

Description

The present invention relates to a process for converting hydrocarbon oils into products of lower average molecular weight and lower boiling point by contacting a hydrocarbon oil containing a relatively low amount of nitrogen over a series of catalysts.

It is known to subject a heavy hydrocarbon feedstock to a hydrocracking process which makes use of a series of catalysts.

From US-A-4,435,275, for instance, it is known to hydrocrack a hydrocarbon feedstock using typically mild hydrocracking conditions by passing the feedstock firstly over a bed of an amorphous hydro-treating catalyst and subsequently without intermediate separation or liquid recycle passing the hydrotreated feedstock over a zeolitic hydrocracking catalyst. The zeolite in the hydrocracking catalyst can be selected from faujasite, zeolite X, zeolite Y, mordenite or zeolite ZSM-20.

From EP-A-0247678 a hydrocracking process is known wherein a feedstock is contacted with a zeolitic catalyst comprising a particular modified zeolite Y having a unit cell size below 2.445 nm (24.45 Å).

The products of lower average molecular weight and lower boiling point thus obtained by hydrocracking include gaseous material, i.e. in general C_{1-4} hydrocarbons, naphtha and a middle distillate fraction, i.e. a kerosine fraction and a gas oil fraction. It is evident that the cut between hydrocracked products may be made at various boiling points.

Further, in GB-A-1161725 a two-stage hydrocracking process has been described wherein use is made of a zeolite X catalyst in a first stage and an amorphous catalyst in a second stage. Said process is aimed at the production of gasoline.

Since the gaseous products are not very much wanted and since there is an increasing demand for middle distillates, it would be advantageous to have a two-stage process available for converting hydrocarbon oils that shows a considerable selectivity towards middle distillates and a low gas make.

It has now surprisingly been found that a good yield of middle distillates and low gas make can be obtained if a hydrocarbon oil containing a relatively low amount of nitrogen is passed over a catalyst system comprising a series of a catalyst which comprises a wide pore zeolite and an amorphous silica-alumina containing catalyst.

The present invention thus relates to a process for converting hydrocarbon oils into products of lower average molecular weight and lower boiling point comprising contacting a hydrocarbon oil which contains less than 200 ppm N at elevated temperature and pressure in the presence of hydrogen with a catalyst A comprising a zeolite having a pore diameter of at least 0.65 nm which comprises a modified Y zeolite having a unit cell size below 2.445 nm (24.45 Å), a binder and at least one hydrogenation component of a Group VI and/or Group VIII metal, and wherein the hydrocarbon oil is subsequently, without intermediate separation or liquid recycle, contacted with an amorphous silica-alumina containing catalyst B comprising at least one hydrogenation component of a Group VI and/or Group VIII metal.

In a preferred embodiment of the process according to the present invention catalysts A and B are applied in such a manner that the catalyst A/catalyst B volume ratio is in the range of 0.25-4.0, preferably 0.5-2.0. Suitably, the amorphous silica-alumina containing catalyst B comprises silica in an amount of 10-90% by weight, preferably 20-80% by weight. Preferably, catalyst B comprises at least one component of nickel and/or cobalt and at least one component of molybdenum and/or tungsten or at least one component of platinum and/or palladium. Suitable catalysts B comprise commercially available catalysts.

Preferably, the modified Y zeolite has a pore volume of at least 0.25 ml/g wherein between 10% and 60%, preferably between 10% and 40% of the total pore volume 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. Halena (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 can be obtained when modified Y zeolites are used having a water adsorption capacity of at least 8%, preferably at least 10% by weight on zeolite, and in particular between 10% and 15% by weight of zeolite. The water adsorption capacity of the modified Y zeolites present in catalyst A 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 zeolite present in catalyst A is below 2.445 nm (24.45 Å) (as determined

by ASTM-D-3492, the zeolite being present in its NH_4^+ -form) and preferably below 2.440 nm (24.40 Å), in particular below 2.435 nm (24.35 Å). 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 to be used in the process according to the present invention preferably 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.

Preferably catalyst A comprises an amount of modified Y zeolite which ranges between 5% and 90%, preferably between 15% and 50% of the combined amount of modified Y zeolite and binder.

Suitably, catalyst A comprises at least one component of nickel and/or cobalt and at least one component of molybdenum and/or tungsten or at least one component of platinum and/or palladium.

The binder(s) present in catalyst A suitably comprise(s) inorganic oxides or mixtures of inorganic oxides. Both amorphous and crystalline binders can be applied. Examples of suitable binders comprise silica, alumina, clays, zirconia, titania, magnesia, thoria, and mixtures thereof. Preference is given to the use of alumina as binder.

Depending on the unit cell size desired 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 catalyst A. Preference is given to modified Y zeolites having a molar ratio between 8 and 15.

The amount(s) of hydrogenation component(s) in catalyst A suitably ranges 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 component(s) may be in the oxidic and/or 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 the present process.

Suitably, catalyst A is prepared by co-mulling the wide pore zeolite with the Group VI and/or Group VIII metal compound and the binder. Suitably, (a) solid Group VI and/or Group VIII metal compound(s) is (are) used in the co-mulling procedure. The solid Group VI and/or Group VIII compound(s), preferably molybdenum and/or tungsten, are suitably water-insoluble. Suitable water-insoluble compounds comprise Group VI and/or Group VIII metal oxides, sulphides and acids. For example, molybdenum oxides, tungsten oxides, molybdenum sulphides, tungsten sulphides, molybdenum acid and tungsten acid. The manufacture of such compounds is known in the art.

Apart from for instance a molybdenum and/or tungsten compound other hydrogenation components, in particular nickel and/or cobalt and/or platinum and/or palladium may be present in catalyst A. Such other hydrogenation components can suitably be added to the co-mulling mixture in the form of a solution containing the hydrogenation components. Preferably, the hydrogenation components are selected from the group consisting of nickel, cobalt, molybdenum and tungsten. In particular the hydrogenation-metal is nickel and/or cobalt, most preferably it is nickel. The solution is advantageously an aqueous solution. It will be understood that catalyst A may also suitably be prepared by means of various conventional methods, i.e. ion-exchange or impregnation. The co-mulling can suitably be carried out in the presence of a peptizing agent, such as an acid, e.g. a mineral acid or acetic acid. Shaping of the catalyst A particles can be done in any method known in the art. A very convenient way to shape the particles is by extrusion.

The process according to the present invention is preferably carried out over catalyst A in the presence of hydrogen and at a temperature of 250-500 °C and at a pressure of 20-300 bar, more preferably at a temperature of 300-450 °C and a pressure of 90-200 bar.

The process according to the present invention is preferably carried out over catalyst B in the presence of hydrogen and at a temperature of 250-500 °C and a pressure of 20-300 bar, more preferably at a temperature of 300-450 °C and a pressure of 90-200 bar.

Preferably, catalysts A and B are applied in a stacked-bed configuration.

Feedstocks which can suitably be applied in the process according to the present invention comprise all sorts of hydrocarbonaceous feedstocks as long as they fulfil the requirement to contain less than 200 ppm N. Suitably, the feedstocks 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 or combinations thereof, which may have been hydrotreated before being contacted with catalyst A. The feedstocks can for instance suitably be con-

tacted with an alumina containing hydrotreating catalyst prior to contact with catalyst A.

Preference is made to hydrocarbon oils which contain less than 50 ppm N, more preferably less than 30 ppm N.

Preferably, the process according to the present invention is carried out in such a way that part of the effluent, in particular substantially unconverted material, from catalyst B is recycled to catalyst A.

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

Example I

a) Composition of a stacked-bed which comprises a first bed of catalyst A and a second bed of catalyst B, whereby both catalysts are in calcined form. Catalyst A comprises 11% by weight of a modified Y zeolite having a unit cell size of 2.432 nm (24.32 Å), a water adsorption capacity (at 25 °C and a p/p_0 value of 0.2) of 11.0% 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 of at least 8 nm, 62.5% by weight of aluminium oxide (ex Condea), 5% by weight of nickel and 16% by weight of tungsten.

Catalyst A has been prepared by co-mulling a mixture comprising a modified Y zeolite, hydrated aluminium oxide, acetic acid, water, nickel nitrate solution and ammonium meta tungstate.

Catalyst B comprises 83.5 %wt of amorphous silica-alumina (ex American Cyanamid), 3.6% by weight of nickel and 7.9% by weight of molybdenum.

The stacked-bed has a catalyst A/catalyst B volume ratio of 1.

b) An experiment was carried out in accordance with the present invention by subjecting the stacked-bed as described hereinabove to a hydrocracking performance test involving a hydrotreated heavy vacuum gas oil having the following properties:

C (%wt)	: 86.64
H (%wt)	: 13.25
S (ppm)	: 75
N (ppm)	: 13
d (70/4)	: 1.4716
I.B.P. (°C)	: 325
10/20	: 381/406
30/40	: 426/443
50/60	: 461/478
70/80	: 497/519
90	: 547
F.B.P.	: > 548

The stacked-bed was firstly subjected to a presulphiding treatment by slowly heating in a 10% v H_2S/H_2 -atmosphere to a temperature of 370 °C. Both catalysts A and B were tested in a 1:1 dilution with 0.2 mm SiC particles under the following operation conditions: WHSV 0.75 kg/l/hr, H_2S partial pressure 3 bar, total pressure 130 bar and a gas/feed ratio of 1500 NI/kg. The experiment was carried out in once-through operation. The temperature required for 70% conversion of the 370 °C⁺ fraction was noted, whereafter the temperature was adjusted to obtain a 80% conversion of the 370 °C⁺ fraction.

The following results were obtained:

Temperature required (70% conv. of 370 °C⁺): 360 °C. Distribution of 370 °C⁺ product (in % by weight) at 80% conversion:

$C_1 - C_4$	: 3
$C_5 - 150$ °C	: 33
150 °C - 370 °C	: 64

Comparative Example

An experiment was carried out in substantially the same manner as described in Example I except that a catalyst bed (in volume essentially equal to the volume of the stacked bed as described in Example I) was used comprising a catalyst as described hereinbelow. The catalyst used comprises 8.4% by weight of a modified Y zeolite having a unit cell size of 2.432 nm (24.32 Å), a water adsorption capacity (at 25 °C and a p/p_0 value of 0.2) of 11.0% 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 of at least 8 nm, 50.2% by weight of amorphous silica-alumina (ex Condea), 25% by weight of aluminium oxide (ex American Cyanamid), 3% by weight of nickel and 10% by weight of tungsten. The catalyst has been prepared by co-mulling a mixture comprising a modi-

fied Y zeolite, amorphous silica-alumina, hydrated aluminium oxide, acetic acid, water, nickel nitrate solution and ammonium meta tungstate.

The following results were obtained:

Temperature required (70% conv. 370 °C⁺): 358 °C.

Distribution of 370 °C⁻ product (in % by weight) at 80% conversion:

C₁ - C₄ : 5

C₅ - 150 °C : 37

150 °C - 370 °C : 58

It will be clear from the above results that the experiment according to the present invention yields less gaseous material (C₁ - C₄) and more middle distillates (150 °C - 370 °C), than the comparative experiment which is not according to the present invention.

Claims

1. Process for converting hydrocarbon oils into products of lower average molecular weight and lower boiling point comprising contacting a hydrocarbon oil which contains less than 200 ppm N at elevated temperature and pressure in the presence of hydrogen with a catalyst A comprising a zeolite having a pore diameter of at least 0.65 nm which comprises a modified Y zeolite having a unit cell size below 2.445 nm (24.45 Å), a binder and at least one hydrogenation component of a Group VI and/or Group VIII metal, and wherein the hydrocarbon oil is subsequently, without intermediate separation or liquid recycle, contacted with an amorphous silica-alumina containing catalyst B comprising at least one hydrogenation component of a Group VI and/or Group VIII metal.
2. Process according to claim 1, wherein catalysts A and B are applied in such a manner that the catalyst A/catalyst B volume ratio is in the range of 0.25-4.0.
3. Process according to claim 1 or 2, wherein catalyst B comprises silica in an amount of 10-90% by weight.
4. Process according to any one of claims 1-3, wherein the binder comprises an inorganic oxide or mixture of inorganic oxides.
5. Process according to any one of claims 1-4, wherein the modified Y zeolite has a water adsorption capacity (at 25 °C and a p/p₀ value of 0.2) of at least 8% by weight of modified Y zeolite.
6. Process according to any one of claims 1-5, wherein the modified Y zeolite has 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.
7. Process according to any one of claims 1-6, wherein catalyst A comprises an amount of modified Y zeolite which ranges between 5 and 90% of the combined amount of modified Y zeolite and binder.
8. Process according to any one of claims 1-7, wherein the hydrogenation component comprises at least one component of nickel and/or cobalt and at least one component of molybdenum and/or tungsten or at least one component of platinum and/or palladium.
9. Process according to any one of claims 1-8, wherein catalyst A has been prepared by co-mulling the wide pore zeolitic catalyst with a Group VI and/or Group VIII metal compound and the binder.
10. Process according to any one of claims 1-9, wherein part of the effluent from catalyst B is recycled to catalyst A.
11. Process according to any one of claims 1-10, wherein the hydrocarbon oil to be converted has been subjected to a hydrotreating process.
12. Process according to any one of claims 1-11, wherein catalysts A and B are applied in a stacked-bed configuration.



fied Y zeolite, amorphous silica-alumina, hydrated aluminium oxide, acetic acid, water, nickel nitrate solution and ammonium meta tungstate.

The following results were obtained:

5 Temperature required (70% conv. 370 °C): 358 °C.

Distribution of 370 °C product (in % by weight) at 80% conversion:

C₁ - C₄ : 5

C₅ - 150 °C : 37

150 °C - 370 °C : 58

10 It will be clear from the above results that the experiment according to the present invention yields less gaseous material (C₁ - C₄) and more middle distillates (150 °C - 370 °C), than the comparative experiment which is not according to the present invention.

15 Claims

1. Process for converting hydrocarbon oils into products of lower average molecular weight and lower boiling point comprising contacting a hydrocarbon oil which contains less than 200 ppm N at elevated temperature and pressure in the presence of hydrogen with a catalyst A comprising a zeolite having a pore diameter of at least 0.65 nm which comprises a modified Y zeolite having a unit cell size below 2.445 nm (24.45 Å), a binder and at least one hydrogenation component of a Group VI and/or Group VIII metal, and wherein the hydrocarbon oil is subsequently, without intermediate separation or liquid recycle, contacted with an amorphous silica-alumina containing catalyst B comprising at least one hydrogenation component of a Group VI and/or Group VIII metal.
2. Process according to claim 1, wherein catalysts A and B are applied in such a manner that the catalyst A/catalyst B volume ratio is in the range of 0.25-4.0.
3. Process according to claim 1 or 2, wherein catalyst B comprises silica in an amount of 10-90% by weight.
- 30 4. Process according to any one of claims 1-3, wherein the binder comprises an inorganic oxide or mixture of inorganic oxides.
5. Process according to any one of claims 1-4, wherein the modified Y zeolite has a water adsorption capacity (at 25 °C and a p/p₀ value of 0.2) of at least 8% by weight of modified Y zeolite.
- 35 6. Process according to any one of claims 1-5, wherein the modified Y zeolite has 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.
- 40 7. Process according to any one of claims 1-6, wherein catalyst A comprises an amount of modified Y zeolite which ranges between 5 and 90% of the combined amount of modified Y zeolite and binder.
8. Process according to any one of claims 1-7, wherein the hydrogenation component comprises at least one component of nickel and/or cobalt and at least one component of molybdenum and/or tungsten or at least one component of platinum and/or palladium.
- 45 9. Process according to any one of claims 1-8, wherein catalyst A has been prepared by co-mulling the wide pore zeolitic catalyst with a Group VI and/or Group VIII metal compound and the binder.
- 50 10. Process according to any one of claims 1-9, wherein part of the effluent from catalyst B is recycled to catalyst A.
11. Process according to any one of claims 1-10, wherein the hydrocarbon oil to be converted has been subjected to a hydrotreating process.
- 55 12. Process according to any one of claims 1-11, wherein catalysts A and B are applied in a stacked-bed configuration.



Patentansprüche

1. Verfahren zum Umwandeln von Kohlenwasserstoffölen in Produkte mit niedrigerem durchschnittlichem Molekulargewicht und niedrigerem Siedepunkt, umfassend das Kontaktieren eines Kohlenwasserstofföls, das weniger als 200 Tpm N enthält, bei erhöhter Temperatur und Druck, in Gegenwart von Wasserstoff mit einem Katalysator A, umfassend einen Zeolith mit einem Porendurchmesser von mindestens 0,65 nm, der einen modifizierten Zeolith Y mit einer Elementarzellengröße von unter 2,445 nm (24,45 Å), ein Bindemittel und mindestens eine hydrierend wirkende Komponente eines Metalls der Gruppe VI und/oder VIII enthält, und in welchem Verfahren das Kohlenwasserstofföl anschließend ohne zwischenabtrennung oder Flüssigkeitsrückführung im Kreislauf, mit einem amorphen Siliciumdioxid-Aluminiumoxid enthaltenden Katalysator B, der mindestens eine hydrierend wirkende Komponente eines Metalls der Gruppe VI und/oder VIII enthält, kontaktiert wird.
2. Verfahren nach Anspruch 1, in welchem die Katalysatoren A und B so eingesetzt werden, daß das Volumenverhältnis von Katalysator A zu Katalysator B im Bereich von 0,25 bis 4,0 liegt.
3. Verfahren nach Anspruch 1 oder 2, in welchem der Katalysator B Siliciumdioxid in einer Menge von 10 bis 90 Gewichtsprozent enthält.
4. Verfahren nach einem der Ansprüche 1 bis 3, in welchem das Bindemittel ein anorganisches Oxid oder eine Mischung von anorganischen Oxiden umfaßt.
5. Verfahren nach einem der Ansprüche 1 bis 4, in welchem der modifizierte Zeolith Y eine Wasseradsorptionskapazität (bei 25°C und einem p/p_0 -Wert von 0,2) von mindestens 8 Gewichtsprozent, bezogen auf den modifizierten Zeolith Y aufweist.
6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem der modifizierte Zeolith Y ein Porenvolumen von mindestens 0,25 ml/g aufweist, wobei zwischen 10 und 60 % des Gesamtporenvolumens aus Poren mit einem Durchmesser von mindestens 8 nm bestehen.
7. Verfahren nach einem der Ansprüche 1 bis 6, in welchem der Katalysator A eine Menge eines modifizierten Zeoliths Y enthält, die im Bereich zwischen 5 und 90% der kombinierten Menge aus modifiziertem Zeolith Y und Bindemittel liegt.
8. Verfahren nach einem der Ansprüche 1 bis 7, in welchem die hydrierend wirkende Komponente mindestens eine Komponente aus Nickel und /oder Kobalt und mindestens eine Komponente aus Molybdän und/oder Wolfram oder mindestens eine Komponente aus Platin und/oder Palladium enthält.
9. Verfahren nach einem der Ansprüche 1 bis 8, in welchem der Katalysator A durch Vermahlen im Kollergang des großporigen zeolitischen Katalysators mit einer Metallverbindung eines Metalls der Gruppe VI und/oder VIII und dem Bindemittel hergestellt worden ist.
10. Verfahren nach einem der Ansprüche 1 bis 9, in welchem ein Teil des Abstroms von Katalysator B im Kreislauf zu Katalysator A rückgeführt wird.
11. Verfahren nach einem der Ansprüche 1 bis 10, in welchem das umzuwandelnde Kohlenwasserstofföl einem Hydrobehandlungsverfahren unterworfen worden ist.
12. Verfahren nach einem der Ansprüche 1 bis 11, in welchem die Katalysatoren A und B in Schichtbettkonfiguration eingesetzt werden.

Revendications

1. Procédé de transformation d'huiles hydrocarbonées en produits de poids moléculaire moyen plus faible et de plus faible point d'ébullition dans lequel on met en contact une huile hydrocarbonée qui contient moins de 200 ppm de N à une température et à une pression élevées en présence d'hydrogène avec un catalyseur A comprenant une zéolithe ayant un diamètre de pore d'au moins 0,65 nm qui comprend une zéolithe Y modifiée ayant une taille cellulaire unitaire inférieure à 2,445 nm (24,45 Å), un liant et au moins



- un composant d'hydrogénation d'un métal du groupe VI et/ou du groupe VIII, et où l'huile hydrocarbonée est ensuite mise en contact, sans intermédiaire de séparation ou recyclage de liquide, avec une silice-alumine amorphe contenant le catalyseur B comprenant au moins un composant d'hydrogénation d'un métal du groupe VI et/ou du groupe VIII.
2. Procédé selon la revendication 1, dans lequel on applique les catalyseurs A et B d'une manière telle que le rapport volumique catalyseur A/catalyseur B soit dans l'intervalle de 0,25 - 4,0.
 3. Procédé selon la revendication 1 ou 2, dans lequel le catalyseur B comprend de la silice en une quantité de 10 - 90% en poids.
 4. Procédé selon l'une quelconque des revendications 1 - 3, dans lequel le liant comprend un oxyde inorganique ou un mélange d'oxydes inorganiques.
 5. Procédé selon l'une quelconque des revendications 1 - 4, dans lequel la zéolithe Y modifiée a une capacité d'adsorption d'eau (à 25°C et une valeur p/p_0 de 0,2) d'au moins 8% en poids de zéolithe Y modifiée.
 6. Procédé selon l'une quelconque des revendications 1 - 5, dans lequel la zéolithe Y modifiée a un volume de pores d'au moins 0,25 ml/g où entre 10% et 60% du volume total de pores est constitué de pores ayant un diamètre d'au moins 8 nm.
 7. Procédé selon l'une quelconque des revendications 1 - 6, dans lequel le catalyseur A comprend une quantité de zéolithe Y modifiée qui se situe entre 5 et 90% de la quantité combinée de zéolithe Y modifiée et de liant.
 8. Procédé selon l'une quelconque des revendications 1 - 6, dans lequel le composant d'hydrogénation comprend au moins un composant de nickel et/ou cobalt et au moins un composant de molybdène et/ou tungstène ou au moins un composant de platine et/ou palladium.
 9. Procédé selon l'une quelconque des revendications 1 - 8, dans lequel on a préparé le catalyseur A en préparant une pâte commune du catalyseur zéolithique à larges pores avec un composé métallique du groupe VI et/ou du groupe VIII et le liant.
 10. Procédé selon l'une quelconque des revendications 1 - 9, dans lequel on recycle une partie de l'effluent provenant du catalyseur B vers le catalyseur A.
 11. Procédé selon l'une quelconque des revendications 1 - 10, dans lequel l'huile hydrocarbonée à transformer a été soumise à un procédé d'hydrotraitement.
 12. Procédé selon l'une quelconque des revendications 1 - 11, dans lequel les catalyseurs A et B sont appliqués dans une configuration de lit empilé.