

Process for the preparation of catalytically active cross-linked metal silicate

Citation for published version (APA):

Gaaf, J., Santen, van, R. A., & Shell International Research (NL) (1983). Process for the preparation of catalytically active cross-linked metal silicate.

Document status and date:

Published: 01/01/1983

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

EP0090442B1

Publication Title:

Process for the preparation of catalytically active cross-linked metal silicates

Abstract:

Highly active and selective hydroisomerization catalysts are prepared by heating to 300 DEG -450 DEG C. at subatmospheric pressure, a mixture of nickel synthetic mica montmorillonite (Ni-SMM) with a hydroxy aluminum polymeric solution. The resulting pillared Ni-SMM catalyst, preferably Pd-loaded, is especially useful in hydroisomerizing C4-C7 paraffins.

Data supplied from the esp@cenet database - <http://ep.espacenet.com>

⑫ **EUROPEAN PATENT SPECIFICATION**

- ⑬ Date of publication of patent specification: **11.11.87** ⑮ Int. Cl.⁴: **B 01 J 29/06, C 07 C 5/27,**
C 07 C 9/16
- ⑰ Application number: **83200323.0**
- ⑱ Date of filing: **07.03.83**

⑳ **Process for the preparation of catalytically active cross-linked metal silicate.**

㉑ Priority: **29.03.82 NL 8201289**

㉒ Date of publication of application:
05.10.83 Bulletin 83/40

㉓ Publication of the grant of the patent:
11.11.87 Bulletin 87/46

㉔ Designated Contracting States:
BE DE FR GB SE

㉕ References cited:
US-A-3 844 938
US-A-3 966 642
US-A-4 271 043

IND. ENG. CHEM. PROD. RES. DEVELOP, Vol.
13, No. 2, 1974; E. SWIFT et al.: "Superactive
nickel-aluminosilicate catalysts for
hydroisomerization and hydrocracking of light
hydrocarbons", pages 106-110.

㉖ Proprietor: **SHELL INTERNATIONALE**
RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)

㉗ Inventor: **Gaaf, Jan**
Badhuisweg 3
NL-1031 CM Amsterdam (NL)
Inventor: **Van Santen, Rutger Anthony**
Badhuisweg 3
NL-1031 CM Amsterdam (NL)

㉘ Representative: **Aalbers, Onno et al**
P.O. Box 302
NL-2501 CH The Hague (NL)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

EP 0 090 442 B1

Description

The invention relates to a process for the preparation of a catalytically active cross-linked metal silicate by mixing an at least partly crystalline metal silicate having a crystal lattice largely consisting of a triple layer structure with octahedrally co-ordinated aluminium in the centre layer entirely or partly replaced by nickel and/or cobalt and tetrahedrally co-ordinated silicon in the two outer layers partly replaced by aluminium, is mixed with one or more polymerized hydroxy metal complexes, optionally loading the metal silicate with one or more metals of group VIII of the Periodic System and/or compounds thereof, and heating the mixture. The invention further relates to the use of such a metal silicate as a catalyst in the catalytic conversion of hydrocarbons in the presence of hydrogen.

It is known from US—A—4,271,043 to prepare pillared interlayered smectite-type of metal silicates as described hereinabove and to use such pillared (i.e. cross-linked) metal silicates as catalysts in processes for the conversion of hydrocarbon mixtures, such as cracking and isomerization, with or without the presence of hydrogen.

It has now been found that the catalytic activity of cross-linked metal silicates depends mainly on their manner of preparation; in particular it has been found that heating at subatmospheric pressure during preparation has a substantial effect on the performance of the catalyst. For example, the reaction rate during catalytic hydroisomerization of straight-chain paraffins is considerably higher when cross-linked metal silicates are used that during their preparation were heated at subatmospheric pressure than when cross-linked metal silicates are used that were not subjected to this treatment at subatmospheric pressure.

The invention therefore relates to a process for the preparation of catalytically active cross-linked metal silicate by mixing an at least partly crystalline metal silicate having a crystal lattice largely consisting of a triple layer structure with octahedrally co-ordinated aluminium in the centre layer entirely or partly replaced by nickel and/or cobalt and tetrahedrally co-ordinated silicon in the two outer layers partly replaced by aluminium, is mixed with one or more polymerized hydroxy metal complexes, optionally loading the metal silicate with one or more metals of Group VIII of the Periodic System and/or compounds thereof, and heating the mixture, characterized in that the heating is performed at least temporarily at subatmospheric pressure.

Hereinafter smectites, which class of compounds includes, inter alia, montmorillonite, fitting the above description, are referred to as metal silicates.

Particularly suitable metal silicates for the process according to the invention consist at least partly of synthetic micamontmorillonite in which aluminium has been partly replaced by nickel, which type of substances has been described by Swift, H. E. and Black, E. R. in *Ind. Eng. Chem. Prod. Res. Dev.* 13 (1974), pp. 106—110.

The quantity of nickel in the metal silicates is preferably from 20 to 36% by weight, based on dried non-(cross-linked) metal silicate.

The metal silicates used in the process according to the invention are preferably prepared via a hydrothermal synthesis route.

A metal silicate consisting of synthetic mica-montmorillonite in which aluminium has been partly replaced by nickel (abbreviated: Ni-SMM) can be suitably prepared by entirely or partly replacing the sodium ions in an aqueous dispersion of sodium silicate by protons with the aid of an ion exchanger in the H-form and subsequently adding a nickel salt, an aluminium alcoholate, ammonia and optionally ammonium fluoride. The slurry obtained is partly evaporated and the resultant gel is subsequently heated at 250—350°C for several hours in an autoclave. The product obtained after filtration is dried at 70—200°C.

Ni-SMM can also be suitably prepared by adding a nickel salt, an aluminium alcoholate and ammonium fluoride to an aqueous dispersion of silica, optionally partly evaporating the resultant slurry, adding ammonia, and subsequently introducing the resultant mixture into an autoclave and subjecting it to the same treatment as described in the preparation method first-mentioned.

After suspension in water, the nickel-substituted metal silicate prepared by any of the above methods is mixed with one or more polymerized hydroxy metal complexes, preferably largely or entirely consisting of aluminium hydroxy chloride. The aluminium hydroxy chloride acting as cross-linking agent can suitably be prepared by refluxing aluminium with dilute hydrochloric acid, filtering the resultant solution and subsequently ageing the filtrate for a few days.

The mixture of metal silicate and hydroxy metal complex(es) is preferably heated to a temperature of 300—450°C, which heating is preferably effected for at least 15 minutes at an absolute pressure of at most 0.1 bar.

Most preference is given to a process according to the invention in which the mixture is heated to a temperature of 340—420°C for at least 1 hour, and preferably for at most 100 hours, at an absolute pressure of at most 0.05 bar.

Before the mixture of metal silicate and hydroxy metal complex(es) is heated at subatmospheric pressure, according to the present process the mixture is preferably first subjected to a drying treatment at temperatures from 70°C to 200°C, followed by calcination at temperatures from 300°C to 400°C at atmospheric or elevated pressure.

In the process according to the invention the metal silicate is preferably loaded with one or more noble

metals of Group VIII of the Periodic System and/or compounds thereof, as stated in the "Handbook of Chemistry and Physics", 55th edition, CRC Press, Ohio, U.S.A. (1975).

Before being mixed with hydroxy metal complex(es), the metal silicate is preferably loaded with 0.2—2% by weight of palladium, based on dried non-cross-linked metal silicate. The loading of the metal silicate with noble metal can be effected by means of any process for the preparation of catalysts known in the art, such as impregnation, ion exchange or precipitation. In the present process it is preferred to apply the Group VIII noble metals to the metal silicate from an aqueous solution containing the metals in the form of cations. Especial preference is given to ammonia-containing solutions in which the Group VIII noble metals are present in the form of cationic complexes.

The invention also relates to a process for the catalytic conversion of hydrocarbons, in particular in the presence of hydrogen, with the aid of catalysts prepared according to the process described above.

Prior to conversion the catalyst is preferably activated by treatment with hydrogen at a temperature from 150°C to 420°C, in particular for at least several hours at a temperature from 300°C to 400°C and at at least atmospheric pressure.

It has been found that in the catalytic isomerization of paraffins having 4—7 carbon atoms in the presence of hydrogen, the first order reaction rate is considerably higher (while maintaining a high selectivity (generally above 98%)) when a catalyst is used that has been prepared according to the invention by heating the above-mentioned mixture for some time at subatmospheric pressure than when using a catalyst that has been prepared by heating the same mixture exclusively at atmospheric or elevated pressure.

In the above-mentioned hydroisomerization according to the invention the starting material used is one or more paraffins, especially having 4—7 carbon atoms, preferably consisting substantially or entirely of n-pentane or n-hexane or mixtures of both. Very suitably, tops obtained in the atmospheric distillation of petroleum are used as starting material.

It is intended that in the hydroisomerization according to the invention the largest possible proportion of the paraffins present in the feed is converted into isomers of said paraffins with a higher degree of branching, while cracking into products having a smaller number of carbon atoms than the molecules in the feed should be as low as possible.

Suitable conditions for effecting the hydroisomerization according to the invention are:

a temperature between 150 and 330°C;

a space velocity between 0.2 and 20 kg of paraffin/kg of catalyst/hour;

a hydrogen-paraffin molar ratio from 0.5:1 to 50:1 and a total pressure between 1 and 70 bar.

Preferred conditions are:

a temperature between 220°C and 280°C;

a space velocity between 1 and 5 kg of paraffin/kg of catalyst/hour;

a hydrogen-paraffin molar ratio from 1:1 to 15:1 and a total pressure between 20 and 50 bar.

Another application of the catalysts obtained by the process according to the invention resides in the catalytic hydrocracking of hydrocarbon oils. Catalytically active cross-linked metal silicates are especially suitable for the hydrocracking of relatively large hydrocarbon molecules on account of the ready accessibility of the catalyst for these molecules because of the permanent enlargement of the space between the various triple layers in cross-linked metal silicates in relation to non-cross-linked metal silicates.

When performing hydroconversion processes according to the invention it is often not necessary to use pure hydrogen, and then hydrogen-containing gases can also be used. Very suitable is a hydrogen-rich gas obtained in the catalytic reforming of hydrocarbon mixtures, such as naphthas.

Example I—Preparation of Ni-SMM A

A quantity of 79.7 g of nickel acetate-4 aq is dissolved in 200 ml of water, after which in that solution 40 g of dried silica and 47 g of aluminium isopropoxide are consecutively suspended with stirring and 0.82 g of ammonium fluoride is dissolved. Subsequently the resultant mixture is heated at 90°C for 20 hours with stirring, after which 8 ml of ammonia (25% by weight of NH_3) is added and the mixture is heated to 300°C in an autoclave, which temperature is maintained for 40 hours. Then the autoclave is cooled to ambient temperature and the resultant product is filtered, washed with water and dried at 110°C. The dried product contains 23.2% by weight of nickel.

Preparation of Ni-SMM B

A quantity of 79.2 g of nickel acetate-4 aq is dissolved in 335 ml of water, after which to this solution are consecutively added with stirring: 33.3 g of silica, predried for 2 hours at 200°C, 39.2 g of aluminium isopropoxide and 0.68 g of ammonium fluoride. The resultant suspension is evaporated with stirring for 17 hours at a temperature of 90°C to a volume of 250 ml, after which 6.7 ml of NH_4OH (25% by weight of NH_3) is added and the resultant mixture is treated for 40 hours at a temperature of 300°C in an autoclave. Subsequently, the autoclave is cooled and the product filtered, washed with water and finally dried at 110°C. The resultant clay contains 23.7% by weight of nickel.

Preparation of the cross-linking agent

A quantity of 10.0 g of aluminium strip is refluxed for 5 hours with 50 ml of hydrochloric acid (1N), after which the resultant aluminium hydroxychloride solution, which contains 33 g of aluminium/litre, is filtered off and the filtrate is aged for 10 days before being used as a cross-linking agent. The aluminium hydroxychloride may be described as aluminium chloride in which the chloride ions have been partly replaced by hydroxide ions.

Cross-linking of Ni-SMM A and B

A quantity of 10 g of Ni-SMM (A or B) of the <0.18 mm sieve fraction is suspended in 400 ml of water, after which 50 ml of aluminium hydroxychloride solution, containing 33 g of aluminium/litre, is added and the mixture stirred for 20 hours at 70°C. Subsequently, the cross-linked Ni-SMM is filtered off, washed with water and dried at 110°C.

The Table below shows the results of X-ray diffraction measurements of 001 lattice spacings for non-cross-linked and for cross-linked Ni-SMM A and B.

TABLE I

Sample	001 lattice spacings in nm	
	Non-cross-linked	Cross-linked
Ni-SMM A	1.26	1.61
Ni-SMM B	1.26	1.7

Table I shows that the 001 lattice spacing is considerably enlarged as a result of the cross-linking of the Ni-SMM.

Preparation of catalyst A

A quantity of 5 g of the dried, non-cross-linked Ni-SMM A is suspended in a solution of 83 mg of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ in 100 ml of water and stirred for 16 hours, after which the product is washed with 200 ml of water, filtered off and dried at 110°C. The resultant product contains 0.7% by weight of palladium and is subsequently cross-linked in the same way as described above under "Cross-linking of Ni-SMM A and B".

After drying, the cross-linked and palladium-loaded Ni-SMM A is calcined for 2 hours at 350°C in air at atmospheric pressure and subsequently heated at 350°C for 16 hours at an absolute pressure of 1×10^{-6} bar.

The resultant catalyst A is pressed into tablets and ground in a mortar, after which the catalyst particles of the 0.18—0.59 mm sieve fraction are heated at 350°C and an absolute pressure of 1×10^{-6} bar for a further 4 hours.

Preparation of catalyst B

A quantity of 5 g of the dried cross-linked Ni-SMM B is suspended in a solution of 83 mg of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ in 100 ml of water and stirred for 16 hours, after which the product is washed with 200 ml of water, filtered off and dried at 110°C. The resultant product contains 0.7% by weight of palladium and is subsequently calcined in air at 400°C for 2 hours at atmospheric pressure and subsequently heated for 16 hours at 400°C and an absolute pressure of 1×10^{-6} bar.

The resultant catalyst B is pressed into tablets, ground in a mortar and the catalyst particles of the 0.18—0.59 mm sieve fraction are heated at 400°C and an absolute pressure of 1×10^{-6} bar for a further 4 hours.

Preparation of catalyst C

After drying, the cross-linked and palladium-loaded Ni-SMM A, as obtained in the preparation of catalyst A, is calcined in air for 2 hours at 350°C and at atmospheric pressure.

Preparation of catalyst D

After drying, the cross-linked and palladium-loaded Ni-SMM B obtained in the preparation of catalyst B is calcined at 400°C and at atmospheric pressure of 2 hours.

The catalysts A and B have been prepared in accordance with the process of the invention; C and D are comparative catalysts not according to the invention.

Example II—Hydroisomerization of pentane

Pentane hydroisomerization experiments are carried out in a microflow reactor with a length of 35 cm and an internal diameter of 1 cm, containing 2 g of catalyst particles (of the 0.18—0.59 mm sieve fraction).

Before being used for the catalytic conversion of hydrocarbons, the catalysts A, B, C and D are treated with hydrogen in the isomerization reactor at a pressure of 1 bar and a temperature of 343°C for 16 hours.

After the activation treatment of the catalyst with hydrogen has taken place at 343°C in the microflow reactor, the temperature of the latter, both for the use of catalyst A, B, C and D, is reduced to 250°C and the pre-dried n-pentane feed is subsequently passed across the catalyst together with pure hydrogen.

The reaction conditions of the hydroisomerization step are:

5 temperature: 250°C

total pressure: 30 bar

hydrogen/pentane molar ratio: 1.25

space velocity: 2 g of pentane/g of catalyst/hour.

The product stream is continuously analyzed by means of gas-liquid chromatography.

10 In Table II below, "k" is the first order reaction rate constant expressed in g of converted pentane per g of catalyst per hour, and "Selectivity, %" is the percentage by weight of isomerized pentane based on converted pentane.

TABLE II

Exp. No.	Catalyst	Temp. (°C) of calcination (press.=1 bar)	Temp. (°C) of the vacuum treatment	k (gram·gram ⁻¹ ·h ⁻¹)	Selectivity, %
1	A	350	350	3.6	98.8
2	B	400	400	2.3	98.1
3	C	350	—	0.5	99.6
4	D	400	—	2.0	97.3

30 The heating of cross-linked Ni-SMM at subatmospheric pressure results in a higher k-value for the hydroisomerization of pentane while maintaining high selectivity, in comparison with the use of cross-linked Ni-SMM which has been calcined at exclusively atmospheric pressure.

Claims

35 1. A process for the preparation of catalytically active cross-linked metal silicate by mixing an at least partly crystalline metal silicate, having a crystal lattice largely consisting of a triple layer structure with octahedrally co-ordinated aluminium in the centre layer entirely or partly replaced by nickel and/or cobalt and tetrahedrally co-ordinated silicon in the two outer layers partly replaced by aluminium, with one or more polymerized hydroxy metal complexes, optionally loading the metal silicate with one or more metals of Group VIII of the Periodic System and/or compounds thereof, and heating the mixture, characterized in that the heating is performed at least temporarily at subatmospheric pressure.

2. A process as claimed in claim 1, characterized in that the metal silicate consists at least partly of synthetic mica-montmorillonite in which aluminium has been partly replaced by nickel.

45 3. A process as claimed in claim 1 or 2, characterized in that the polymerized hydroxy metal complex used is aluminium hydroxy chloride.

4. A process as claimed in any one or more of the preceding claims, characterized in that the mixture is heated to a temperature of 300°C—450°C.

5. A process as claimed in any one or more of the preceding claims, characterized in that the mixture is heated at least temporarily at an absolute pressure of at most 0.1 bar.

50 6. A process as claimed in claim 5, characterized in that the mixture is heated for at least one hour at a temperature of 340°C—420°C and at an absolute pressure of at most 0.05 bar.

7. A process as claimed in any one or more of the preceding claims, characterized in that the mixture is dried at temperatures of 70°C—200°C, subsequently calcined at temperatures of 300°C—400°C and atmospheric or elevated pressure, and is subsequently maintained at an elevated temperature for at least 15 minutes at a subatmospheric pressure.

8. A process as claimed in any one or more of the preceding claims, characterized in that before mixing with hydroxy metal complex(es) the metal silicate is loaded with 0.2—2% by weight of palladium, based on dried non-cross-linked metal silicate.

60 9. A process for the catalytic conversion of hydrocarbons in the presence of hydrogen, characterized in that in such a process a catalyst is used which has been prepared in accordance with any one or more of the preceding claims.

10. A process as claimed in claim 9, characterized in that prior to conversion the catalyst is activated by treatment with hydrogen at a temperature of 150°C—420°C, preferably of 300°C to 400°C.

65 11. A process as claimed in claim 9 or 10, characterized in that paraffins having 4—7 carbon atoms are

catalytically isomerized in the presence of hydrogen at a temperature between 150 and 300°C, a space velocity between 0.2 and 20 kg of paraffin/kg of catalyst/hour, a hydrogen/paraffin molar ratio from 0.5:1 to 50:1 and a total pressure between 1 and 70 bar.

5 Patentansprüche

1. Ein Verfahren zu Herstellung von katalytisch aktivem vernetztem Metallsilikat durch Vermischen eines mindestens teilweise kristallinen Metallsilikats mit einer Kristallgitterstruktur, welche großenteils aus einer Dreischichtenstruktur besteht, wobei octahedrisch koordiniertes Aluminium in der Zentralschicht
10 vollständig oder teilweise durch Nickel und/oder Kobalt und tetrahedrisch koordiniertes Silizium in den beiden äußeren Schichten teilweise durch Aluminium ersetzt ist, mit einem oder mehreren polymerisierten Hydroxymetallkomplexen, wobei das Metallsilikat gegebenenfalls mit einem oder mehreren Metallen der Gruppe VIII des periodischen Systems und/oder Verbindungen derselben beladen wird und Erhitzen der Mischung, dadurch gekennzeichnet, daß das Erhitzen mindestens zeitweilig bei unteratmosphärischem
15 Druck durchgeführt wird.

2. Ein Verfahren, wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß das Metallsilikat mindestens teilweise aus synthetischem Glimmer-Montmorillonit besteht, in welchem Aluminium teilweise durch Nickel ersetzt worden ist.

3. Ein Verfahren, wie in Anspruch 1 oder 2 beansprucht, dadurch gekennzeichnet, daß der verwendete
20 polymerisierte Hydroxymetallkomplex Aluminiumhydroxychlorid ist.

4. Ein Verfahren, wie in irgendeinem oder mehreren der vorhergehenden Ansprüche beansprucht, dadurch gekennzeichnet, daß die Mischung auf eine Temperatur von 300°C bis 450°C erhitzt wird.

5. Ein Verfahren, wie in irgendeinem oder mehreren der vorhergehenden Ansprüche beansprucht, dadurch gekennzeichnet, daß die Mischung mindestens zeitweilig bei einem absoluten Druck von
25 höchstens 0,1 bar erhitzt wird.

6. Ein Verfahren wie in Anspruch 5 beansprucht, dadurch gekennzeichnet, daß die Mischung mindestens eine Stunde bei einer Temperatur von 340°C bis 420°C und bei einem absoluten Druck von höchstens 0,05 bar erhitzt wird.

7. Ein Verfahren, wie in irgendeinem oder mehreren der vorhergehenden Ansprüche beansprucht, dadurch gekennzeichnet, daß die Mischung bei Temperaturen von 70°C bis 200°C getrocknet, anschließend
30 bei Temperaturen von 300°C bis 400°C und bei atmosphärischem oder erhöhtem Druck kalziniert wird und anschließend mindestens 15 Min. lang bei unteratmosphärischem Druck auf erhöhter Temperatur gehalten wird.

8. Ein Verfahren, wie in irgendeinem oder mehreren der vorhergehenden Ansprüche beansprucht,
35 dadurch gekennzeichnet, daß das Metallsilikat vor dem Vermischen mit dem (den) Hydroxymetallkomplex(en) mit 0,2 bis 2 Gewichtsprozent Palladium, bezogen auf getrocknetes, nicht vernetztes Metallsilikat, beladen wird.

9. Ein Verfahren zur katalytischen Umwandlung von Kohlenwasserstoffen in Anwesenheit von Wasserstoff, dadurch gekennzeichnet, daß in einem solchen Verfahren ein Katalysator verwendet wird, der gemäß einem oder mehreren der vorhergehenden Ansprüche hergestellt worden ist.

10. Ein Verfahren, wie in Anspruch 9, beansprucht, dadurch gekennzeichnet, daß der Katalysator vor Durchführung der Umwandlung durch Behandlung mit Wasserstoff bei einer Temperatur von 150°C bis 420°C, vorzugsweise von 300°C bis 400°C, aktiviert wird.

11. Ein Verfahren, wie in Anspruch 9 oder 10 beansprucht, dadurch gekennzeichnet, daß Paraffine mit 4
45 bis 7 Kohlenstoffatomen in Anwesenheit von Wasserstoff bei einer Temperatur zwischen 150°C und 300°C, einer Raumgeschwindigkeit zwischen 0,2 und 20 kg Paraffin/kg Katalysator/Stunde, einem Molverhältnis Wasserstoff zu Paraffin von 0,5:1 bis 50:1 und einem Gesamtdruck zwischen 1 und 70 bar katalytisch isomerisiert werden.

50 Revendications

1. Procédé pour la préparation d'un silicate métallique réticulé à activité catalytique par mélange d'un silicate métallique au moins partiellement cristallin, ayant un réseau cristallin largement constitué par une structure à trois couches, l'aluminium de coordinence 8, dans la couche centrale, étant entièrement ou
55 partiellement remplacé par du nickel et/ou du cobalt, et le silicium de coordinence 4, dans les deux couches externes, étant partiellement remplacé par de l'aluminium, avec un ou plusieurs complexes métalliques hydroxylés polymérisés, le chargement éventuel du silicate métallique avec un ou plusieurs métaux du groupe VIII de la Classification Périodique et/ou des composés de ces métaux, et le chauffage du mélange, caractérisé en ce que le chauffage est réalisé au moins temporairement à une pression inférieure à la
60 pression atmosphérique.

2. Procédé selon la revendication 1, caractérisé en ce que le silicate métallique est constitué au moins partiellement d'une mica-montmorillonite synthétique dans laquelle l'aluminium a été en partie remplacé par du nickel.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le complexe métallique hydroxylé
65 polymérisé utilisé est de l'oxychlorure d'aluminium.

0 090 442

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le mélange est chauffé à une température de 300°C—450°C.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le mélange est chauffé au moins temporairement sous une pression absolue au plus égale à 0,1 bar.

5 6. Procédé selon la revendication 5, caractérisé en ce que le mélange est chauffé au moins pendant une heure à une température de 340°C—420°C et sous une pression absolue au plus égale à 0,05 bar.

7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le mélange est séché à des températures de 70°C—200°C, calciné ensuite à des températures de 300°C—400°C et sous une pression atmosphérique ou élevée, et maintenu ensuite à une température élevée pendant au moins

10 15 minutes sous une pression inférieure à la pression atmosphérique.

8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que, avant le mélange avec un ou des complexes métalliques hydroxylés, le silicate métallique est chargé avec 0,2—2% en poids de palladium, par rapport au silicate métallique non réticulé séché.

9. Procédé pour la conversion catalytique d'hydrocarbures en présence d'hydrogène, caractérisé en ce que, dans ce procédé, on utilise un catalyseur qui a été préparé selon l'une quelconque des revendications

15 précédentes.

10. Procédé selon la revendication 9, caractérisé en ce que, avant la conversion, le catalyseur est activé par traitement à l'hydrogène, à une température de 150°C—420°C, de préférence de 300°C à 400°C.

11. Procédé selon la revendication 9 ou 10, caractérisé en ce que des paraffines comportant 4—7

20 atomes de carbone sont isomérisées catalytiquement en présence d'hydrogène, à une température comprise entre 150 et 300°C, à une vitesse spatiale comprise entre 0,2 et 20 kg de paraffine/kg de catalyseur/heure, à un rapport molaire hydrogène/paraffine de 0,5:1 à 50:1 et sous une pression totale comprise entre 1 et 70 bars.

25

30

35

40

45

50

55

60

65