and a loss of ignition (550 °C) of 6.8% by weight is mixed with 337 g of amorphous silica-alumina (ex Akzo) with a loss of ignition of 18.4% by weight. To this powdery mixture were added a slurry of 500 g of water and 175 g of hydrated aluminium oxide (boehmite, ex Condea) having a loss on ignition of 21.4% by weight and 6.8 g of acetic acid. After mulling the mixture obtained, it was extruded in a Bonnot extruder provided with a die plate producing 1.5 mm extrudates. The extrudates were dried at 120 °C for 2 hours and finally calcined for 2 hours at 500 °C. The extrudates obtained had a water pore volume of 0.73 ml/g.

A nickel/tungsten solution was made up containing 107.2 g of nickel nitrate solution (14% by weight of nickel), 76 g of water and 68.4 g of ammonium metatungstate (69.5% by weight of tungsten). 25.2 g of the nickel/tungsten solution was diluted with water to 36.5 ml and used to impregnate 50 g of the extrudates described hereinabove. After homogenizing the impregnated extrudates for 1 hour using a rolling device, the extrudates were dried for 1 hour at 120 °C and calcined for 1 hour at 500 °C. They contained 2.6% by weight of nickel and 8.2% by weight of tungsten. The ready catalyst contained 36.6% by weight of modified Y zeolite, 41.8% by weight of amorphous cracking component and 21.6% by weight of binder, on a dry basis.

b) Hydrocracking experiments.

The catalyst as described in Example IIa was subjected to a presulphiding treatment as described in Example Ib and thereafter tested in a 1:1 dilution with 0.2 mm SiC particles under the operating conditions as described in Example Ib.

The catalyst performance is expressed at 50% by weight conversion of 320 °C⁺ boiling point material in the feed after allowing the catalyst to stabilize.

The following results were obtained:

Temperature required (50% conv. of 320 °C⁺): 334 °C.

Distribution of 320 °C⁻ product (in % by weight):

C ₁ -C ₄	9
C ₅ -140°C	41
140°C-320°C	49

The chemical hydrogen consumption amounted to 0.9% by weight on feed.

Example III

a) Preparation of the catalyst.

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 SiO₂/Al₂O₃ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 6.85.

The material obtained was then subjected to an ion exchange treatment with 0.16 M aluminium sulphate for one hour under reflux conditions followed by a treatment with 1 M ammonium nitrate under the same conditions. This treatment was repeated once. The modified Y zeolite obtained had a unit cell size of 2.432 nm and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 10.2.

317 g of modified Y zeolite having a unit cell size of 2.432 nm, a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 10.2, a water adsorption capacity (at 25 °C and a p/p_0 value of 0.2) of 10.6% by weight, a nitrogen pore volume of 0.47 ml/g wherein 27% of the total pore volume is made up of pores having a diameter > 8 nm and a loss of ignition (550°C) of 21% by weight is mixed with 356 g of amorphous silica-alumina (ex Crosfield) with a loss of ignition of 30% by weight and 168 g of hydrated aluminium oxide (boehmite, ex Condea) having a loss of ignition of 25.8% by weight. A solution of 18.8 g of acetic acid and 342 g of water was added to this mixture. After mulling, the resulting mixture was extruded in a Bonnot extruder provided with a die plate producing 1.5 mm extrudates. The extrudates were dried for 2 hours at 120°C and calcined for 2 hours at 500°C. The extrudates obtained had a water pore volume of 0.71 ml/g.

A nickel/tungsten solution was made up containing 214 g of nickel nitrate solution (14% by weight of nickel), 150 g of water and 136.7 g of ammonium metatungstate (69.5% by weight of tungsten). 65.7 g of the nickel/tungsten solution was diluted with water to 93 ml and used to impregnate 131 g of the extrudates described hereinabove. After homogenizing the impregnated extrudates for 1 hour using a rolling device, the extrudates were dried for 2 hours at 120 °C and finally calcined at 500°C for 1 hour. They contained 2.6% by weight of nickel and 8.2% by weight of tungsten. The ready catalyst contained 37.7% by weight of modified Y zeolite, 42.3% by weight of amorphous cracking component and 20.0% by weight of binder, on a dry basis.

b) Hydrocracking experiments.

The catalyst as described in Example IIIa was subjected to a presulphiding treatment as described in Example Ib and thereafter tested as described in Example IIb.

The catalyst performance is expressed at 50% by weight conversion of 320°C+ boiling point material in the feed after allowing the catalyst to stabilize.

The following results were obtained:

Temperature required (50% conv. of 320°C+) : 330°C.

Distribution of 320°C- product (in % by weight):

C ₁ -C ₄	7
C ₅ -140°C	40
140°C-320°C	53

The chemical hydrogen consumption amounted to 0.8% by weight on feed.

Comparative Example A

a) Preparation of catalyst.

113.8 g of a commercially available ultra-stable Y-zeolite having a unit cell size of 2.456 nm, a water adsorption capacity (at 25°C and a p/p_0 value of 0.2) of 24% by weight 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 and a loss of ignition (550°C) of 21% by weight was mixed with 626 g of amorphous silica-alumina (ex Akzo) having a loss of ignition (550°C) of 18.5% by weight. To this powdery mixture were added a slurry of 500 g of water and 191 g of hydrated aluminium oxide (boehmite, ex Condea) having a loss of ignition of 22% by weight and 7.5 g of acetic acid. After mulling the mixture obtained, it was extruded in a Bonnot extruder provided with a die plate producing 1.5 mm extrudates. The extrudates 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 0.80 ml/g. A nickel/tungsten solution was made up containing 107.3 g of nickel nitrate (14% by weight of nickel), 76 g of water and 68.4 g of ammonium metatungstate (69.5% by weight of tungsten). 40 ml of a solution containing water and 25.2 g of the nickel/tungsten solution was used to impregnate 50 g of the extrudates described hereinabove. After homogenizing the impregnated extrudates for 1 hour using a rolling device, the extrudates were dried for 2 hours at 120°C and calcined for 1 hour at 500°C. They contained 2.6% by weight of nickel and 8.2% by weight of tungsten. The ready catalyst contained 12.2% by weight of zeolite, 67.3% by weight of amorphous cracking component and 20.5% by weight of binder, on a dry basis.

b) Hydrocracking experiments.

The catalyst as described in Comparative Example A a) was subjected to a presulphiding treatment as described in Example Ib and thereafter tested as described in Example Ib.

The catalyst performance is expressed at 50% by weight conversion of 320°C+ boiling point material in the feed after allowing the catalyst to stabilize.

The following results were obtained:

Temperature required (50% conv. of 320°C+) : 361°C.

Distribution of 320°C- product (in % by weight):

C ₁ -C ₄	9
C ₅ -140°C	56
140°C-320°C	35

The chemical hydrogen consumption amounted to 1.0% by weight on feed.

Comparative Example B

a) Preparation of catalyst.

379.3 g of a commercially available ultra-stable Y-zeolite having a unit cell size of 2.456 nm, a water adsorption capacity (at 25°C and a p/p₀ value of 0.2) of 24% by weight 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 and a loss of ignition (550°C) of 21% by weight was mixed with 368 g of amorphous silica-alumina (ex Akzo) having a loss of ignition (550°C) of 18.5% by weight. To this powdery mixture was added a slurry containing 191.1 g of hydrated aluminium oxide (boehmite, ex Condea), 500 g of water and 7.5 g of acetic acid. After mulling the mixture obtained, it was extruded in a Bonnot extruder with a die plate producing 1.5 mm extrudates. The extrudates 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 0.71 ml/g.

50 g of the extrudates thus obtained were impregnated with 36 ml of a solution comprising water and 25.2 g of a solution made up of 107.2 g of nickel nitrate (14% by weight of nickel), 76 g of water and 68.3 g ammonium metatungstate (69.5% by weight of tungsten). After homogenizing the impregnated extrudates for 1 hour using a rolling device, the impregnated extrudates were dried for 2 hours at 120°C and calcined for 1 hour at 500°C. They contained 2.6% by weight of nickel and 8.2% by weight of tungsten. The ready catalyst contained 40.4% by weight of zeolite, 39.2% by weight of amorphous cracking component and 20.4% by weight of binder, on a dry basis.

b) Hydrocracking experiments.

The catalyst as described in Comparative Example B a) was subjected to a presulphiding treatment as described in Example I b and thereafter tested as described in Example I b.

The catalyst performance is expressed at 50% by weight conversion of 320°C+ boiling point material in the feed after allowing the catalyst to stabilize.

The following results were obtained:

Temperature required (50% conv. of 320°C+): 338°C.

Distribution of 320°C- product (in % by weight):

C ₁ -C ₄	22
C ₅ -140°C	58
140°C-320°C	20

The chemical hydrogen consumption amounted to 1.2% by weight on feed.

It will be clear that the catalysts in accordance with the present invention are not only more active but also more selective than catalysts based on known ultra-stable Y zeolites. Also the chemical hydrogen consumption is slightly reduced.

Claims

1. 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 comprising a modified Y zeolite having a unit cell size below 2.445 nm, a degree of crystallinity which is at least retained at increasing SiO₂/Al₂O₃ molar ratios, a water adsorption capacity (at 25 °C and a p/p₀ 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, an amorphous cracking component, 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.

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

3. A process according to claim 1 or 2, wherein use is made of a modified Y zeolite having a water adsorption capacity of at least 10% by weight of modified zeolite.

4. A process according to claim 3, wherein use is made of a modified zeolite having a water adsorption capacity between 10% and 15% by weight of modified zeolite.

5. A process according to any one of claim 1-4, wherein use is made of a modified Y zeolite having a unit cell size below 2.440 nm, in particular below 2.435 nm.

6. A process according to any one of claims 1-5, wherein use is made of a catalyst comprising 50-90% by weight of modified Y zeolite and amorphous cracking component and 10-50% by weight of binder.

7. A process according to claim 6, wherein use is made of a catalyst comprising 60-85% by weight of modified Y zeolite and amorphous cracking component and 15-40% by weight of binder.

8. A process according to any one of claims 1-7, wherein use is made of a catalyst wherein the amount of modified Y zeolite ranges between 5 and 85% of the combined amount of modified Y zeolite and amorphous cracking component.

9. A process according to claim 8, wherein use is made of a catalyst wherein the amount of modified Y zeolite ranges between 10 and 75% of the combined amount of modified Y zeolite and amorphous cracking component.

10. A process according to any one of claims 1-9, wherein use is made of a silica-based amorphous cracking component.

11. A process according to claim 10, wherein use is made of silica-alumina as amorphous cracking component.

12. A process according to claim 10 or 11, wherein use is made of an amorphous cracking component containing 50-95% by weight of silica.



Comparative Example B

a) Preparation of catalyst.

379.3 g of a commercially available ultra-stable Y-zeolite having a unit cell size of 2.456 nm, a water adsorption capacity (at 25°C and a p/p₀ value of 0.2) of 24% by weight 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 and a loss of ignition (550°C) of 21% by weight was mixed with 368 g of amorphous silica-alumina (ex Akzo) having a loss of ignition (550°C) of 18.5% by weight. To this powdery mixture was added a slurry containing 191.1 g of hydrated aluminium oxide (boehmite, ex Condea), 500 g of water and 7.5 g of acetic acid. After mulling the mixture obtained, it was extruded in a Bonnot extruder with a die plate producing 1.5 mm extrudates. The extrudates 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 0.71 ml/g.

50 g of the extrudates thus obtained were impregnated with 36 ml of a solution comprising water and 25.2 g of a solution made up of 107.2 g of nickel nitrate (14% by weight of nickel), 76 g of water and 68.3 g ammonium metatungstate (69.5% by weight of tungsten). After homogenizing the impregnated extrudates for 1 hour using a rolling device, the impregnated extrudates were dried for 2 hours at 120°C and calcined for 1 hour at 500°C. They contained 2.6% by weight of nickel and 8.2% by weight of tungsten. The ready catalyst contained 40.4% by weight of zeolite, 39.2% by weight of amorphous cracking component and 20.4% by weight of binder, on a dry basis.

b) Hydrocracking experiments.

The catalyst as described in Comparative Example B a) was subjected to a presulphiding treatment as described in Example I b and thereafter tested as described in Example I b.

The catalyst performance is expressed at 50% by weight conversion of 320°C+ boiling point material in the feed after allowing the catalyst to stabilize.

The following results were obtained:

Temperature required (50% conv. of 320°C+): 338°C.

Distribution of 320°C- product (in % by weight):

C ₁ -C ₄	22
C ₅ -140°C	58
140°C-320°C	20

The chemical hydrogen consumption amounted to 1.2% by weight on feed.

It will be clear that the catalysts in accordance with the present invention are not only more active but also more selective than catalysts based on known ultra-stable Y zeolites. Also the chemical hydrogen consumption is slightly reduced.

Claims

1. 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 comprising a modified Y zeolite having a unit cell size below 2.445 nm, a degree of crystallinity which is at least retained at increasing SiO₂/Al₂O₃ molar ratios, a water adsorption capacity (at 25 °C and a p/p₀ 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, an amorphous cracking component, 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.

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

3. A process according to claim 1 or 2, wherein use is made of a modified Y zeolite having a water adsorption capacity of at least 10% by weight of modified zeolite.

4. A process according to claim 3, wherein use is made of a modified zeolite having a water adsorption capacity between 10% and 15% by weight of modified zeolite.

5. A process according to any one of claim 1-4, wherein use is made of a modified Y zeolite having a unit cell size below 2.440 nm, in particular below 2.435 nm.

6. A process according to any one of claims 1-5, wherein use is made of a catalyst comprising 50-90% by weight of modified Y zeolite and amorphous cracking component and 10-50% by weight of binder.

7. A process according to claim 6, wherein use is made of a catalyst comprising 60-85% by weight of modified Y zeolite and amorphous cracking component and 15-40% by weight of binder.

8. A process according to any one of claims 1-7, wherein use is made of a catalyst wherein the amount of modified Y zeolite ranges between 5 and 85% of the combined amount of modified Y zeolite and amorphous cracking component.

9. A process according to claim 8, wherein use is made of a catalyst wherein the amount of modified Y zeolite ranges between 10 and 75% of the combined amount of modified Y zeolite and amorphous cracking component.

10. A process according to any one of claims 1-9, wherein use is made of a silica-based amorphous cracking component.

11. A process according to claim 10, wherein use is made of silica-alumina as amorphous cracking component.

12. A process according to claim 10 or 11, wherein use is made of an amorphous cracking component containing 50-95% by weight of silica.



13. A process according to any one of claims 1-12 wherein use is made of a binder comprising an inorganic oxide.

14. A process according to claim 13, wherein use is made of silica, alumina or a clay as binder.

15. A process according to any one of claims 1-14, wherein use is made of a modified Y zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of from 4 to 25.

16. A process according to claim 15, wherein use is made of a modified Y zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of from 8 to 15.

17. A process according to any one of claims 1-16, wherein use is made of a catalyst comprising 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.

18. A process according to claim 17, wherein use is made of a hydrogenation component 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.

19. A process according to claim 18, wherein use is made of hydrogenation component(s) of Group VI in sulphided form.

20. A process according to any one of claims 1-19, wherein at least 10% by weight of polynaphthenic components is converted in addition to the hydrocarbon oil conversion 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 at a gross conversion level of at least 40% by weight per pass.

21. A process according to claim 20, wherein at least 25% by weight of polynaphthenic components is converted in addition to the hydrocarbon oil conversion carried out at a temperature between 300 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 at a gross conversion level of at least 40% by weight per pass.

22. Catalyst composition comprising a modified Y zeolite having a unit cell size below 2.445 nm, a degree of crystallinity which is at least retained at increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios, a water adsorption capacity (at 25 °C and p/p_0 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, an amorphous cracking component, 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, and wherein 50-90% by weight of the catalyst is made up of modified Y zeolite and amorphous cracking component and 10-50% by weight is made up of binder.

23. Catalyst composition according to claim 22, wherein 60-85% by weight of the catalyst is made up of modified Y zeolite and amorphous cracking component and 15-40% by weight is made up of binder.

24. Catalyst compositions according to claim 22 or 23, 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.

25. Catalyst composition according to any one of claims 22-24, wherein the modified Y zeolite has a water adsorption capacity between 10% and 15% by weight of modified zeolite.

26. Catalyst composition according to any one of claims 22-25, wherein the modified Y zeolite has a unit cell size below 2.440 nm, in particular below 2.435 nm.

27. Catalyst composition according to any one of claims 22-26, wherein the amount of modified zeolite Y ranges between 10 and 75% of the combined amount of modified Y zeolite and amorphous cracking component.

28. Catalyst composition according to any one of claims 22-27, wherein the amorphous cracking component is a silica-based cracking component.

29. Catalyst composition according to any one of claims 22-28, wherein the modified Y zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of from 4 to 25, in particular of from 8 to 15.

30. Catalyst composition according to any one of claims 22-29, wherein the catalyst comprises 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.

Revendications

1. Procédé de conversion d'huiles hydrocarbonées en produits de masse moléculaire moyenne plus faible et de point d'ébullition moyen plus faible, comprenant la mise en contact d'une huile hydrocarbonée, à une température élevée sous une pression élevée, en présence d'hydrogène, avec un catalyseur comprenant une zéolite Y modifiée ayant une taille de cellule élémentaire inférieure à 2,445 nm, un degré de cristallinité qui est au moins conservé lorsque les rapports molaires $\text{SiO}_2/\text{Al}_2\text{O}_3$ augmentent, une capacité d'adsorption d'eau (à 25°C et pour une valeur p/p_0 de 0,2) d'au moins 8% en poids de la zéolite modifiée et un volume poreux d'au moins 0,5 ml/g, dans lequel entre 10% et 60% du volume poreux total est constitué de pores ayant un diamètre d'au moins 8 nm, un constituant de craquage amorphe, un liant et au moins un constituant d'hydrogénation d'un métal du groupe VI et/ou au moins un constituant d'hydrogénation d'un métal du groupe VIII.

2. Procédé selon la revendication 1, dans lequel on utilise un catalyseur comprenant une zéolite Y modifiée dans laquelle entre 10% et 40% du volume poreux total est constitué par des pores ayant un diamètre d'au moins 8 nm.

3. Procédé selon la revendication 1 ou 2, dans lequel on utilise une zéolite Y modifiée ayant une capacité d'adsorption d'eau d'au moins 10% en poids de la zéolite modifiée.

4. Procédé selon la revendication 3, dans lequel on utilise une zéolite modifiée ayant une capacité d'adsorption d'eau comprise entre 10% et 15% en poids de la zéolite modifiée.

5. Procédé selon l'une quelconque des revendications 1-4, dans lequel on utilise une zéolite Y mo-



difiée ayant une taille de cellule élémentaire inférieure à 2,440 nm, en particulier inférieure à 2,435 nm.

6. Procédé selon l'une quelconque des revendications 1-5, dans lequel on utilise un catalyseur comprenant 50-90% en poids de zéolite Y modifiée et de constituant de craquage amorphe et 10-50% en poids de liant.

7. Procédé selon la revendication 6, dans lequel on utilise un catalyseur comprenant 60-85% en poids de zéolite Y modifiée et de constituant de craquage amorphe et 15-40% en poids de liant.

8. Procédé selon l'une quelconque des revendications 1-7, dans lequel on utilise un catalyseur dans lequel la quantité de zéolite Y modifiée s'échelonne entre 5 et 85% de la quantité combinée de zéolite Y modifiée et de constituant de craquage amorphe.

9. Procédé selon la revendication 8, dans lequel on utilise un catalyseur dans lequel la quantité de zéolite Y modifiée s'échelonne entre 10 et 75% de la quantité combinée de zéolite Y modifiée et de constituant de craquage amorphe.

10. Procédé selon l'une quelconque des revendications 1-9, dans lequel on utilise un constituant de craquage amorphe à base de silice.

11. Procédé selon la revendication 10, dans lequel on utilise de la silice-alumine comme constituant de craquage amorphe.

12. Procédé selon la revendication 10 ou 11, dans lequel on utilise un constituant de craquage amorphe contenant 50-95% en poids de silice.

13. Procédé selon l'une quelconque des revendications 1-12, dans lequel on utilise un liant comprenant un oxyde minéral.

14. Procédé selon la revendication 13, dans lequel on utilise comme liant de la silice, de l'alumine ou une argile.

15. Procédé selon l'une quelconque des revendications 1-14, dans lequel on utilise une zéolite Y modifiée ayant un rapport molaire $\text{SiO}_2/\text{Al}_2\text{O}_3$ de 4 à 25.

16. Procédé selon la revendication 15, dans lequel on utilise une zéolite Y modifiée ayant un rapport molaire $\text{SiO}_2/\text{Al}_2\text{O}_3$ de 8 à 15.

17. Procédé selon l'une quelconque des revendications 1-16, dans lequel on utilise un catalyseur comprenant un ou plusieurs constituants du nickel et/ou du cobalt et un ou plusieurs constituants du molybdène et/ou du tungstène ou un ou plusieurs constituants du platine et/ou du palladium.

18. Procédé selon la revendication 17, dans lequel on utilise un constituant d'hydrogénation comprenant entre 0,05 et 10% en poids de nickel et entre 2 et 40% en poids de tungstène, calculé en métaux pour 100 parties en poids de catalyseur total.

19. Procédé selon la revendication 18, dans lequel on utilise un ou des constituants d'hydrogénation du groupe VI sous forme sulfurée.

20. Procédé selon l'une quelconque des revendications 1-19, dans lequel au moins 10% en poids de constituants polynaphténiques sont convertis en plus de la conversion de l'huile hydrocarbonée réalisée à une température dans l'intervalle de 250°C à 500°C, sous une pression allant jusqu'à 300 bars et à une vitesse spatiale comprise entre 0,1 et 10 kg de

charge par litre de catalyseur et par heure, à un taux de conversion global d'au moins 40% en poids par passe.

21. Procédé selon la revendication 20, dans lequel au moins 25% en poids de constituants polynaphténiques sont convertis en plus de la conversion de l'huile hydrocarbonée réalisée à une température comprise entre 300°C et 450°C, sous une pression comprise entre 25 et 200 bars et à une vitesse spatiale comprise entre 0,2 et 5 kg de charge par litre de catalyseur et par heure, à un taux de conversion global d'au moins 40% en poids par passe.

22. Composition catalytique comprenant une zéolite Y modifiée ayant une taille de cellule élémentaire inférieure à 2,445 nm, un degré de cristallinité qui est au moins conservé lorsque les rapports molaires $\text{SiO}_2/\text{Al}_2\text{O}_3$ augmentent, une capacité d'adsorption d'eau (à 25°C et pour une valeur p/p_0 de 0,2) d'au moins 8% en poids de la zéolite modifiée et un volume poreux d'au moins 0,25 ml/g dans lequel entre 10% et 60% du volume poreux total est constitué par des pores ayant un diamètre d'au moins 8 nm, un constituant de craquage amorphe, un liant et au moins un constituant d'hydrogénation d'un métal du groupe VI et/ou au moins un constituant d'hydrogénation d'un métal du groupe VIII, et dans lequel 50-90% en poids du catalyseur est constitué par de la zéolite Y modifiée et un constituant de craquage amorphe et 10-50% en poids est constitué d'un liant.

23. Composition catalytique selon la revendication 22, dans laquelle 60-85% en poids du catalyseur est constitué de zéolite Y modifiée et de constituant de craquage amorphe et 15-40% en poids est constitué de liant.

24. Composition catalytique selon la revendication 22 ou 23, dans laquelle entre 10% et 40% du volume poreux total de la zéolite Y modifiée est constitué de pores ayant un diamètre d'au moins 8 nm.

25. Composition catalytique selon l'une quelconque des revendications 22-24, dans laquelle la zéolite Y modifiée a une capacité d'adsorption d'eau comprise entre 10% et 15% en poids de la zéolite modifiée.

26. Composition catalytique selon l'une quelconque des revendications 22-25, dans laquelle la zéolite Y modifiée a une taille de cellule élémentaire inférieure à 2,440 nm, en particulier inférieure à 2,435 nm.

27. Composition catalytique selon l'une quelconque des revendications 22-26, dans laquelle la quantité de zéolite Y modifiée s'échelonne entre 10 et 75% de la quantité combinée de zéolite Y modifiée et de constituant de craquage amorphe.

28. Composition catalytique selon l'une quelconque des revendications 22-27, dans laquelle le constituant de craquage amorphe est un constituant de craquage à base de silice.

29. Composition catalytique selon l'une quelconque des revendications 22-28, dans laquelle la zéolite Y modifiée a un rapport molaire $\text{SiO}_2/\text{Al}_2\text{O}_3$ de 4 à 25, en particulier de 8 à 15.

30. Composition catalytique selon l'une quelconque des revendications 22-29, dans laquelle le catalyseur comprend entre 0,05 et 10% en poids de



nickel et entre 2 et 40% en poids de tungstène, calculé en métaux pour 100 parties en poids de catalyseur total.

Patentansprüche

1. Ein Verfahren zur Umwandlung von Kohlenwasserstoffölen in Produkte mit niedrigerem Durchschnittsmolekulargewicht und niedrigerem durchschnittlichen Siedepunkt, umfassend das Kontaktieren eines Kohlenwasserstofföls bei erhöhter Temperatur und erhöhtem Druck in Gegenwart von Wasserstoff mit einem Katalysator, umfassend einen modifizierten Y-Zeolith mit einer Elementarzellengröße von weniger als 2,445 nm, einem Kristallinitätsgrad, welcher bei steigenden $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Molverhältnissen mindestens gleich bleibt, einer Wasseradsorptionskapazität (bei 25°C und einem p/po-Wert von 0,2) von mindestens 8 Gewichtsprozent des modifizierten Zeoliths und einem Porenvolumen von mindestens 0,25 ml/g, wobei zwischen 10% und 60% des Gesamtporenvolumens aus Poren mit einem Durchmesser von mindestens 8 nm bestehen, eine amorphe Crackkomponente, ein Bindemittel und wenigstens eine Hydrierkomponente eines Metalls der Gruppe VI und/oder mindestens eine Hydrierkomponente eines Metalls der Gruppe VIII.

2. Ein Verfahren nach Anspruch 1, in welchem ein Katalysator, enthaltend einen modifizierten Zeolith, bei welchem zwischen 10% und 40% des Gesamtporenvolumens aus Poren mit einem Durchmesser von mindestens 8 nm bestehen, verwendet wird.

3. Ein Verfahren nach Anspruch 1 oder 2, in welchem ein modifizierter Zeolith mit einer Wasseradsorptionskapazität von mindestens 10 Gewichtsprozent des modifizierten Zeolith verwendet wird.

4. Ein Verfahren nach Anspruch 3, in welchem ein modifizierter Zeolith mit einer Wasseradsorptionskapazität zwischen 10 und 15 Gewichtsprozent des modifizierten Zeolith verwendet wird.

5. Ein Verfahren nach einem der Ansprüche 1 bis 4, in welchem ein modifizierter Zeolith mit einer Elementarzellengröße von weniger als 2,440 nm, vorzugsweise weniger als 2,435 nm verwendet wird.

6. Ein Verfahren nach einem der Ansprüche 1 bis 5, in welchem ein Katalysator, enthaltend 50 bis 90 Gewichtsprozent eines modifizierten Y-Zeolith und eine amorphe Crackkomponente und 10 bis 50 Gewichtsprozent eines Bindemittels, verwendet wird.

7. Ein Verfahren nach Anspruch 6, in welchem ein Katalysator, enthaltend 60 bis 85 Gewichtsprozent eines modifizierten Y-Zeolith und eine amorphe Crackkomponente und 15 bis 40 Gewichtsprozent eines Bindemittels, verwendet wird.

8. Ein Verfahren nach einem der Ansprüche 1 bis 7, in welchem ein Katalysator verwendet wird, bei welchem die Menge an modifiziertem Y-Zeolith zwischen 5 und 85% der zusammengesetzten Menge aus modifiziertem Y-Zeolith und der amorphen Crackkomponente beträgt.

9. Ein Verfahren nach Anspruch 8, in welchem ein Katalysator verwendet wird, bei welchem die Menge an modifiziertem Y-Zeolith zwischen 10 und 75% der zusammengesetzten Menge aus modifizier-

tem Y-Zeolith und amorpher Crackkomponente beträgt.

10. Ein Verfahren nach einem der Ansprüche 1 bis 9, in welchem eine amorphe Crackkomponente auf Siliciumdioxidbasis verwendet wird.

11. Ein Verfahren nach Anspruch 10, in welchem Siliciumdioxid-Aluminiumoxid als amorphe Crackkomponente verwendet wird.

12. Ein Verfahren nach Anspruch 10 oder 11, in welchem eine amorphe Crackkomponente, enthaltend 50 bis 95 Gewichtsprozent Siliciumdioxid, verwendet wird.

13. Ein Verfahren nach einem der Ansprüche 1 bis 12, in welchem ein Bindemittel, enthaltend ein anorganisches Oxid, verwendet wird.

14. Ein Verfahren nach Anspruch 13, in welchem Siliciumdioxid, Aluminiumoxid oder ein Ton als Bindemittel verwendet wird.

15. Ein Verfahren nach einem der Ansprüche 1 bis 14, in welchem ein modifizierter Y-Zeolith mit einem Molverhältnis von $\text{SiO}_2/\text{Al}_2\text{O}_3$ von 4 bis 25 verwendet wird.

16. Ein Verfahren nach Anspruch 15, in welchem ein modifizierter Y-Zeolith mit einem Molverhältnis $\text{SiO}_2/\text{Al}_2\text{O}_3$ von 8 bis 15 verwendet wird.

17. Ein Verfahren nach einem der Ansprüche 1 bis 16, in welchem ein Katalysator, enthaltend eine oder mehrere Komponente(n) aus Nickel und/oder Cobalt und eine oder mehrere Komponenten aus Molybdän und/oder Wolfram oder eine oder mehrere Komponenten aus Platin und/oder Palladium, verwendet wird.

18. Ein Verfahren nach Anspruch 17, in welchem eine Hydrierkomponente, enthaltend zwischen 0,05 und 10 Gewichtsprozent Nickel und zwischen 2 und 40 Gewichtsprozent Wolfram, berechnet als Metalle pro 100 Gewichtsteile des gesamten Katalysators, verwendet wird.

19. Ein Verfahren nach Anspruch 18, in welchem (eine) Hydrierkomponente(n) der Gruppe VI in sulfidierter Form eingesetzt wird (werden).

20. Ein Verfahren nach einem der Ansprüche 1 bis 19, in welchem mindestens 10 Gewichtsprozent an Polynaphthenkomponenten zusätzlich zu der Kohlenwasserstoffölmwandlung umgewandelt werden, welche bei einer Temperatur zwischen 250°C und 500°C, einem Druck bis zu 300 bar und einer Raumgeschwindigkeit zwischen 0,1 und 10 kg Zuspaltung pro Liter Katalysator pro Stunde bei einem Bruttoumwandlungsgrad von mindestens 40 Gewichtsprozent pro Durchgang durchgeführt wird.

21. Ein Verfahren nach Anspruch 20, in welchem mindestens 25 Gewichtsprozent der Polynaphthenkomponenten zusätzlich zur Kohlenwasserstoffölmwandlung umgewandelt werden, welche bei einer Temperatur zwischen 300 und 450°C, einem Druck zwischen 25 und 200 bar und einer Raumgeschwindigkeit zwischen 0,2 und 5 kg Zuspaltung pro Liter Katalysator pro Stunde bei einem Bruttoumwandlungsgrad von mindestens 40 Gewichtsprozent pro Durchgang durchgeführt wird.

22. Katalysatorzusammensetzung, enthaltend einen modifizierten Y-Zeolith mit einer Elementarzellengröße von weniger als 2,445 nm einem Kristallinitätsgrad, welcher bei steigenden Molverhältnissen



von $\text{SiO}_2/\text{Al}_2\text{O}_3$ mindestens gleich bleibt, einer Wasseradsorptionskapazität (bei 25°C und einem p/p_0 -Wert von 0,2) von mindestens 8 Gewichtsprozent des modifizierten Zeolith und einem Porenvolumen von mindestens 0,25 ml/g, wobei zwischen 10 und 60% des Gesamtporenvolumens aus Poren mit einem Durchmesser von mindestens 8 nm bestehen, eine amorphe Crackkomponente, ein Bindemittel und mindestens eine Hydrierkomponente eines Metalls der Gruppe VI und/oder mindestens eine Hydrierkomponente eines Metalls der Gruppe VIII, und wobei 50 bis 90 Gewichtsprozent des Katalysators aus modifiziertem Y-Zeolith und einer amorphen Crackkomponente und 10 bis 50 Gewichtsprozent aus einem Bindemittel bestehen.

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23. Katalysatorzusammensetzung nach Anspruch 22, in welcher 60 bis 85 Gewichtsprozent des Katalysators aus einem modifizierten Y-Zeolith und amorpher Crackkomponente und 15 bis 40 Gewichtsprozent aus einem Bindemittel bestehen.

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24. Katalysatorzusammensetzung nach Anspruch 22 oder 23, in welcher 10 bis 40% des Gesamtporenvolumens des modifizierten Y-Zeoliths aus Poren mit einem Durchmesser von mindestens 8 nm bestehen.

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25. Katalysatorzusammensetzung nach einem der Ansprüche 22 bis 24, in welcher der modifizierte Zeolith Y eine Wasseradsorptionskapazität zwischen 10 und 15 Gewichtsprozent des modifizierten Zeolith hat.

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26. Katalysatorzusammensetzung nach einem der Ansprüche 22 bis 25, in welcher der modifizierte Zeolith Y eine Elementarzellengröße von weniger als 2,440 nm, vorzugsweise weniger als 2,435 nm hat.

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27. Katalysatorzusammensetzung nach einem der Ansprüche 22 bis 26, in welcher die Menge an modifiziertem Zeolith Y im Bereich zwischen 10 und 75% der zusammengesetzten Menge an modifiziertem Y-Zeolith und amorpher Crackkomponente beträgt.

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28. Katalysatorzusammensetzung nach einem der Ansprüche 22 bis 27, in welcher die amorphe Crackkomponente eine Crackkomponente auf Siliciumdioxid-Basis ist.

29. Katalysatorzusammensetzung nach einem der Ansprüche 22 bis 28, in welcher der modifizierte Y-Zeolith ein Molverhältnis $\text{SiO}_2/\text{Al}_2\text{O}_3$ von 4 bis 25, vorzugsweise von 8 bis 15 aufweist.

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30. Katalysatorzusammensetzung nach einem der Ansprüche 22 bis 29, in welcher der Katalysator zwischen 0,05 und 10 Gewichtsprozent Nickel und zwischen 2 und 40 Gewichtsprozent Wolfram, berechnet als Metalle pro 100 Gewichtsteile des Gesamtkatalysators, enthält.

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