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(54) HYDROCARBON CONVERSION CATALYST AND PROCESSES FOR THE PRODUCTION AND USE THEREOF

(71) We, SNAM PROGETTI S.P.A. (formerly known as Snam Progetti S.p.A.), an Italian Company, of Corso Venezia, 16, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalyst suitable for use in hydrocarbon conversion reactions, to processes for preparing the catalyst and to processes employing the catalyst. The catalyst of the present invention is particularly suitable for use in converting paraffinic hydrocarbons, either separately or in admixture, to products which are more commercially desirable.

Examples of reactions which can be catalyzed by the catalyst of the present invention are hydrocarbon hydrocracking and isomerization, for example the selective isomerization of 2,2-dimethylbutane to 2,3-dimethylbutane and the selective isomerization of normal paraffins containing from 10 to 30 carbon atoms.

Processes for hydrocarbon isomerization and hydrocracking are much in use. Isomerization processes enable branched-chain saturated hydrocarbons to be obtained from straight-chain saturated hydrocarbons. When in admixture with other paraffinic hydrocarbons, branched-chain saturated hydrocarbons increases the antiknock value of the paraffinic hydrocarbons, thereby obviating or reducing the need to use additives based on, for example, lead alkyls; the addition of branched-chain hydrocarbons to available hydrocarbon cuts, to produce a mixture for use as a fuel for internal combustion engines, thus allows the octane number of the fuel to be increased in a very simple and economic way. However, during isomerization, hydrocracking generally also take place as a secondary reaction which produces undesirable low molecular weight hydrocarbons, although this is offset to some extent by the fact that hydrocracking of heavy distillates or heavy gas oils produces some light fractions rich in isoparaffins and therefore usable as fuel oils.

Hydrocarbon hydrocracking can be carried out according to well known techniques by allowing a suitable petroliferous fraction to react, in the presence of a catalyst and at a high pressure, with hydrogen in a reactor kept at a desired temperature.

According to the present invention, there is provided a catalyst suitable for use in processes for the isomerization or hydrocracking of hydrocarbons, which comprises a material having a crystal matrix in the form of planar and non-porous layers having on its surface identical centres of controlled acidity, the acidity being of the type caused by displacement of charge or of the protonic type or of the Lewis acid type, and at least one noble metal finely dispersed throughout at least the surface regions of the material, the noble metal(s) being selected from platinum, palladium, irridium, osmium, rhodium and ruthenium.

The catalyst according to the present invention enables high selectivities at levels of conversions very near to the best obtainable thermodynamically to be achieved, when the catalyst is employed under suitable conditions.

Preferably the finely dispersed metal is platinum and/or palladium.

The centres of controlled acidity are produced artificially by different methods, and the grade of acidity depends on the method of preparation used to obtain the catalyst.

As mentioned above, the centres of controlled acidity can be one of several different types, in particular:

(a) an acidity of the type caused by displacement of charge;

(b) an acidity of the protonic type; and

(c) an acidity of the Lewis acid type.

In providing material having acidity of type (a) or type (b) or type (c), there may be utilized a material having a crystalline matrix in the form of planar and non-porous and having, inside the crystal lattice, some deficiencies of charge which require, in order to obtain electric neutrality, compensation from cations on the external surface of the layers; for example certain natural and synthetic minerals of the clay type meet these requirements, and among those particular preferred are phyllosilicates having a high density of charge (from 0.4 to 1 electronic charge per semi cell Si_4O_{10}) tetrahedral coordination. Examples of such minerals are:

smectites of the "beidellite" type (e.g. beidellites and nontronites) and

minerals having limited expansion of the "vermiculite" type (e.g. vermiculites, hydrobiotites and illites).

The acidity of type (a) is produced by subjecting the previously described minerals when in a finely subdivided state (i.e. in the form of particles having a particle size smaller than 40μ) to cationic exchange with bi- or poly-valent cations of a metal selected from Groups IIIb, IVb, VIb, VIIb and VIII (including the lanthenides) of the Periodic Table as given in the Handbook of Chemistry and Physics, 49th. Edition, 1968—1969, published by the Chemical Rubber Publishing Company, preferably cations of lanthanum, cerium, titanium or manganese.

The acidity of the type (b) is produced by subjecting the previously described minerals to cationic exchange with ammonium ions and subsequent heating at a temperature suitable for decomposition of the ammonium ion, generally in the range from 300 to 600° C., preferably at approximately 450°C. for about 10 hours.

The acidity of the type (c) is produced by heating the previously described materials to effect partial dehydration of hydroxyl groups linked to aluminium present in the octahedral layers of the materials; also, but not limitatively, such an acidity is possessed by the metakolinite obtained by heating the mineral kaolinite between 350 and 450°C.

The noble metal of the catalyst of the present invention preferably constitutes from 0.01 to 5 percent by weight of the catalyst and can be combined with the material having the crystal matrix by impregnation using a compound of the noble metal. For example, in the case of platinum, the impregnation can be made using H_2PtCl_6 or $Pt(NH_3)_4(OH)_2$. The incorporation of the noble metal is carried out regardless of the type of acidity present on the surface of the material having the crystal matrix and therefore regardless of the process adopted to obtain this acidity.

The catalyst of the present invention offers a degree of conversion and selectivity which industrially is attractive. Moreover it is more economical than conventional catalysts either from the point of view of the low cost of the minerals used in its manufacture or from the point of view of the processes in which it is employed, which are easy and inexpensive to carry out. Moreover, the catalyst of the present invention gives results of industrial interest even when it has only a low content of noble metal which, in the case of catalyst for use in isomerization is preferably approximately 0.15% by weight, which is much lower than that required by conventional catalysts.

Moreover, it is to be noted that it is possible to obtain catalysts with different grades of acidity merely by changing one or more of the starting material having the crystal matrix, the nature of the cation involved in the cation exchange and the preparative method. In fact, for a starting material having a certain deficiency of charge (as mentioned above), the use of different cations in effecting cationic exchange allows there to be obtained catalysts having different acidity whereby it is possible to obtain, from the same hydrocarbon feed material and under the same reaction conditions, different reaction products; different reaction products are also obtained by the use of different materials having the crystal matrix which have been subjected to cationic exchange with the same cation.

Another aspect of the present invention is an isomerization process which employs the catalyst of the present invention. The isomerization of paraffinic hydrocarbons, either singly or in admixture, and particularly of 2,2-dimethylbutane to 2,3-dimethylbutane, can be carried out under variable conditions of temperature, pressure and space velocity to obtain a desired percentage conversion per pass. The temperature used is genrally dependent on the catalyst used and is usually in the range from 100 to 600°C., preferably from 300 to 450°C. The pressure is selected so as to ensure that the process is carried out with the reactant(s) in the vapour phase and, depending on the particular temperature used, the pressure is usually from atmospheric pressure to 160 kg/cm^2. The liquid hourly space velocity (LHSV) is preferably from 0.1 to 20. The term "liquid hourly space velocity" is used herein to mean the ratio between the volume of liquid hydrocarbon fed per hour and the catalyst volume.

The isomerization process of the present invention can be carried out either in a continuous or discontinuous manner. A preferred isomerization process is a process for transforming 2,2-dimethylbutane into 2,3-dimethylbutane in view of the higher octane number of the latter.

Isomerization of 2,2-dimethylbutane is preferably carried out in a continuous manner as follows. A fresh feed constituted by almost pure hexane is isomerized in a first reaction zone containing a suitable catalyst, for example catalyst of the present invention. A mixture, in thermodynamic equilibrium, of paraffinic C_6 aliphatic hydrocarbons is obtained, from which 2,2-dimethylbutane is separated by distillation. This compound is sent to a second reaction zone containing catalyst of the present invention where isomerization of 2,2-dimethylbutane into 2,3-dimethylbutane takes place. The reaction product is forward to a separation column from the top of which is recovered unreacted 2,2-dimethylbutane which is recycled to the second reaction zone, while from the bottom of the column is withdrawn 2,3-dimethylbutane together with a controlled amount of 2-methylpentane. By this procedure, 2,3-dimethylbutane is obtained as the predominant product. It is to be observed that both reaction zones may be operated with the catalyst of the present invention. It is nevertheless possible for the first zone to be operated with a catalyst of a different type, for instance that described in British Patent Specification No. 1081120. In any case, it is absolutely necessary that the second zone is operated with the catalyst of the present invention.

A further aspect of the present invention is a hydrocracking process which employs a catalyst according to the present invention. The feedstock to be treated is a liquid C_{10}—C_{30} hydrocarbon feedstock. The process is effected at a temperature usually in the range from 150 to 450°C., at a pressure usually in the range from 35 to 150 atmospheres and at a liquid hourly space velocity usually in the range from 0.1 to 10. The reaction product can be subjected to conventional treatments of debutanization and fractionation.

The following Examples illustrate the present invention. In the Examples, the term "conversion" is expressed as a percentage and is defined as:

$$\left(\frac{\text{number of molecules reacted}}{\text{number of molecules fed}}\right)\times 100$$

and the term "selectivity" is expressed as a percentage and is defined as:

$$\left(\frac{\text{number of molecules of desired product}}{\text{number of molecules reacted}}\right)\times 100$$

Selective isomerization of 2,2-dimethylbutane

Example 1

To prepare the catalyst there was used a beidellite which had an equivalent surface area of 54 Å^2. An "equivalent surface area" is the area at the disposal of a single monovalent cation.

10 Grams of this beidellite were subjected to conventional ion exchange at a temperature of 60 to 70°C. using a 2*N* aqueous solution of lanthanum nitrate. The treatment was repeated three times to ensure complete ion exchange.

The resulting material, after careful washing to remove all foreign ions present, was subjected to impregnation with a solution of chloroplatinic acid, and thereafter dried and calcined at 350°C. Sufficient of the chloroplatinic acid solution was used to provide a final catalyst having a platinum content of 0.15% by weight.

The catalyst was used in the isomerization of 2,2-dimethylbutane in a flow microreactor under the following reaction conditions:

Temperature	390°C.
Pressure	30 kg/cm^2
Catalyst	1.5 g
LHSV	1
H_2/Hydrocarbon molar ratio	5:1
ppm H_2O in the feedstock	50

The results obtained are reported in the following Table 1. The catalyst was tested three times, each time under the same conditions, and the discrepancies between the results of tests A, B and C in Table 1 are accounted for by the limited sensitivity of the analytical apparatus.

The degree of hydration of the catalyst during isomerization was controlled by the addition of a suitable amount of water to the feed hydrocarbon. Generally the amount added was 50—100 ppm of water; in the particular case of Example 1, the amount added was 50 ppm of water.

TABLE 1

Composition of the reaction product	Test A	Test B	Test C
2,2-dimethylbutane (2,2-DMB)	73.6	73.5	78.6
2,3-dimethylbutane (2,3-DMB)	21.9	22.8	18.1
2-methylpentane (2-MP)	2.3	2.0	1.7
3-methylpentane (3-MP)	2.2	1.7	1.6
n-hexane (nC_6)	traces	traces	traces
Conversion (%)	26.4	26.5	21.6
Selectivity to 2,3-DMB (%)	83.0	86.0	84.6

The selectivity to 2,3-DMB is the ratio:—

$$\frac{\text{2,3-DMB}}{\text{2,3-DMB}+\text{2-MP}+\text{3-MP}+\text{nC}_6} \cdot 100$$

Products resulting from cracking and hydrocracking were substantially absent.

Example 2

A vermiculite having an equivalent surface area of 37 Å^2 was finely milled to provide particles having a diameter smaller than 40 microns. The resulting material was washed several times to remove any soluble impurities present and was then subjected to cationic exchange with a 2*N* solution of lanthanum nitrate, impregnated with chloroplatinic acid, dried and calcined, all as set forth in Example 1, to provide a catalyst having a platinum content of 0.15% by weight.

The catalyst was used in the isomerization at various temperatures T of 2,2-dimethylbutane in a flow microreactor under the following conditions:—

Pressure	20 kg/cm^2
Catalyst	1.5 g
LHSV	1
Hydrogen/Hydrocarbon molar ratio	5:1
ppm H_2O in the feedstock	50

The results obtained are reported in the following Table 2.

TABLE 2

Composition of the reaction product	Test A T=390°C	Test B T=390°C	Test C T=410°C	Test D T=390°C
2,2-dimethylbutane	78.7	75.5	69.0	73.7
2,3-dimethylbutane	20.2	22.6	27.5	23.0
2-methylpentane	0.6	1.0	1.8	1.7
3-methylpentane	0.5	0.9	1.7	1.6
Conversion (%)	21.3	24.5	31.0	26.3
Selectivity to 2,3-DMB (%)	94.8	92.2	88.7	87.5

Example 3

In this Example, the vermiculite of the type described in Example 2 was used; it was subjected to exchange with an ammonium salt (in this case the acetate, although the nitrate could equally well have been used) and then to calcination (between 400 and 500°C, in this case 450°C) to cause removal of NH_3 and formation of a protonic type acidity.

10 grams of the vermiculite were subjected to conventional ion exchange with a solution of ammonium acetate, washed, heated for three hours at a temperature of 450°C, impregnated with chloroplatinic acid, dried and calcined to provide a catalyst having a platinum content of 0.15% by weight.

The catalyst was used in the isomerization at various temperatures T of 2,2-dimethylbutane in a flow reactor under the following conditions:

Pressure	20 kg/cm^2
Catalyst	1.5 g
LHSV	1
H_2/Hydrocarbon molar ratio	5:1

The results obtained are reported in the following Table 3.

TABLE 3

Reaction product	T=400°C	T=420°C
2,2-DMB	91.7	30.9
2,3-DMB	6.0	11.6
2-methylpentane	1.4	26.2
3-methylpentane	0.7	16.4
n-C_6	0.2	14.9
Conversion (%)	8.3	69.1
Selectivity to 2,3-DMB (%)	72.3	16.8

Example 4

10 grams of kaolinite, which had been purified by settling and subsequently washed in order to remove any dissolved impurities, were impregnated with chloroplatinic acid and subsequently heated at a temperature of 420°C. for 15 hours to provide a catalyst consisting of metastable kaolinite containing 0.15% by weight of platinum.

The catalyst was used in the isomerization at various temperatures T and flow rates of

2,2-dimethylbutane in a microreactor under the following conditions:

Pressure	20 kg/cm^2
Catalyst	15 g
H_2/Hydrocarbon molar ratio	5:1

The results obtained are reported in the following Table 4.

TABLE 4

Reaction product (other than compounds obtained by cracking)	T=420°C LHSV=1	T=450°C LHSV=0.5	T=420°C LHSV=0.5
2,2-DMB	91.6	83.4	63.7
2,3-DMB	6.8	14.6	24.4
2-methylpentane	0.9	1.6	8.2
n-hexane	—	—	0.6
Conversion (%)	8.4	16.6	36.3
Selectivity with respect to 2,3-DMB (%)	80.9	87.9	87.2

The kaolinite-based catalyst, unlike the vermiculite-based catalysts of Examples 2 and 3, caused isomerization and a small degree of cracking. The small quantities of compounds produced by the cracking are not specified in Table 4. In Table 4 the selectivity is defined as:—

$$\frac{2,3\text{-DMB}}{(2,3\text{-DMB}+2\text{-MP}+nC_6+A}$$

where A is the summation of the numbers of carbon atoms in the molecules of the compounds produced by the cracking, divided by 6.

Selective isomerization of normal hexadecane

Example 5

20 Grams of a catalyst constituted by 0.15% by weight of Pt supported on 99.85% by weight of vermiculite which had been ion exchanged with titanium were used in the isomerization of normal hexadecane under the following reaction conditions:

Temperature	330°C
Pressure	50 kg/cm^2
LHSV	1
H_2/Hydrocarbon molar ratio	5:1

In the reaction product, there was 15% (by moles) of C_3—C_{15} hydrocarbons and 85% (by moles) of C_{16} hydrocarbons (iso and straight chain); the percentage of iso-C_{16} in the total C_{16} in the product was 85%. By "C_3—C_{15}" is meant all the products derived by hydrocracking, which is desirably as small as possible since the products of interest are the hydrocarbons having the same molecular weight as the feedstock but having a branched structure. Therefore, the relevant indices of the catalyst behaviour, are the ratio between iso-hexadecanes and the sum of all the C_{16} hydrocarbons, and the fraction of feedstock cracked to C_3—C_{15} hydrocarbons.

Selective isomerization of heavy paraffinic cuts

Example 6

20 Grams of a catalyst constituted by 0.15% by weight of Pt supported on 99.85% by weight of vermiculite which had been ion exchanged with titanium were used in the selective isomerization of the normal heavy paraffins present in a gas oil cut having a boiling range of from 250 to 350°C., with the aim of reducing the pour point of the cut itself, under the following conditions:

Temperature	340°C
Pressure	50 kg/cm^2
LHSV	1
H_2/Hydrocarbon molar ratio	5:1

The reaction product contained 22 per cent by weight of material having a boiling point up to 250°C. and 78 per cent by weight of material having a boiling point higher than 250°C. The product fraction having a boiling point higher than 250°C had a d_{15} of 0.795 and a pour point of +3°C, whereas the feed had a d_{15} of 0.804 and a pour point of +19°C.

Normal hexadecane hydrocracking.

Example 7

20 Grams of a catalyst constituted by 0.15% by weight of Pt supported on 99.85% by weight of vermiculite which had been ion exchanged with titanium were used in the hydrocracking of *n*-hexadecane.

The reaction conditions were as follows:

Temperature	350°C
Pressure	50 kg/cm^2
LHSV	0.5
H_2/Hydrocarbon molar ratio	10:1

The conversion of n-hexadecane was 80%, and the molar distribution of the constituents of the reaction product and the product characteristics were as follows:—

$C_3 = 6.5\%$

$C_4 = 8.3\%$

$C_5 = 12\%$

$C_6 = 15.8\%$

$C_7 = 12.7\%$

$C_8 = 10.8\%$

$C_9 = 10.4\%$

$C_{10} = 8.5\%$

$C_{11} = 6.7\%$

$C_{12} = 1.8\%$

$C_{16} = 6.5\%$

$$\frac{n\text{-}C_4 = 44.1\%}{\text{total } C_4}$$

$$\frac{n\text{-}C_5 = 35.3\%}{\text{total } C_5}$$

$$\frac{n\text{-}C_6 = 36.0\%}{\text{total } C_6}$$

where C_3, C_4, C_5 etc. represent the isoparaffinic and the *n*-paraffinic hydrocarbons having the number of carbon atoms indicated in the subscript.

WHAT WE CLAIM IS:—

1. A catalyst suitable for use in processes for the isomerization or hydrocracking of hydrocarbons, which comprises a material having a crystal matrix in the form of planar and non-porous layers and having on its surface identical centres of controlled acidity, the acidity being of the type caused by displacement of charge or the protonic type or of the Lewis acid type, and at least one noble metal finely dispersed throughout at least the surface regions of the material, noble metal(s) being selected from platinum, palladium, iridium, osmium, rhodium and ruthenium.

2. A catalyst according to Claim 1, wherein the material having the crystal matrix is a natural or synthetic mineral of the clay type.

3. A catalyst according to Claim 2, wherein the natural or synthetic mineral of the clay type is a smectite of the beidellite type.

4. A catalyst according to Claim 3, wherein the smectite of the beidellite type is beidellite or nontronite.

5. A catalyst according to Claim 2, wherein the natural or synthetic mineral of the clay type is a semi-expandable mineral of the vermiculite type.

6. A catalyst according to Claim 5, wherein the semi-expandable mineral of the vermiculite type is vermiculite, hydrobiotite or illite.

7. A catalyst according to Claim 2, wherein the clay type mineral is metakaolinite.

8. A catalyst according to any preceding claim, wherein the noble metal constitutes from 0.01 to 0.5% by weight of the catalyst.

9. A catalyst according to Claim 8, wherein the noble metal is platinum and/or palladium.

10. A process for the preparation of a catalyst according to any one of Claims 1 to 6 or to Claim 8 or 9 when Claim 8 is directly appendant to any one of Claims 1 to 6, wherein the centres of controlled acidity are formed by subjecting the material having the crystal matrix, when in the form of particles having a particle size smaller than 40μ, to cationic exchange with cations of a metal selected from Groups IIIb, IVb, VIb, VIIb and VIII of the Periodic Table hereinbefore referred to.

11. A process according to Claim 10, wherein the cations are those of lanthanum, cerium, titanium or manganese.

12. A process for the preparation of a catalyst according to any one of Claims 1 to 6 or to Claim 8 or 9 when Claim 8 is directly appendant to any one of Claims 1 to 6, wherein the centres of controlled acidity are formed by subjecting the material having the crystal matrix to cationic exchange with ammonium ions and subsequent heating at a temperature from 300 to 600°C.

13. A process according to Claim 12, wherein the subsequent heating is effected at approximately 450°C. for about ten hours.

14. A process for the preparation of a catalyst either according to any one of Claims 1 to 6 or to Claim 8 or 9 when Claim 8 is directly appendant to any one of Claims 1 to 6, wherein the centres of controlled acidity are obtained by heating the material having a crystal matrix at a temperature from 350 to 450°C, or according to Claim 7 or to Claim 8 or 9 when Claim 8 is appendant to Claim 7, wherein the centres of controlled acidity are obtained by heating kaolinite at a temperature from 350 to 450°C.

15. A process for the isomerization of one or more saturated hydrocarbons, which comprises contacting the saturating hydrocarbon(s) in the vapour phase with a catalyst according to any one of Claims 1 to 9 at a temperature in the range from 100 to 600°C, a pressure in the range from 1 to 160 kg/cm^2 and a liquid hourly space velocity in the range from 0.1 to 20.

16. A process according to Claim 15, wherein the temperature is in the range from 300 to 450°C.

17. A process according to Claim 15 or 16, wherein the hydrocarbon to be isomerized

is 2,2-dimethylbutane and the product includes 2,3-dimethylbutane.

18. A process for hydrocracking of one or more normally liquid hydrocarbons, which comprises contacting the hydrocarbon(s) with a catalyst according to any one of Claims 1 to 9 at a temperature in the range from 150 to 450°C, a pressure in the range from 35 to 150 atmospheres and a liquid hourly space velocity in the range from 0.1 to 10.

19. A catalyst substantially as described in any one of the foregoing Examples 1 to 5.

20. A process for preparing a catalyst, substantially as described in any one of the foregoing Examples 1 to 5.

21. An isomerization process according to Claim 15, substantially as described in any one of Examples 1 to 6.

22. A hydrocracking process according to Claim 18, substantially as described in Example 7.

23. A hydrocarbon whenever produced by a process according to any one of Claims 15, 16, 17 and 21.

24. A hydrocarbon whenever produced by a process according to Claim 18 or 22.

HASELTINE, LAKE & CO.,
Chartered Patent Agents,
28, Southampton Buildings,
Chancery Lane,
London, WC2A 1AT.
and
Temple Gate House,
Temple Gate,
Bristol BS1 6PT.
and
9 Park Square,
Leeds LS1 2LH.
Agents for the Applicants.

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