

Preparation of a catalyst for normal paraffin isomerization

The invention relates to a process for the preparation of a catalyst suitable for use in the isomerization of normal paraffins.

Catalysts that have been prepared by depositing one or more noble metals of Group VIII on mordenite have a high activity and selectivity for the isomerization of normal paraffins. In order to prepare suitable catalysts for this purpose the exchangeable metal cations originally present in the mordenite are to be replaced almost completely by hydrogen ions. This replacement may be carried out by treating the mordenite with an aqueous solution of an acid or by treating the mordenite with an aqueous solution of an ammonium compound, followed by calcination.

In the past applicant had found (see German Offenlegungsschrift No. 2,500,072) that catalysts prepared by depositing one or more noble metals of group VIII on mordenite, which mordenite had previously been treated with an acid solution, prepared by incorporating potassium and/or sodium ions in the aqueous acid solution with a normality of at least 0.5 and at most 3.0, in an amount which, expressed in g/l, is at least ten times the normality of the aqueous acid solution, and subsequently with an aqueous solution of an ammonium compound, had a greater activity in the isomerization of normal paraffins than catalysts prepared by depositing one or more noble metals of Group VIII on mordenite, which mordenite had been treated in one step either with an aqueous solution of an acid, not containing alkali ions, or with an aqueous solution of an ammonium compound.

From the catalyst base material obtained in the way described above catalyst particles can be prepared by shaping under high pressure. In order to give these catalyst particles sufficient crushing strength for use on a technical scale, it is common practice to mix the catalyst base material thoroughly with an amorphous binder material consisting substantially of one or more oxides of metals of the groups II, III and IV, before subjecting it to shaping under high pressure.

It is known from British Patent Specification No. 1,379,257, to deposit a noble metal of Group VIII on a carrier before mixing the material obtained with mordenite treated in one step or described above. It has been found in the past that the improved activity for the isomerization of normal paraffins, which improvement had been obtained by replacing the classic one-step treatment of the mordenite by the two-step treatment, using an aqueous acid solution in which no alkali metal ions had been incorporated, is fully retained when the catalyst base material is thoroughly mixed with an amorphous binder material, and shaped under high pressure. It was assumed

that this would apply also to the additional improvement obtained by incorporating alkali metal ions in the aqueous acid solution. This assumption was found to be incorrect. It was found experimentally that, if the mordenite present in the catalyst base material had been subjected to the two-step treatment, using an aqueous acid solution in which alkali metal ions had been incorporated, the additional improvement obtained by incorporating alkali metal ions in the aqueous acid solution was completely lost when the catalyst base material was mixed with an amorphous binder material, and shaped under high pressure.

It would be attractive to be able to prepare catalyst particles with sufficient crushing strength for use on a technical scale whilst retaining the earlier established optimum suitability of the isomerization of normal paraffins, which suitability is obtained by subjecting the mordenite to the two step treatment, using an aqueous solution of an acid in which alkali metal ions have been incorporated.

It has now been found that such catalyst particles can be prepared by depositing the noble metals of group VIII not as usual, on the treated mordenite, but on the amorphous binder material consisting substantially of one or more oxides of metals of the groups II, III and IV. By thoroughly mixing the treated mordenite and the amorphous binder material which contains the noble metal of group VIII and shaping the mixture thus obtained under high pressure, catalysts can be prepared which actually satisfy the two above-mentioned requirements.

The present invention therefore relates to a process the preparation of a catalyst suitable for the isomerization of normal paraffins, in which process a mixture comprising

a) an amorphous material consisting substantially of one or more oxides of metals of the groups II, III, and IV,

b) mordenite which has first been treated with a solution prepared by incorporating into an aqueous acid solution with a normality of at least 0.5 and at most 3.0, potassium and/or sodium ions, in an amount which, expressed in g/l, is at least ten times the normality of the aqueous acid solution, which mordenite has subsequently been treated with an aqueous solution of an ammonium compound, and

c) one or more noble metals of group VIII and/or compounds thereof, is prepared, and the mixture obtained is subjected to shaping under high pressure, characterized in that said mixture is prepared by depositing one or more noble metals of group VIII and/or compounds thereof on said amorphous material, and mixing the material obtained with the mordenite treated with an acid solution and an ammonium compound.

As acids in the said aqueous solution

according to the invention both organic and inorganic acids may be used. Preference is given to hydrochloric acid. The preferred normality of the aqueous acid solution is between 1.0 and 2.0. For the incorporation of potassium and/or sodium ions in the aqueous solution both organic and inorganic salts may be used. Very attractive results can be obtained by carrying out the treatment with an aqueous acid solution into which potassium and/or sodium ions have been incorporated (also indicated as acid treatment) with an aqueous solution of one or more acids, which solution is saturated with one or more potassium and/or sodium salts. For the acid treatment preference is given to an aqueous acid solution containing sodium ions. It is further preferred to make use of potassium and/or sodium salts derived from the same acid as used for the acid treatment. The acid treatment is preferably carried out at elevated temperature, in particular near the boiling point of the aqueous acid solution.

For the treatment of the mordenite with an aqueous solution of an ammonium compound both organic and inorganic ammonium compounds may be used. The term ammonium compound is meant to denote any compound able to form ammonium ions. It is preferred to use simple inorganic ammonium compounds, in particular ammonium nitrate. The preferred molarity of the aqueous solution of the ammonium compound is 0.1—10. The treatment with the aqueous solution of an ammonium compound may be carried out at room temperature or at elevated temperature.

The time required for each of the treatments depends on concentration, temperature and degree of contact. As a rule, each treatment should continue for at least 30 minutes and preferably for about one hour. It may be advantageous to repeat the acid treatment or the treatment with an ammonium compound, or even both treatments, several times. It is preferred to repeat or continue the treatment with the aqueous solution of an ammonium compound until the mordenite does not give off alkali metal in amounts detectable by analysis.

After the treatment with an ammonium compound the mordenite is in the ammonium form. By calcining the ammonium mordenite, nitrogen atoms incorporated by the treatment are removed and mordenite in the hydrogen form is obtained. The conversion of the ammonium mordenite into the hydrogen form may take place before or after mixing with the amorphous material which contains the noble metal of group VIII.

Examples of oxides suitable for use as carriers for the noble metals of group VIII are alumina, silica, magnesia, zirconia and boria. Preference is given to alumina. The noble metals of group VIII which may be present on the oxide(s) of elements of groups II, III and IV are platinum, palladium, rhodium, ruthenium,

iridium and osmium, of which platinum is the preferred metal. The catalyst may contain two or more noble metals of group VIII. The amount of noble metal of group VIII present in the ready catalyst is preferably 0.01 — 5% w and in particular 0.1 — 1.5% w. The ready catalyst contains preferably 5 — 50% w amorphous material which contains noble metal of group VIII. The noble metals of group VIII are preferably deposited on the oxides by impregnation. The shaping at high pressure may be carried out, for instance, by tableting or extrusion.

Catalysts according to the invention are very suitable for the isomerization of normal paraffins in the presence of hydrogen. The normal paraffins which are subjected to the isomerization treatment contain preferably 4 — 10 and in particular 4 — 7 carbon atoms per molecule. The isomerization of the above-mentioned low-molecular normal paraffins in the presence of hydrogen is usually carried out at a temperature of 150—300°C, at a pressure of 3—50 bar, a space velocity, based on H-mordenite, of 0.5—10 kg.kg⁻¹.h⁻¹ and a molar ratio of hydrogen to feed of 0.5:1 to 10:1. The isomerization is preferably carried out under the following conditions: a temperature of 230—280°C, a pressure of 10—40 bar and a space velocity based on H-mordenite, of 1.0—5.0 kg.kg⁻¹.h⁻¹.

The isomerization of low-molecular normal paraffins is an attractive method for the upgrading of light gasoline fractions, such as tops obtained by straight-run distillation. In comparison with isoparaffins with the same number of carbon atoms, normal paraffins have a low octane number; their presence in light gasoline fractions is therefore undesirable. By conversion of the normal paraffins present in the fractions into isoparaffins the octane number is increased. Isoparaffins also present in these gasoline fractions may be removed from them before the isomerization, for instance by distillation or by means of molecular sieves. Since isomerization of normal paraffins is an equilibrium reaction, the product leaving the isomerization reactor still contains an amount of unconverted paraffins. These paraffins may be separated from the isomerization product, for instance by distillation or by means of molecular sieves, and recycled to the isomerization process. It is also possible to add the isomerization product to the original mixture of normal and isoparaffins, to remove the isoparaffins from this mixture, for instance by distillation or with molecular sieves, and to isomerize the remaining mixture of normal paraffins according to the invention.

The invention will now be explained with reference to the following example.

Example

In the investigation five catalysts were involved, which had been prepared as follows:

Catalyst 1

A mixture of 20 g sodium mordenite and 200 ml 1.5 N HCl was boiled under reflux for one hour. The solid material was filtered off and washed with water. Subsequently, the solid material was boiled under reflux for one hour with 200 ml of a 1.0 molar NH_4NO_3 solution. This treatment with NH_4NO_3 was repeated twice, each time with a fresh NH_4NO_3 solution. After each treatment the solid material was filtered off and washed with water. Eventually platinum was deposited on the NH_4 mordenite thus obtained by treating it with an aqueous solution of a platinum compound. The solid material was filtered off and dried at 120°C . The Pt/ NH_4 mordenite thus obtained was tabletted at a pressure of 50 tonnes and ground. From the ground material a fraction with particle diameters between 0.2 and 0.6 mm was separated by sieving. This sieve fraction was converted into catalyst 1 by calcining at 500°C .

Catalyst 2

The catalyst was prepared in substantially the same way as catalyst 1, the difference being that in the present case the Pt/ NH_4 mordenite was thoroughly mixed with a powdered alumina in a weight ratio of 4:1, before being pelletized.

Catalyst 3

This catalyst was prepared in substantially the same way as catalyst 1, the difference being that in the present case use was made of 1.5 N HCl to which 400 g NaCl/l had been added.

Catalyst 4

This catalyst was prepared in substantially the same way as catalyst 3, the difference being that in the present case the Pt/ NH_4 mordenite was thoroughly mixed, in a weight ratio of 4:1, with the same alumina powder as used in the preparation of catalyst 2, before being tabletted.

Catalyst 5

A Pt/Alumina composite containing 1.2 pbw platinum per 100 pbw alumina was prepared by treating the alumina powder which was also used in the preparation of the catalysts 2 and 4 with an aqueous solution of a platinum compound, followed by drying and calcining at 500°C . NH_4 mordenite, obtained as intermediate product in the preparation of the catalysts 3 and 4, was dried at 120°C and thoroughly mixed in a weight ratio of 4:1 with the above-mentioned Pt/Alumina composite. The mixture was tabletted at a pressure of 50 tonnes and ground. From the ground material a fraction with particle diameters between 0.2 and 0.6 mm was separated by sieving. This sieve fraction was converted into catalyst 5 by calcining at 500°C .

Isomerization experiments

The above-mentioned five catalysts, all containing 0.3 pbw platinum, based on

100 pbw H-mordenite, were used for the isomerization of n-pentane. The isomerization was carried out under the following conditions:

Temperature : 250°C

5 Pressure : 30 bar

Space velocity, based on H-mordenite : $2 \text{ kg.kg}^{-1}.\text{h}^{-1}$.

Molar ratio H_2/feed : 1.25

Duration of the experiment : 25 hours

10 The results of these experiments are listed in the table. The percentages, by weight of isopentane in the product are the averages between the run hours 10 and 25.

Table

Experiment No.	Catalyst No.	%w isopentane in product
20 1	1	64.1
2	2	64.0
3	3	67.3
4	4	63.5
25 5	5	66.9

25 Of the experiments 1—5, only experiment 5 is an isomerization experiment according to the present invention. In this experiment a catalyst was used which had been prepared according to the invention. The other experiments are outside the scope of the invention, and have been included for comparison.

30 Comparison of the results of the experiments 1 and 2 shows that mixing of the Pt/H mordenite with the Al_2O_3 binder before shaping under high pressure has no influence on the behaviour of the ready catalyst particles in the isomerization experiment.

35 Comparison of the results of the experiments 3 and 4 shows the improvement in the behaviour of the H-mordenite in the isomerization experiment as a result of the incorporation of sodium ions in the acid solution is completely lost when the Pt/H mordenite is mixed with the Al_2O_3 binder prior to shaping under high pressure.

40 The result of experiment 5 shows that in the preparation of the catalyst particles according to the present invention the improvement of the behaviour of the H-mordenite in the isomerization experiment as a result of incorporating sodium ions in the acid solution is fully retained in the ready catalyst particles.

Claims

1. A process for the preparation of a catalyst suitable for the isomerization of normal paraffins, in which process a mixture comprising

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least 0.5 and at most 3.0, potassium and/or sodium ions, in an amount which, expressed in g/l, is at least ten times the normality of the aqueous acid solution, which mordenite has subsequently been treated with an aqueous solution of an ammonium compound, and

c) one or more noble metals of group VIII and/or compounds thereof, is prepared, and the mixture obtained is subjected to shaping under high pressure, characterized in that said mixture is prepared by depositing one or more noble metals of group VIII and/or compounds thereof on said amorphous material, and mixing the material obtained with the mordenite treated with an acid solution and an ammonium compound.

2. A process according to claim 1, characterized in that the acid treatment is carried out at elevated temperature, using an aqueous hydrochloric acid solution with a normality between 1.0 and 2.0, which solution has been saturated with sodium chloride.

3. A process according to claim 1 or 2, characterized in that the treatment with the ammonium compound is carried out with an aqueous solution of ammonium nitrate having a molarity of 0.1—10.

4. A process according to any one of claims 1—3, characterized in that as an amorphous material use is made of alumina.

5. A process according to any one of claims 1—4, characterized in that platinum has been deposited on the amorphous material.

6. A process according to any one of claims 1—5, characterized in that the ready catalyst contains 0.1—1.5% w noble metal of group VIII.

7. A process according to any one of claims 1—6, characterized in that the ready catalyst contains 5—50% w amorphous material loaded with noble metal of group VIII.

Revendications

1. Un procédé pour la préparation d'un catalyseur propre à l'isomérisation d'hydrocarbures paraffiniques normaux, dans lequel procédé un mélange comportant:

a) une matière amorphe se composant essentiellement d'un ou de plusieurs oxydes de métaux des groupes II, III et IV du tableau périodique;

b) de la mordenite qui a été traitée d'abord par une solution qu'on a préparée en introduisant dans une solution acide aqueuse d'une normalité d'au moins 0,5 et de 3,0 au maximum, une quantité d'ions de potassium et/ou de sodium qui, exprimée en g/l, est d'au moins dix fois la normalité de la solution acide aqueuse, laquelle mordenite a été traitée subsequmment par une solution aqueuse d'un composé d'ammonium, et

c) un ou plusieurs métaux nobles du groupe VIII du tableau périodique et/ou des composés de ceux-ci;

est préparé, et le mélange obtenu est soumis à un façonnage sous haute pression, procédé caractérisé en ce qu'on prépare ledit mélange en déposant un ou plusieurs métaux nobles du groupe VIII du tableau périodique et/ou des composés de ceux-ci sur ladite matière amorphe, et en mélangeant la matière obtenue avec la mordenite traitée par une solution acide et un composé d'ammonium.

2. Un procédé selon la revendication 1, caractérisé en ce qu'on exécute le traitement acide à une température élevée en utilisant une solution aqueuse d'acide chlorhydrique d'une normalité entre 1,0 et 2,0, laquelle solution a été saturée avec du chlorure de sodium.

3. Un procédé selon l'une des revendications 1 ou 2, caractérisé en ce que le traitement par le composé d'ammonium est exécuté avec une solution aqueuse de nitrate d'ammonium ayant une molarité de 0,1 à 10.

4. Un procédé selon l'une des revendications 1 à 3, caractérisé en ce qu'on utilise de l'alumine en tant que matière amorphe.

5. Un procédé selon l'une des revendications 1 à 4, caractérisé en ce que du platine a été déposé sur la matière amorphe.

6. Un procédé selon l'une des revendications 1 à 5, caractérisé en ce que le catalyseur fini contient 0,1 à 1,5% en poids de métal noble du groupe VIII du tableau périodique.

7. Un procédé selon l'une des revendications 1 à 6, caractérisé en ce que le catalyseur fini contient 5 à 50% en poids de matière amorphe, chargée de métal noble du groupe VIII du tableau périodique.

Patentansprüche

1. Verfahren zur Herstellung eines für die Isomerisierung von Normalparaffinen geeigneten Katalysators; in dem Verfahren wird ein Gemisch hergestellt, das

a) ein amorphes Material, das in der Hauptsache aus einem oder mehreren Oxiden von Metallen der II., III. und IV. Gruppe des Periodensystems besteht,

b) Mordenit, das zunächst mit einer Lösung behandelt worden ist, die dadurch hergestellt wurde, dass in die wässrige Lösung einer Säure mit einer Normalität von mindestens 0,5 und höchstens 3,0 Kalium- und/oder Natriumionen in einer Menge eingebracht wurden, die in g/l ausgedrückt mindestens das Zehnfache der Normalität der wässrigen Lösung der Säure beträgt, und das anschliessend mit der wässrigen Lösung einer Ammoniumverbindung behandelt worden ist, und

c) ein oder mehrere Edelmetalle der VIII. Gruppe des Periodensystems und/oder deren Verbindungen

umfasst; das erhaltene Gemisch wird einer Formung unter hohem Druck unterworfen, dadurch gekennzeichnet, dass das genannte Gemisch durch Abscheiden von einem oder mehreren Edelmetallen der VIII. Gruppe des Perioden-



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systems und/oder deren Verbindungen auf dem genannten amorphen Material und Mischen des erhaltenen Materials mit dem mit einer Säurelösung und einer Ammoniumverbindung behandelten Mordenit hergestellt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Säurebehandlung bei höherer Temperatur mit einer wässrigen Salzsäurelösung mit einer Normalität zwischen 1,0 und 2,0 erfolgt, die mit Natriumchlorid gesättigt worden ist.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass die Behandlung mit der Ammoniumverbindung mit einer wässrigen Ammoniumnitratlösung mit einer Molarität von 0,1—10 erfolgt.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass als amorphes Material Tonerde verwendet wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass Platin auf dem amorphen Material abgeschieden worden ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, dass der fertige Katalysator 0,1—1,5 Gew.-% Edelmetall der VIII. Gruppe des Periodensystems enthält.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass der hergestellte Katalysator 5—50 Gew.-% amorphes Material enthält, das mit Edelmetall der VIII. Gruppe des Periodensystems beladen ist.

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