CATALYST COMPOSITIONS AND THEIR USE IN HYDROCARBON CONVERSION PROCESSES

The present invention relates to catalytic compositions and hydrocarbon conversion processes using them.

Many hydrocarbon conversion processes in the petroleum industry are carried out using catalyst compositions based on zeolite Y. The zeolite Y has very often been subjected to certain stabilising and/or dealumination process steps during its preparation which result in its having a reduced unit cell constant (a_o) and an increased silica to alumina molar ratio. These stabilised zeolites, as well as the as-synthesised zeolite Y, possess relatively few pores that are larger than 2 nanometres (nm) in diameter and therefore have a limited mesopore volume (a mesopore has a diameter typically in the range from 2 to 60 nm).

US-A-5 354 452 discloses a process in which ultrastable Y zeolites having a silica to alumina molar ratio of 6 to 20, and superultrastable Y zeolites having a silica to alumina molar ratio of at least 18 and a unit cell constant (a_o) of 2.420 to 2.448 nm (24.20 to 24.48 Å) are subjected to a hydrothermal treatment with steam at 1000 to 1200 °F followed by an acid treatment at 140 to 220 °F. The hydrothermally-treated zeolite is characterised by a unit cell constant (a_o) typically in the range from 2.427 to 2.439 nm (24.27 to 24.39 Å), a secondary pore volume contained in mesopores having a diameter in the range from 10 to 60 nm (100 to 600 Å) of 0.09 to 0.13 ml/g, and a total pore volume of 0.16 to 0.20 ml/g, whereas the acidified, hydrothermally-treated zeolite is characterised by a unit cell constant (a_o) typically in the range from 2.405 to 2.418 nm (24.05 to

24.18 Å), a secondary pore volume contained in mesopores having a diameter in the range from 10 to 60 nm (100 to 600 Å) of 0.11 to 0.14 ml/g, and a total pore volume of 0.16 to 0.25 ml/g.

It has now surprisingly been found possible to prepare catalyst compositions containing certain 'Y-type' molecular sieves with even higher mesopore volumes which may advantageously be used in the conversion of hydrocarbon oils, e.g. by catalytic cracking or hydrocracking, to produce desirable products in greater yield and selectivity.

In accordance with the present invention, there is provided a catalyst composition comprising a molecular sieve having a structure substantially the same as zeolite Y, a unit cell constant (a_o) less than or equal to 2.485 nm and a mesopore volume, contained in mesopores having a diameter in the range from 2 to 60 nm, of at least 0.05 ml/g, and a binder, wherein the relationship between the unit cell constant (a_o) and the mesopore volume is defined as follows:

Unit Cell Constant (nm)	Mesopore Volume (ml/g)
$2.485 \geq a_o > 2.460$	≥ 0.05
$2.460 \geq a_o \geq 2.450$	≥ 0.18
$2.450 > a_o > 2.427$	≥ 0.23
$2.427 \geq a_o$	≥ 0.26

The molecular sieve used in the catalyst compositions of the invention is defined as having a structure substantially the same as zeolite Y. This definition is intended to embrace molecular sieves derived not only from zeolite Y per se but also from modified zeolites Y in which a proportion of the aluminium ions have been replaced by other metal ions such as iron, titanium, gallium, tin, chromium or scandium ions but whose structures are not significantly different from that of zeolite Y, as may be determined by X-ray crystallography.

Examples of suitable iron- and/or titanium-modified zeolites Y are those disclosed in US Patents Nos. 5 176 817 and 5 271 761, and examples of suitable chromium- and/or tin-modified zeolites Y are those disclosed in EP-A-321 177.

However, the molecular sieve used in the catalyst compositions of the invention is preferably derived from a zeolite Y per se, e.g. as described in Zeolite Molecular Sieves (Structure, Chemistry and Use) by Donald W. Breck published by Robert E. Krieger Publishing Company Inc., 1984; and US Patents Nos. 3 506 400, 3 671 191, 3 808 326, 3 929 672 and 5 242 677.

The molecular sieve used in the present compositions has a unit cell constant (a_o) less than or equal to (≤) 2.485 nm (24.85 Å), preferably less than or equal to (≤) 2.460 nm (24.60 Å), e.g. in the range from 2.427 to 2.485 nm (24.27 to 24.85 Å), preferably in the range from 2.427 to 2.460 nm (24.27 to 24.60 Å). Advantageously, the molecular sieve has a unit cell constant (a_o) up to 2.440 nm (24.40 Å), e.g. in the range from 2.427 to 2.440 nm (24.27 to 24.40 Å), or a unit cell constant (a_o) in the range from 2.450 to 2.460 nm (24.50 to 24.60 Å).

The mesopore volume of the molecular sieve, as contained in mesopores having a diameter in the range from 2 to 60 nm, will vary depending on the unit cell constant (a_o). The relationship between the unit cell constant (a_o) and the mesopore volume is as follows:

Unit Cell Constant (nm)	Mesopore Volume (ml/g)
$2.485 \geq a_o > 2.460$	≥ 0.05
$2.460 \geq a_o \geq 2.450$	≥ 0.18
$2.450 > a_o > 2.427$	≥ 0.23
$2.427 \geq a_o$	≥ 0.26

The molecular sieve may have a mesopore volume of up to 0.8 ml/g, e.g. in the range from 0.05, preferably from 0.18, more preferably from 0.23, still more preferably

from 0.26, advantageously from 0.3 and particularly from 0.4 ml/g, up to 0.6 ml/g, especially up to 0.8 ml/g.

The molecular sieves useful in the present invention may conveniently be prepared by a hydrothermal treatment in which a zeolite Y or modified zeolite Y as described above is contacted hydrothermally with an aqueous solution having dissolved therein one or more salts, acids, bases and/or water-soluble organic compounds at a temperature above the boiling point of the solution at atmospheric pressure for a period of time sufficient to provide the zeolite with an increased mesopore volume in mesopores having a diameter in the range from 2 to 60 nm. On completion of the hydrothermal treatment, the product is separated, washed (using deionized water or an acid, e.g. nitric acid, solution) and recovered. The product obtained by this treatment will generally have a unit cell size (unit cell constant) and a silica to alumina molar ratio similar to those of the starting zeolite. However, if desired, the product may be subjected to additional stabilisation and/or dealumination treatments as are well known in the art in order to change the unit cell size and/or the silica to alumina molar ratio.

In the preparation of the aqueous hydrothermal treatment solution, examples of salts which may be used include ammonium, alkali metal (e.g. sodium and potassium) and alkaline earth metal salts of strong and weak, organic and inorganic acids, (e.g., nitric and hydrochloric acids); examples of acids which may be used include strong inorganic acids such as nitric acid and hydrochloric acid as well as weak organic acids such as acetic acid and formic acid; examples of bases which may be used include inorganic bases such as ammonium, alkali metal and alkaline earth metal hydroxides together with organic bases such as quaternary ammonium hydroxides, amine complexes and pyridinium salts; and examples of

water-soluble organic compounds which may be used include C_1-C_6 alcohols and ethers. The concentration and amount of the aqueous solution contacted with the starting zeolite is adjusted to provide at least 0.1 part by weight (pbw) of dissolved solute per part by weight of zeolite, on a dry weight basis.

The pH of the aqueous hydrothermal treatment solution may vary between 3 and 10 and depending on the (modified) zeolite Y to be treated, a high or a low pH may be preferred. Thus, if the starting zeolite has a unit cell constant (a_o) of from 2.450 to 2.460 nm (2.460 nm $\geq a_o \geq$ 2.450 nm), it is desirable to maintain or adjust the pH of the solution prior to contact with the zeolite to a value of 4.5 to 8; if the starting zeolite has a unit cell constant (a_o) of from greater than 2.427 to less than 2.450 nm (2.450 nm $> a_o >$ 2.427 nm), then the pH of the solution should desirably be maintained or adjusted to a value of 3 to 8; and if the starting zeolite has a unit cell constant (a_o) less than or equal to 2.427 nm (2.427 nm $\geq a_o$), then the pH of the solution should desirably be maintained or adjusted to a value of 3 to 7.

The temperature of the hydrothermal treatment should be above the atmospheric boiling point of the aqueous solution. Although temperatures up to 400 °C can be used, a temperature in the range from 110 or 115 to 250 °C is usually satisfactory. Good results can be obtained using a temperature in the range from 140 to 200 °C.

The treatment time is inversely related to the treatment temperature. Thus, at a higher temperature, a shorter time will be required to effect a given increase in mesopore volume. The treatment time may vary between 5 minutes and 24 hours but is usually in the range from 2 to 12 hours.

The duration of the hydrothermal treatment and the temperature at which it is applied should be such as to provide a mesopore volume in the final product which is at least 5%, preferably at least 10%, larger than the mesopore volume in the starting zeolite.

A preferred molecular sieve to use in the catalyst composition of the present invention is one prepared by a process comprising contacting a (modified) zeolite Y as hereinbefore defined hydrothermally with an aqueous solution having dissolved therein one or more salts, acids, bases and/or water-soluble organic compounds at a temperature above the atmospheric boiling point of the solution, followed by separation and washing with an acid solution.

The acid solution may be an aqueous solution of one or more acids selected from inorganic and organic acids, e.g. nitric acid, hydrochloric acid, acetic acid, formic acid and citric acid. Compared to using (deionized) water, washing with an acid solution has the advantage of further enhancing the middle distillate selectivity of the increased mesopore molecular sieve.

As binder in the catalyst compositions of the invention, it is convenient to use an inorganic oxide or a mixture of two or more such oxides. The binder may be amorphous or crystalline. Examples of suitable binders include alumina, silica, magnesia, titania, zirconia, silica-alumina, silica-zirconia, silica-boria and mixtures thereof. A preferred binder to use is alumina, or alumina in combination with a dispersion of silica-alumina in an alumina matrix, particularly a matrix of gamma alumina.

The catalyst composition of the present invention preferably contains from 1 to 80 %w (per cent by weight) of the molecular sieve and from 20 to 99 %w binder, based on the total dry weight of molecular sieve and binder.

More preferably, the catalyst composition contains from 10 to 70 %w of the molecular sieve and from 30 to 90 %w binder, in particular from 20 to 50 %w of the molecular sieve and from 50 to 80 %w binder, based on the total dry weight of molecular sieve and binder.

Depending on the application of the present catalyst compositions (e.g. in hydrocracking), they may further comprise at least one hydrogenation component. Examples of hydrogenation components useful in the present invention include Group 6B (e.g. molybdenum and tungsten) and Group 8 metals (e.g. cobalt, nickel, iridium, platinum and palladium), their oxides and sulphides. The catalyst composition preferably contains at least two hydrogenation components, e.g. a molybdenum and/or tungsten component in combination with a cobalt and/or nickel component. Particularly preferred combinations are nickel/tungsten and nickel/molybdenum. Very advantageous results are obtained when the metals are used in the sulphide form.

The catalyst composition may contain up to 50 parts by weight of hydrogenation component, calculated as metal per 100 parts by weight of total catalyst composition. For example, the catalyst composition may contain from 2 to 40, more preferably from 5 to 25 and especially from 10 to 20, parts by weight of Group 6 metal(s) and/or from 0.05 to 10, more preferably from 0.5 to 8 and advantageously from 2 to 6, parts by weight of Group 8 metal(s), calculated as metal per 100 parts by weight of total catalyst composition.

The present catalyst compositions may be prepared in accordance with techniques conventional in the art.

A convenient method for preparing a catalyst composition for use in cracking comprises mixing binder material with water to form a slurry or sol, adjusting the pH of the slurry or sol as appropriate and then

adding a powdered molecular sieve as defined above together with additional water to obtain a slurry or sol with a desired solids concentration. The slurry or sol is then spray-dried. The spray-dried particles thus formed may be used directly or may be calcined prior to use.

One method for preparing a catalyst composition for use in hydrocracking comprises mulling a molecular sieve as defined above and binder in the presence of water and optionally a peptising agent, extruding the resulting mixture into pellets and calcining the pellets. The pellets thus obtained are then impregnated with one or more solutions of Group 6B and/or Group 8 metal salts and again calcined.

Alternatively, the molecular sieve and binder may be co-mulled in the presence of one or more solutions of Group 6B and/or Group 8 metal salts and optionally a peptising agent, and the mixture so formed extruded into pellets. The pellets may then be calcined.

The present invention further provides a process for converting a hydrocarbonaceous feedstock into lower boiling materials which comprises contacting the feedstock at elevated temperature with a catalyst composition according to the invention.

The hydrocarbonaceous feedstocks useful in the present process can vary within a wide boiling range. They include lighter fractions such as kerosine fractions as well as heavier fractions such as gas oils, coker gas oils, vacuum gas oils, deasphalted oils, long and short residues, catalytically cracked cycle oils, thermally or catalytically cracked gas oils, and syncrudes, optionally originating from tar sands, shale oils, residue upgrading processes or biomass. Combinations of various hydrocarbon oils may also be employed. The feedstock will generally comprise hydrocarbons having a boiling point of

at least 330 °C. In a preferred embodiment of the invention, at least 50 %w of the feedstock has a boiling point above 370 °C. The feedstock may have a nitrogen content of up to 5000 ppmw (parts per million by weight) and a sulphur content of up to 6 %w. Typically, nitrogen contents are in the range from 250 to 2000 ppmw and sulphur contents are in the range from 0.2 to 5 %w. It is possible and may sometimes be desirable to subject part or all of the feedstock to a pre-treatment, for example, hydrodenitrogenation, hydrodesulphurisation or hydrodemetallisation, methods for which are known in the art.

If the process is carried out under catalytic cracking conditions (i.e. in the absence of added hydrogen), the process is conveniently carried out in an upwardly or downwardly moving catalyst bed, e.g. in the manner of conventional Thermofor Catalytic Cracking (TCC) or Fluidised Catalytic Cracking (FCC) processes. The process conditions are preferably a reaction temperature in the range from 400 to 900 °C, more preferably from 450 to 800 °C and especially from 500 to 650 °C; a total pressure of from 1 x 10^5 to 1 x 10^6 Pa (1 to 10 bar), in particular from 1 x 10^5 to 7.5 x 10^5 Pa (1 to 7.5 bar); a catalyst composition/feedstock weight ratio (kg/kg) in the range from 5 to 150, especially 20 to 100; and a contact time between catalyst composition and feedstock of from 0.1 to 10 seconds, advantageously from 1 to 6 seconds.

However, the process according to the present invention is preferably carried out under hydrogenating conditions, i.e. under catalytic hydrocracking conditions, e.g. residue hydrocracking conditions.

Thus, the reaction temperature is preferably in the range from 250 to 500 °C, more preferably from 300 to 450 °C and especially from 350 to 450 °C.

The total pressure is preferably in the range from 5×10^6 to 3×10^7 Pa (50 to 300 bar), more preferably from 7.5×10^6 to 2.5×10^7 Pa (75 to 250 bar) and even more preferably from 1×10^7 to 2×10^7 Pa (100 to 200 bar).

The hydrogen partial pressure is preferably in the range from 2.5×10^6 to 2.5×10^7 Pa (25 to 250 bar), more preferably from 5×10^6 to 2×10^7 Pa (50 to 200 bar) and still more preferably from 6×10^6 to 1.8×10^7 Pa (60 to 180 bar).

A space velocity in the range from 0.05 to 10 kg feedstock per litre catalyst composition per hour ($kg.l^{-1}.h^{-1}$) is conveniently used. Preferably the space velocity is in the range from 0.1 to 8, particularly from 0.1 to 5, $kg.l^{-1}.h^{-1}$. Furthermore, total gas rates (gas/feed ratios) in the range from 100 to 5000 Nl/kg are conveniently employed. Preferably, the total gas rate employed is in the range from 250 to 2500 Nl/kg.

The present invention will be further understood from the following illustrative examples in which the unit cell constant (a_o) was determined according to standard test method ASTM D 3942-80, the relative crystallinity (%) was determined by comparing X-ray crystallography data for the increased mesopore zeolite Y with that for a standard corresponding zeolite Y of the prior art, and the surface properties (i.e. surface area (m^2/g) and mesopore volume (ml/g)) were determined using nitrogen adsorption at 77 °K (-196 °C).

Example 1

(i) Preparation of a molecular sieve with increased mesopore volume

A very ultrastable zeolite Y (VUSY) having a silica to alumina molar ratio of 7.4, a unit cell constant (a_o) of 2.433 nm (24.33 Å), a surface area of 691 m^2/g and a mesopore volume of 0.177 ml/g was added to an aqueous 4N

solution of ammonium nitrate (NH_4NO_3) in an amount such that, on a dry weight basis, the ratio of the number of grams of ammonium nitrate to the number of grams of zeolite Y was 1.5. The resulting slurry was placed in a 2 litre stirred autoclave and the slurry was heated at 150 °C for 12 hours. After cooling, the contents of the autoclave were filtered to yield a molecular sieve having a structure substantially the same as zeolite Y which, after 2 three-hour washes at 93 °C with a nitric acid solution (2 milli-equivalents (meq) hydrogen ions (H^+) per gram of zeolite) and drying at 110 °C, was found to have a silica to alumina molar ratio of 13.2, a unit cell constant (a_o) of 2.429 nm (24.29 Å), a relative crystallinity of 87%, a surface area of 756 m^2/g and a mesopore volume of 0.322 ml/g.

(ii) Preparation of a catalyst composition

To a mixture consisting of a molecular sieve prepared as described in (i) above (5 g), amorphous 55/45 silica-alumina (104 g) and high microporosity precipitated alumina (50 g) was added water (145 g) and acetic acid (96%, 4 g). The mixture was first mulled and was then extruded, following the addition of an extrusion aid, into pellets of cylindrical shape. The pellets were dried for 2 hours at 120 °C and subsequently calcined for 2 hours at 530 °C. The pellets so obtained had a circular end surface diameter of 1.6 mm and a water pore volume of 0.72 ml/g. The pellets comprised 4 %w of the molecular sieve and 96 %w binder (66 %w silica-alumina and 30 %w alumina), on a dry weight basis.

10.07 g of an aqueous solution of nickel nitrate (14 %w nickel) and 16.83 g of an aqueous solution of ammonium metatungstate (39.8 %w tungsten) were combined and the resulting nickel/tungsten solution was diluted with water (18 g) and homogenised. 25.0 g of the pellets were impregnated with the homogenised nickel/tungsten

solution, dried for 1 hour at 120 °C and finally calcined for 2 hours at 500 °C. The pellets contained 3.9 %w nickel and 18.9 %w tungsten, based on total composition.

Example 2

(i) Preparation of a molecular sieve with increased mesopore volume

A very ultrastable zeolite Y (VUSY) having a silica to alumina molar ratio of 8.4, a unit cell constant (a_o) of 2.434 nm (24.34 Å), a surface area of 727 m^2/g and a mesopore volume of 0.180 ml/g was added to an aqueous 4N solution of ammonium nitrate (NH_4NO_3) in an amount such that, on a dry weight basis, the ratio of the number of grams of ammonium nitrate to the number of grams of zeolite Y was 1.5. The resulting slurry was placed in a 2 litre stirred autoclave and the slurry was heated at 200 °C for 6 hours. After cooling, the contents of the autoclave were filtered to yield a molecular sieve having a structure substantially the same as zeolite Y which, after 2 three-hour washes at 93 °C with a nitric acid solution (2 milli-equivalents (meq) hydrogen ions (H^+) per gram of zeolite) and drying at 110 °C, was found to have a silica to alumina molar ratio of 10.0, a unit cell constant (a_o) of 2.427 nm (24.27 Å), a relative crystallinity of 71%, a surface area of 605 m^2/g and a mesopore volume of 0.423 ml/g.

(ii) Preparation of a catalyst composition

In the manner described in Example 1(ii), a molecular sieve prepared as described in (i) above (5 g) was combined with amorphous 55/45 silica-alumina (82 g) and high microporosity precipitated alumina (40 g) to form cylindrically-shaped pellets which, after drying and calcination, had a circular end surface diameter of 1.2 mm and a water pore volume of 0.717 ml/g. The pellets comprised 5 %w of the molecular sieve and 95 %w

binder (65 %w silica-alumina and 30 %w alumina), on a dry weight basis.

8.34 g of an aqueous solution of nickel nitrate (14.1 %w nickel) and 8.29 g of an aqueous solution of ammonium metatungstate (67.3 %w tungsten) were combined and the resulting nickel/tungsten solution was diluted with water (7.2 g) and homogenised. 25.0 g of the pellets were impregnated with the homogenised nickel/tungsten solution, dried for 1 hour at 120 °C and finally calcined for 2 hours at 500 °C. The pellets contained 3.9 %w nickel and 18.9 %w tungsten, based on total composition.

Example 3

(i) Preparation of a molecular sieve with increased mesopore volume

A very ultrastable zeolite Y (VUSY) having a silica to alumina molar ratio of 7.4, a unit cell constant (a_o) of 2.433 nm (24.33 Å), a surface area of 691 m^2/g and a mesopore volume of 0.177 ml/g was added to an aqueous 4N solution of ammonium nitrate (NH_4NO_3) in an amount such that, on a dry weight basis, the ratio of the number of grams of ammonium nitrate to the number of grams of zeolite Y was 1.5. The resulting slurry was placed in a 2 litre stirred autoclave and the slurry was heated at 180 °C for 12 hours. After cooling, the contents of the autoclave were filtered to yield a molecular sieve having a structure substantially the same as zeolite Y which, after 2 three-hour washes at 93 °C with a nitric acid solution (2 milli-equivalents (meq) hydrogen ions (H^+) per gram of zeolite) and drying at 110 °C, was found to have a silica to alumina molar ratio of 10.2, a unit cell constant (a_o) of 2.428 nm (24.28 Å), a relative crystallinity of 57%, a surface area of 519 m^2/g and a mesopore volume of 0.458 ml/g.

(ii) Preparation of a catalyst composition

In the manner described in Example 1(ii), a molecular sieve prepared as described in (i) above (7 g) was combined with amorphous 55/45 silica-alumina (125 g) and high microporosity precipitated alumina (60 g) to form cylindrically-shaped pellets which, after drying and calcination, had a circular end surface diameter of 1.6 mm and a water pore volume of 0.792 ml/g. The pellets comprised 4 %w of the molecular sieve and 96 %w binder (66 %w silica-alumina and 30 %w alumina), on a dry weight basis.

13.12 g of an aqueous solution of nickel nitrate (14.1 %w nickel) and 12.94 g of an aqueous solution of ammonium metatungstate (67.3 %w tungsten) were combined and the resulting nickel/tungsten solution was diluted with water (13.69 g) and homogenised. 32.53 g of the pellets were impregnated with the homogenised nickel/tungsten solution, dried for 1 hour at 120 °C and finally calcined for 2 hours at 500 °C. The pellets contained 3.9 %w nickel and 18.9 %w tungsten, based on total composition.

Example 4

Hydrocracking experiment

Each of the catalyst compositions of Examples 1 to 3 was assessed for middle distillates selectivity in a hydrocracking performance test. The test involved contacting a hydrocarbonaceous feedstock (a hydrotreated heavy vacuum gas oil) with the catalyst compositions (pre-sulphided in conventional manner) in a once-through operation under the following operating conditions: a space velocity of 1.5 kg gas oil per litre catalyst composition per hour ($kg.l^{-1}.h^{-1}$), a hydrogen sulphide partial pressure of 5.5×10^5 Pa (5.5 bar), an ammonia partial pressure of 7.5×10^3 Pa (0.075 bar), a total

pressure of 14 x 10^6 Pa (140 bar) and a gas/feed ratio of 1500 Nl/kg.

The hydrotreated heavy vacuum gas oil had the following properties:

Carbon content	: 86.5 %w
Hydrogen content	: 13.4 %w
Sulphur content	: 0.007 %w
Nitrogen content	: 16.1 ppmw
Density (70/4)	: 0.8493 g/ml
Kinematic viscosity at 100 °C	: 8.81 mm^2/s (cS)
Initial boiling point	: 345 °C
10 %w boiling point	: 402 °C
20 %w boiling point	: 423 °C
30 %w boiling point	: 441 °C
40 %w boiling point	: 456 °C
50 %w boiling point	: 472 °C
60 %w boiling point	: 490 °C
70 %w boiling point	: 508 °C
80 %w boiling point	: 532 °C
90 %w boiling point	: 564 °C
Final boiling point	: 741 °C

The performance of each catalyst composition was assessed at 65 %w net conversion of feed components boiling above 370 °C. The selectivities for middle distillates (i.e. the fraction boiling in the temperature range from 150 to 370 °C) shown by the catalyst compositions of Examples 1 to 3 are given in Table I following.

Table I

Catalyst composition of Example	Middle distillates selectivity at 65%w net conversion (%w/w)
1	70.5
2	72.5
3	72.5

As can be seen from Table I above, the catalyst compositions of Examples 1 to 3 according to the invention show high middle distillate selectivity.

Example 5

(i) Preparation of a molecular sieve with increased mesopore volume

A very ultrastable zeolite Y (VUSY) having a silica to alumina molar ratio of 7.9, a unit cell constant (a_o) of 2.431 nm (24.31 Å), a surface area of 550 m^2/g and a mesopore volume of 0.141 ml/g was added to an aqueous 4N solution of ammonium nitrate (NH_4NO_3) in an amount such that, on a dry weight basis, the ratio of the number of grams of ammonium nitrate to the number of grams of zeolite Y was 1.5. The resulting slurry was placed in a 2 litre stirred autoclave and the slurry was heated to 200 °C for 6 hours. After cooling, the contents of the autoclave were filtered to yield a molecular sieve having a structure substantially the same as zeolite Y which, after 2 three-hour washes at 93 °C with de-mineralized water and drying at 110 °C, was found to have a silica to alumina molar ratio of 8.5, a unit cell constant (a_o) of 2.432 nm (24.32 Å), a relative crystallinity of 69%, a surface area of 481 m^2/g and a mesopore volume of 0.41 ml/g.

(ii) Preparation of a catalyst composition

In the manner described in Example 1(ii), a molecular sieve prepared as described in (i) above (22.3 g) was combined with high microporosity precipitated alumina (110.0 g) to form cylindrically-shaped pellets which, after drying and calcination, had a circular end surface diameter of 1.6 mm and a water pore volume of 0.642 ml/g. The pellets comprised 20 %w of the molecular sieve and 80 %w alumina binder, on a dry weight basis.

8.92 g of an aqueous solution of nickel nitrate (13.9 %w nickel) and 7.85 g of an aqueous solution of ammonium metatungstate (67.3 %w tungsten) were combined and the resulting nickel/tungsten solution was diluted with water (6.6 g) and homogenised. 22.76 g of the pellets were impregnated with the homogenised nickel/-tungsten solution, dried for 1 hour at 120 °C and finally calcined for 2 hours at 500 °C. The pellets contained 4.0 %w nickel and 17.0 %w tungsten, based on total composition.

Example 6

Hydrocracking experiment

The catalyst composition of Example 5, which is a catalyst composition according to the present invention, was assessed for middle distillates selectivity in a hydrocracking performance test. The test involved contacting a hydrocarbonaceous feedstock (a hydrotreated heavy vacuum gas oil) with the catalyst composition of Example 5 (pre-sulphided in conventional manner) in a once-through operation under the following operating conditions: a space velocity of 1.5 kg gas oil per litre catalyst composition per hour ($kg.l^{-1}.h^{-1}$), a hydrogen sulphide partial pressure of 5.5×10^5 Pa (5.5 bar), an ammonia partial pressure of 1.65×10^4 Pa (0.165 bar), a total pressure of 14×10^6 Pa (140 bar) and a gas/feed ratio of 1500 Nl/kg.

The hydrotreated heavy vacuum gas oil had the following properties:

Carbon content	: 86.7 %w
Hydrogen content	: 13.3 %w
Sulphur content	: 0.007 %w
Nitrogen content	: 19.0 ppmw
Density (70/4)	: 0.8447 g/ml
Initial boiling point	: 349 °C
10 %w boiling point	: 390 °C
20 %w boiling point	: 410 °C
30 %w boiling point	: 427 °C
40 %w boiling point	: 444 °C
50 %w boiling point	: 461 °C
60 %w boiling point	: 478 °C
70 %w boiling point	: 498 °C
80 %w boiling point	: 523 °C
90 %w boiling point	: 554 °C
Final boiling point	: 620 °C

The performance of the catalyst composition was assessed at 65 %w net conversion of feed components boiling above 370 °C. The selectivity for middle distillates (i.e. the fraction boiling in the temperature range from 150 to 370 °C) shown by the catalyst composition of Example 5 was found to be high at 69.0 %w/w.



C L A I M S

1. A catalyst composition comprising a molecular sieve having a structure substantially the same as zeolite Y, a unit cell constant (a_o) less than or equal to 2.485 nm and a mesopore volume, contained in mesopores having a diameter in the range from 2 to 60 nm, of at least 0.05 ml/g, and a binder, wherein the relationship between the unit cell constant (a_o) and the mesopore volume is defined as follows:

Unit Cell Constant (nm)	Mesopore Volume (ml/g)
$2.485 \geq a_o > 2.460$	≥ 0.05
$2.460 \geq a_o \geq 2.450$	≥ 0.18
$2.450 > a_o > 2.427$	≥ 0.23
$2.427 \geq a_o$	≥ 0.26

2. A catalyst composition according to claim 1, wherein the molecular sieve is derived from a zeolite Y.

3. A catalyst composition according to claim 1 or claim 2, wherein the molecular sieve has a unit cell constant (a_o) less than or equal to 2.460 nm.

4. A catalyst composition according to any one of claims 1 to 3, wherein the molecular sieve has a mesopore volume of up to 0.8 ml/g.

5. A catalyst composition according to any one of the preceding claims, wherein the molecular sieve has a mesopore volume in the range from 0.3 to 0.8 ml/g.

6. A catalyst composition according to any one of the preceding claims, wherein the molecular sieve has a mesopore volume in the range from 0.4 to 0.6 ml/g.

7. A catalyst composition according to any one of the preceding claims, wherein the molecular sieve has been prepared by a process comprising contacting a (modified) zeolite Y hydrothermally with an aqueous solution having

dissolved therein one or more salts, acids, bases and/or water-soluble organic compounds at a temperature above the atmospheric boiling point of the solution, followed by separation and washing with an acid solution.

8. A catalyst composition according to any one of the preceding claims, wherein the binder is an inorganic oxide.

9. A catalyst composition according to any one of the preceding claims, wherein the binder is selected from alumina, silica, magnesia, titania, zirconia, silica-alumina, silica-zirconia, silica-boria and mixtures thereof.

10. A catalyst composition according to any one of the preceding claims which further comprises at least one hydrogenation component.

11. A catalyst composition according to claim 10, wherein the at least one hydrogenation component is selected from Group 6B and Group 8 metals, their oxides and sulphides.

12. A catalyst composition according to claim 10 or claim 11, wherein the at least one hydrogenation component is selected from molybdenum, tungsten, cobalt, nickel, platinum and palladium, their oxides and sulphides.

13. A process for converting a hydrocarbonaceous feedstock into lower boiling materials which comprises contacting the feedstock at elevated temperature with a catalyst composition as defined in any one of the preceding claims.

14. A process according to claim 13, wherein the feedstock is contacted with a catalyst composition as defined in any one of claims 10 to 12 under hydrogenating conditions.

15. A process according to claim 14 which is carried out at a temperature in the range from 250 to 500 °C and a total pressure in the range from 5×10^6 to 3×10^7 Pa.

16. A process according to claim 14 or claim 15, wherein a space velocity in the range from 0.05 to 10 kg feedstock per litre catalyst composition per hour ($kg.l^{-1}.h^{-1}$) is used.

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(57) Abstract

The present invention provides a catalyst composition, and a hydrocarbon conversion process using it, which comprises a molecular sieve having a structure substantially the same as zeolite Y, a unit cell constant (a_o) less than or equal to 2.485 nm and a mesopore volume, contained in mesopores having a diameter in the range from 2 to 60 nm, of at least 0.05 ml/g, and a binder, wherein the relationship between the unit cell constant (a_o) and the mesopore volume is defined as in table (I).