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[Continued on next page]

(54) Title: METHANOL CONVERSION PROCESS

$$x(M_{1/n}XO_2):yYO_2:SiO_2 \qquad (I)$$

(57) Abstract: A process for the conversion of methanol to hydrocarbons within the C_5 to C_{17} range is described which comprises contact of a feed comprising methanol with a zeolite microporous crystalline material having an empirical formula (I) wherein M is selected from H^+, an inorganic cation of charge +n, and mixtures thereof, X is at least one chemical element having an oxidation state of +3, Y is at least one second chemical element other than Si having an oxidation state +4, x has a value between 0 and about 0.3, y has a value between 0 and about 0.1, and recovery of hydrocarbons within the C_5 to C17 range from the conversion product.

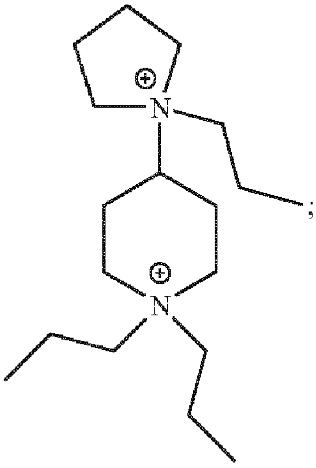

FIGURE 1

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METHANOL CONVERSION PROCESS

FIELD OF INVENTION

[0001] This invention relates to a process for the conversion of methanol to hydrocarbons over a zeolite catalyst.

BACKGROUND ART

[0002] Processes for converting lower alcohols such as methanol to hydrocarbons are known and have become of great interest in recent times because they offer an attractive way of producing liquid hydrocarbon fuels, especially gasoline, from sources which are not of liquid petroliferous origin. In particular, they provide a way by which methanol can be converted to gasoline boiling range products in good yields. The methanol, in turn, may be readily obtained from coal by gasification to synthesis gas and conversion of the synthesis gas to methanol by well-established industrial processes. As an alternative, the methanol may be obtained from natural gas by other conventional processes.

[0003] This process is the well known methanol to gasoline process as developed and operated my ExxonMobil as the ExxonMobil MTG process. This technology is extensively discussed and described in the review “Methanol-to-hydrocarbons: process technology”, Author: Frerich J. Keil, in Microporous and Mesoporous Materials, Volume 29, Issues 1–2, June 1999, Pages 49–66.

[0004] The conversion of methanol to hydrocarbon products may take place in a fluidized bed process as described, for example, in U.S. Pat. Nos. 4,071,573 and 4,138,440, or in a fixed bed as described in U.S. Pat. Nos. 3,998,899, 3,931,349 and 4,035,430. In the fixed bed process, the methanol is usually first subjected to a dehydrating step, using a catalyst such as gamma-alumina, to form an equilibrium mixture of methanol, dimethyl ether (DME) and water. This mixture is then passed over a catalyst such as zeolite ZSM-5 which brings about the conversion to the hydrocarbon products which are mainly in the range of light gas to gasoline. The water may be removed from the methanol dehydration products prior to conversion to hydrocarbons as may the methanol which can be recycled to the dehydration step, as described in

U.S. Pat. No. 4,035,430. Removal of the water is desirable because the catalyst may tend to become deactivated by the presence of the water vapor at the reaction temperatures employed, but this step is by no means essential.

[0005] In the operation of the fixed bed process, a major problem which has to be dealt with is the thermal balance. The conversion of the oxygenated feed stream (methanol, DME) to the hydrocarbons is a strongly exothermic reaction liberating approximately 1480 kJ. (1400 Btu) of heat per kilogram of methanol. In an adiabatic reactor this would result in a temperature rise which would lead to extremely fast catalyst aging rates or even to damage to the catalyst. Furthermore, the high temperatures which might occur could cause undesirable products to be produced or the product distribution could be unfavorably changed. It is therefore necessary that some method should be provided to maintain the catalyst bed within desired temperature limits by dissipating the heat of the reaction.

[0006] A degree of control over the temperature of the catalyst bed can be achieved by suitable choice of bed configuration but this expedient is generally insufficient by itself and other methods must be employed. One particularly efficaceous method is to employ a light gas portion of the hydrocarbon product as recycle, as described in U.S. Pat. No. 3,931,349. An alternative proposal is set out in U.S. Pat. No. 4,035,430. The process described in this patent employs a number of sequential catalyst beds and recycle gas may be injected between the successive beds to control the exotherm.

[0007] The currently preferred catalyst for the MTG process is ZSM-5, which is an aluminosilicate zeolite mineral of MFI structure type belonging to the pentasil family of zeolites. Conventional MTG processes are optimized to work with this catalyst and there are relatively few alternative catalysts.

[0008] There is a continuing need for alternative processes for the conversion of methanol to hydrocarbons especially hydrocarbons in the C_5 to C_{17} range such as gasoline (C_5 to C_{12}) or kerosene (C_{11} to C_{12}).

DISCLOSURE OF THE INVENTION

[0009] In the present invention methanol is converted to hydrocarbons in the C_5 to C_{17} range in the presence of a zeolite microporous crystalline material ITQ-39.

[0010] Thus the present invention in one aspect provides a process for the conversion of methanol to hydrocarbons within the C_5 to C_{17} range, which process comprises contact of a feed comprising methanol with a zeolite microporous crystalline material ITQ-39 and recovery of hydrocarbons within the C_5 to C_{17} range from the conversion product.

[0011] The process of the present invention may be operated under typical MTG operating conditions as described in “Methanol-to hydrocarbons : process technology”, Author: Frerich J. Keil, in Microporous and Mesoporous Materials, Volume 29, Issues 1–2, June 1999, Pages 49–66, U.S. Pat. No. 4,071,573, U.S. Pat. No.4,138,440, U.S. Pat. No. 3,998,899, U.S. Pat. No. 3,931,349 and U.S. Pat. No. 4,035,430, the whole contents of which are incorporated herein by reference.

[0012] The catalyst used in the process of the present invention is a zeolite microporous crystalline material ITQ-39, comprising, in the heated state and in the absence of defects in its crystalline framework manifested by the presence of silanols, the empirical formula:

$$x(M1/nXO2):yYO2:SiO2,$$

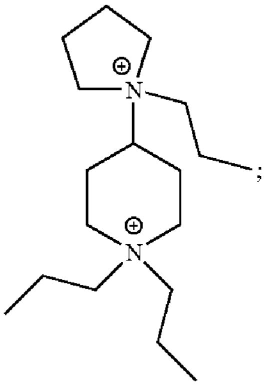
[0013] wherein M is selected from H^+, an inorganic cation of charge +n, and mixtures thereof, X is at least one chemical element having an oxidation state of +3, Y is at least one second chemical element other than Si having an oxidation state +4, x has a value between 0 and about 0.3, y has a value between 0 and about 0.1, and wherein the synthesized material has an X-ray diffraction pattern having at least values of angle 2θ(degrees) and relative intensities (I/I_0) shown in Table 1.

TABLE 1

2θ(degrees) ±0.5	Intensity (I/I_0)
7.8	f
8.5	d(h)
15.8	d
19.3	d
21.4	m
22.0	f

22.8	mf
26.2	d
27.5	d
32.0	d
43.5	d

[0014] Processes for synthesising the microporous crystalline material, comprising the steps of: forming a reaction mixture comprising: a source of SiO2, a source of one or more tetravalent elements Y selected from the group consisting of Ge, Ti, Sn, V and mixtures thereof, a source of one or more trivalent elements X selected from the group consisting of Al, B, Ga, Fe, Cr and mixtures thereof, a source of inorganic cations M having a charge +n, a source of an organic dication SDA-1 having the structure of Formula 1



[0015] a source of fluoride ions and water; heating the reaction mixture to a temperature of between about 80ºC and about 200ºC until crystallisation is achieved; and forming the microporous crystalline material, wherein the material has a composition in the ranges:

[0016] $SDA\text{-}1(OH)_2/SiO_2=0.01\text{-}1.0$,

[0017] $M_{1/n}OH/SiO_2=0\text{-}1.0$,

[0018] $X_2O_3/SiO_2=0\text{-}0.15$,

[0019] $YO_2/SiO_2=0\text{-}0.1$,

[0020] $F/SiO_2=0.1-3.0$, and

[0021] $H_2O/SiO_2=0.5-50$.

[0022] In one embodiment described herein, the microporous crystalline materials produced can be palletized in accordance with known techniques and used as a catalyst or catalyser component in processes of transformation of organic compounds or as an absorbent in a processes of absorption and separation of organic compounds. The material used in the above applications can be in its acid form and/or exchanged with suitable cations.

BRIEF DESCRIPTION OF THE FIGURES

[0023] FIG. 1 illustrates the organic dication, in the presence of which the zeolite ITQ-39 is synthesised.

[0024] FIG. 2 illustrates characteristic peaks of the X-ray diffraction pattern of the ITQ-39 material, as synthesised according to example 5.

[0025] FIG. 3 illustrates characteristic peaks of the X-ray diffraction pattern of the material of example 5 after heating.

DETAILED DESCRIPTION

[0026] Presently described is a methanol conversion process that utilises microporous crystalline zeolite, identified as "zeolite ITQ-39". This material, both in heated and synthesised forms without heating, have an X-ray diffraction patterns that are different from other known zeolite materials, and therefore, characteristic of this material. One example embodiment described herein is a zeolite microporous crystalline material that has, in the heated state and in the absence of defects in its crystalline framework manifested by the presence of silanols, the empirical formula:

[0027] $x(M_{1/n}XO_2):yYO_2:SiO_2$

[0028] wherein M is selected from H^+, an inorganic cation of charge +n, and mixtures thereof, X is at least one chemical element having an oxidation state of +3, Y is at least one second chemical element other than Si having an oxidation state +4, x has a value between 0 and about 0.3, y has a value between 0 and about 0.1, and wherein the synthesized material has an X-ray diffraction pattern with at least the values of angle 2θ (degrees) and relative intensities (I/I_0) shown in Table I, I_0 being the intensity of the most intense peak to which a value of 100 is assigned:

TABLE I

2θ(degrees) ±0.5	Intensity (I/I_0)
7.8	f
8.5	d(h)
15.8	d
19.3	d
21.4	m
22.0	f
22.8	mf
26.2	d
27.5	d
32.0	d
43.5	d

[0029] wherein d has a weak intensity between 0 and 20%, m has a medium intensity between 20 and 40%, f has a strong intensity between 40 and 60%, mf has a very strong intensity between 60 and 100%, and h has a peak of diffraction appearing as a shoulder.

[0030] The zeolite microporous crystalline material described herein, after heating to eliminate the occluded organic compounds inside, has an X-ray diffraction pattern with at least the values of angle 2θ (degrees) and relative intensities (I/I_0) indicated in Table II:

TABLE II

2θ(degrees) ±0.5	Intensity (I/I_0)
7.8	mf
8.6	d(h)
14.8	d
15.8	d
19.4	d
21.4	m
22.1	f
23.0	mf

26.3	m
27.6	d
32.0	d
43.9	d

[0031] wherein d, m, f, mf and h have the same meanings as described for Table I.

[0032] In one example embodiment, the constituents of the microporous crystalline material can be as follows. Element X is selected from the group consisting of Al, Ga, B, Fe, Cr and mixtures thereof. Element Y is selected from the group consisting of Ge, Ti, Sn, V and mixtures thereof. In the empirical formula above, x has a value of less than about 0.3 and y has a value of less than about 0.05.

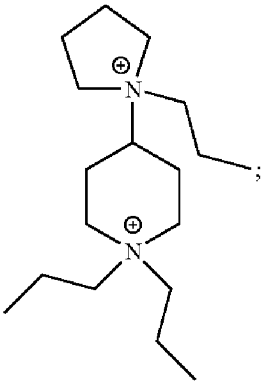
[0033] According to another example embodiment, the zeolite microporous crystalline material has, in the heated state and in the absence of defects in its crystalline framework manifested by the presence of silanols, the empirical formula:

$$x(M_{1/n}XO_2):_yYO_2:SiO_2$$

[0034] wherein M is selected from H^+, an inorganic cation of charge +n, and mixtures thereof, X is at least one chemical element having an oxidation state of +3, selected from the group consisting of Al, Ga, B, Fe, Cr and mixtures thereof, Y is at least one second chemical element other than Si having an oxidation state of +4, selected from the group consisting of Ge, Ti, Sn, V and mixtures thereof, x has a value between 0 and about 0.3, y has a value between 0 and about 0.05, wherein the synthesized material has an X-ray diffraction pattern with at least the values of angle 2θ (degrees) and relative intensities previously mentioned (Table I) and this material has in the heated state an X-ray diffraction pattern with at least the values of angle 2θ (degrees) and relative intensities (I/I_0) previously mentioned (Table II).

[0035] The X-ray diffraction patterns of the microporous crystalline material, ITQ-39, were obtained by the powder method using a fixed divergence slit of 1/4° and using the Kα radiation of Cu. It should be taken into account that the diffraction data listed for this sample of zeolite ITQ-39 as simple or unique lines can be formed by multiple overlaps or superpositions of reflections that, under certain conditions such as differences in crystallographic changes, can appear as resolved or partially resolved lines. Generally, crystallographic changes can include small variations in the unit cell parameters and/or changes in the crystal symmetry without these producing a change in structure. Thus, the positions, widths and relative intensities of the peaks depend to a certain extent on the chemical composition of the material and on the degree of hydration and crystal size.

[0036] When the framework of the microporous crystalline material is exclusively composed of silicon and aluminium oxides in a molar ratio of Si/Al=13 and it has been synthesised in the presence of fluoride anions using the quaternary diammonium dication having the formula:



[0037] Zeolite ITQ-39 presents an X-ray diffraction pattern as illustrated in FIG. 2. This diffraction pattern is characterised by the values of angle 2θ (degrees) and relative intensities (I/I_0) shown in Table III.

TABLE III	
2θ (degrees)	intensities (I/I_0)
7.8198	49.56
8.6885	13.82
15.7045	4.51
19.2097	7.54
21.3591	32.59
22.0000	45.40
22.7964	100.00
25.0561	9.92

26.2576	13.17
27.4230	7.01
28.7596	6.87
29.4369	5.87
31.9616	5.07
34.1133	1.72
36.1252	1.17
36.7736	2.03
42.6035	1.28
43.4655	5.76

[0038] The X-ray diffraction pattern of zeolite ITQ-39 after being heated at 580℃., to eliminate occluded organic compounds inside, is illustrated in FIG. 3. This diffraction pattern is characterised by the values of angle 2θ (degrees)and relative intensities (I/I_0) that are shown in Table IV. Comparing the X-ray diffraction patterns of zeolite ITQ-39 as synthesised and after heating to various temperatures shows the great thermal stability of the material.

TABLE IV

2θ (degrees)	intensities (I/I_0)
7.8461	100.00
8.7039	37.71
11.0092	1.47
13.6688	2.40
14.7903	5.20
15.7731	5.95
19.2573	5.47
21.4378	28.77
22.1339	44.61
22.9739	95.99
25.1759	15.59
26.3257	20.77
27.6284	12.92
29.1717	12.52

32.1493	7.69
34.3923	2.64
36.4259	1.95
43.9105	4.31

[0039] Further described herein, in another example embodiment, is a process for synthesising the microporous crystalline material. The process for synthesising the microporous crystalline material comprises the steps of: forming a reaction mixture comprising one or more sources of SiO_2, one or more sources of the organic cation SDA-1, one or more sources of fluoride ions, and water; heating the reaction mixture to a temperature of between about 80°C. and about 200°C. until crystallisation is achieved; and forming the microporous crystalline material. The reaction mixture has a composition, in terms of molar ratios, in the ranges:

$SDA\text{-}1(OH)_2/SiO_2=0.01\text{-}1.0$,
$F/SiO_2=0.1\text{-}3.0$, and
$H_2O/SiO_2=0.5\text{-}50$.

[0040] According to another example embodiment, the reaction mixture comprises one or more sources of SiO_2, one or more sources of the organic cation SDA-1, one or more sources of fluoride ions, and water, and has a composition, in terms of molar ratios, in the ranges:

$SDA\text{-}1(OH)_2/SiO_2=0.01\text{-}1.0$,
$F/SiO_2=0.1\text{-}3.0$, and
$H_2O/SiO_2=0.5\text{-}50$.

[0041] According to yet another example embodiment, the reaction mixture additionally comprises a source of one or more trivalent elements X and has a composition, in terms of molar ratios, in the ranges:

$SDA\text{-}1(OH)_2/SiO_2=0.01\text{-}1.0$,
$X_2O_3/SiO_2=0\text{-}0.15$, excluding the value 0,
$F/SiO_2=0.1\text{-}3.0$, and

H_2O/SiO_2=0.5-50.

[0042] According to still another example embodiment, the reaction mixture additionally comprises a source of one or more other tetravalent elements Y other than Si and has a composition, in terms of molar ratios, in the ranges:

SDA-1$(OH)_2/SiO_2$=0.01-1.0,
YO_2/SiO_2=0-0.1, excluding the value 0,
F/SiO_2=0.1-3.0, and
H_2O/SiO_2=0.5-50.

[0043] According another example embodiment, the reaction mixture additionally comprises a source of one or more other tetravalent elements Y other than Si and source of one or more trivalent elements X, and has a composition, in terms of molar ratios, in the ranges:

SDA-1$(OH)_2/SiO_2$=0.01-1.0,
X_2O_3/SiO_2=0-0.15, excluding the value 0,
YO_2/SiO_2=0-0.1, excluding the value 0,
F/SiO_2=0.1-3.0, and
H_2O/SiO_2=0.5-50.

[0044] In an further example embodiment, the reaction mixture comprises a source of SiO_2, a source of one or more other tetravalent elements Y other than Si selected from the group consisting of Ge, Ti, V, Sn and mixtures thereof, a source of one or more trivalent elements X selected from the group consisting of Al, B, Ga, Fe, Cr and mixtures thereof, a source of inorganic cations M having a charge +n, selected from the alkaline metals, alkaline earths and mixtures thereof, a source of organic cation SDA-1, a source of fluoride ions and water. The reaction mixture has a composition, in terms of molar ratios, in the ranges:

SDA-1$(OH)_2/SiO_2$=0.1-1.0,
$M_{1/n}OH/SiO_2$=0-0.2

X_2O_3/SiO_2=0-0.07

YO_2/SiO_2=0-0.05

F/SiO_2=0.1-2.0,

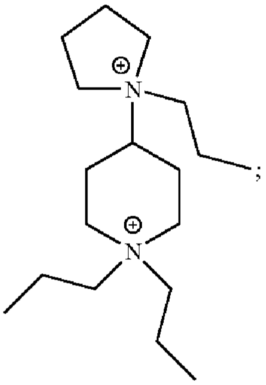
H_2O/SiO_2=1-20.

[0045] The mixture can be heated with or without stirring to a temperature of between 80°C. and 200°C. until crystallisation is achieved.

[0046] The composition of the reaction mixture producing the microporous crystalline material can be generally represented by the following formula, with the values of parameters indicating the molar ratios:

[0047] $r\text{SDA-1(OH)}_2{:}sM_{1/n}OH{:}tX_2O_3{:}uYO_2{:}vF{:}SiO_2{:}wH_2O$

[0048] where M is one or more inorganic cations of charge +n, preferably alkaline metals or alkaline earths; X is one or more trivalent elements, preferably Al, B, Ga, Fe, Cr or mixtures thereof; Y is one or more tetravalent elements other than Si, preferably Ge, Ti, Sn, V or mixtures thereof; SDA-1 is the dication



[0049] F is one or more sources of fluoride ions, preferably HF, NH_4F or mixtures thereof and the values of r, s, t, u, v and w are in the ranges:

r=SDA-1$(OH)_2/SiO_2$=0.01-1.0, preferably 0.1-1.0,

s=$M_{1/n}OH/SiO_2$=0-1.0, preferably 0-0.2,

t=X_2O_3/SiO_2=0-0.15, preferably 0-0.07,
u=YO_2/SiO_2=0-0.1, preferably 0-0.05,
v=F/SiO_2=0.1-3.0, preferably 0.1-2.0, and
w=H_2O/SiO_2=0.5-50, preferably 1-20.

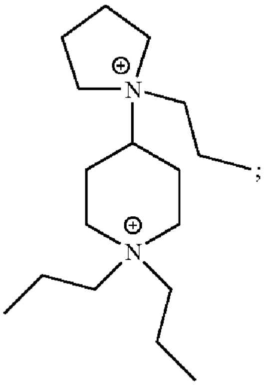
[0050] The components of the synthesis mixture can originate from different sources and the times and conditions of crystallisation may be affected by the same.

[0051] Preferably, the thermal treatment of the mixture is carried out at a temperature of between about 130°C. and about 200°C. The thermal treatment of the reaction mixture can be performed either statically or with stirring of the mixture. After the crystallisation is complete, the solid product is separated by filtration or centrifugation and is dried. Subsequent heating at temperatures higher than 350°C., preferably between about 400°C. and 1000°C. causes decomposition of the occluded organic residues inside the zeolite and their removal, leaving the zeolite channels free.

[0052] The source of SiO_2 can be, for example, tetraethyl orthosilicate, colloidal silica, amorphous silica or a mixture of these.

[0053] The fluoride anion is used as a mobilising agent for the precursor species. The source of fluoride ions is preferably HF, NH4F or mixtures thereof.

[0054] The organic cation or dication SDA-1, is added to the reaction mixture preferably in the form of a salt, for example, a halide, or in the form of a hydroxide and, additionally, a source of alkaline metal, alkaline earth ions or a mixture of both (M) can be added in the form of a hydroxide or a salt. The SDA-1 preferably has a structure



[0055] In one example embodiment, some crystalline ITQ-39 material is added to the reaction mixture as crystallisation promoter in a quantity in the range of about 0.01% to about 20% by weight, preferably between about 0.05% and about 10% by weight with respect to the total added inorganic oxides.

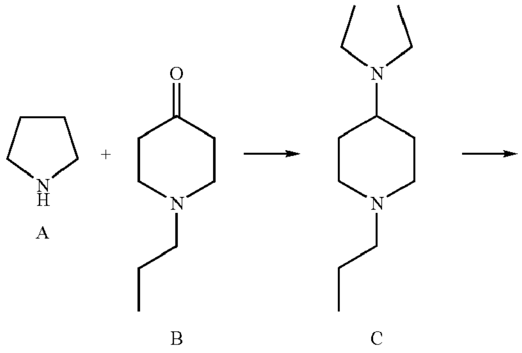
[0056] Additionally, the materials produced herein can be pelletised in accordance with known techniques and used as catalysts or catalyser components in the transformation of organic compounds. The materials can also be used as absorbents in the absorption and separation of organic compounds. As used in these applications, the ITQ-39 material can be in its acid form and/or exchanged with suitable cations.

[0057] In the process of the present invention methanol may be converted into a hydrocarbon product preferably containing a kerosene fraction in a procedure similar to that used in the Mobil methanol to gasoline process.

[0058] When kerosene is the desried product it is preferred that the process is as follows. The crude methanol is initially preheated, vapourised and then superheated to between 300-320°C in a series of heat exchangers. The vapour is then sent to the dimethyl ether (DME) reactor containing a dehydration catalyst such as γ-alumina where approximately 75% of the methanol is partially dehydrated to an equilibrium mixture of DME, water and methanol. The reaction is rapid, reversible and exothermic. The resulting mixture, at a temperature greater than 320°C and preferably between 320 and 420°C is passed into the methanol converter. This reaction is very exothermic and the process gas can be mixed with some recycle gas and then passed to the conversion reactors to absorb some of the heat of reaction. In the conversion reactor which contains zeolite ITQ-39 catalyst, DME and/or methanol is further dehydrated to give the final product containing a kerosene fraction, by a mechanism which may involve the initial formation of light alkenes which can then oligomerize and cyclise with the evolution of further heat. The heat thus recovered can be used elsewhere in the process, for example, pre heating process gas streams or for distillation of the final product. The reactor effluent is cooled and the heat can be recovered, by generating medium pressure steam for use elsewhere in the process. Conversion of methanol is very high and can reach almost 100%. The condensate comprises liquid hydrocarbons, generally in the range C_5 to C_{17} and water. The non condensable fraction used for recycle generally contains low molecular weight hydrocarbons, principally methane, carbon dioxide and hydrogen. Kerosene is recovered from the liquid product by separation from the aqueous component, and distillation.

[0059] Example 1 - Preparation of a Dication in the Form of a Dihydroxide

[0060] The organic dication SDA-1 having the structure of Formula 1 is synthesized following a general process represented in the following schema:



[0061] In this general process, a reductive amination reaction is carried out of 1-propyl-4-piperidone (compound B) with pyrrolidine (compound A) giving rise to the corresponding diamine (compound C). The diamine is diquarternised by propyl halide to be transformed into the SDA-1 dication (compound D).

[0062] More specifically, the organic dication is prepared as follows: 30 g of pyrrolidine is dissolved in 200 mL of methanol and this solution is acidified with HCl (5N in methanol) to reach pH=7.5, continuously cooling the mixture in an external bath at 0 °C. Then, 37 g of 1-propyl-4-piperidone are added, followed by 10.5 g of $NaBH_3CN$. The resulting mixture is maintained at ambient temperature and stirred continuously for 72 hours.

[0063] To this mixture, HCl is added slowly to reach a pH less than 2, displacing the HCN by means of a continuous current of nitrogen. The resulting solution is concentrated by means of a rotavapor and a solution of KOH (25% by weight) is added until reaching a pH higher than 12. In this step, a white precipitate appears. The resulting mixture is saturated with NaCl and poured over water. Finally, the diamine, 1-

propyl-4-pyrrolidin-1-yl-piperidine, is extracted with diethyl ether and dried with anhydrous $MgSO_4$.

[0064] The quarternisation of the diamine is performed as follows: 100 g of propyl idodide are added on a solution of 43.5 g of diamine in 70 mL of MeOH. The mixture is maintained with continuous stirring at ambient temperature for 7 days, after which a white precipitate is formed. The solid is vacuum filtered. The characterisation of this solid by elemental analysis and nuclear magnetic resonance of ^1H and of ^{13}C confirms that it is the diiodide of the cation $[SDA\text{-}1]^{2+}$ illustrated in FIG. 1.

[0065] The iodide of the cation is exchanged for a hydroxide using an ion exchange resin in accordance with the following process: 44 mmol of the iodide of the cation ($[SDA\text{-}1]I_2$) are dissolved in water. 89 g of Dowex SBR resin are added to the solution obtained and this is maintained with stirring until the next day. Then, the mixture is filtered, washed with distilled water and a solution of the dihydroxide ($[SDA\text{-}1](OH)_2$) is obtained. This is evaluated with aqueous HCl using phenolphaline as an indicator, obtaining an exchange efficiency higher than 90%. The final solution contains 0.62 equivalents of hydroxide per 1000 g of solution.

[0066] <u>**Example 2 - Synthesis of ITQ-39**</u>

[0067] <u>A</u>. 0.480 g of Al isopropoxide is added over 10 g of tetraethyl orthosilicate (TEOS). Then, 39.83 g of a solution of $[SDA\text{-}1](OH)_2$ from Example 1 is added. The mixture is left evaporating while stirring until complete elimination of the ethanol from the hydrolysis of the TEOS plus the quantity of water required in reaching the final composition indicated. Finally, 1.03 g of a solution of hydrofluoric acid (48% HF by weight) is added. The composition of the gel is:

$$SiO_2{:}0.0245Al_2O_3{:}0.26[SDA\text{-}1](OH)_2{:}0.51HF{:}2.47H_2O$$

[0068] wherein SDA-1 is the dication illustrated in FIG. 1.

[0069] The gel is heated statically for 7 days in a steel autoclave with an internal Teflon cover at 150°C. The solid obtained after filtration, washing with distilled water and drying at 100°C. is ITQ-39.

[0070] <u>**B.**</u> 0.096 g of Al isopropoxide are added over 5 g of tetraethyl orthosilicate (TEOS). Then, 19.04 g of a solution of $[SDA\text{-}1](OH)_2$ from Example 1 is added. The mixture is allowed to evaporate while stirring until complete elimination of the ethanol from the hydrolysis of the TEOS plus the quantity of water required in reaching the final composition indicated. Finally, 0.5 g of a solution of hydrofluoric acid (48% HF by weight) is added. The composition of the gel is:

SiO_2:0.0098 Al_2O_3:0.25[SDA-1]$(OH)_2$:0.50 HF:2.43H_2O

[0071] where SDA-1 is the dication illustrated in FIG. 1.

[0072] The gel is statically heated for 12 days in steel autoclave with an internal Teflon cover at 135[deg.] C. The solid obtained after filtration, washing with distilled water and drying at 100[deg.] C. is ITQ-39.

[0073] C. 0.384 g of Al isopropoxide are added over 2 g of tetraethyl orthosilicate (TEOS). Then, 8.96 g of a solution of [SDA-1](OH)2 from Example 1 is added. The mixture is allowed to evaporate while stirring until complete elimination of the ethanol from the hydrolysis of the TEOS plus the quantity of water required in reaching the final composition indicated. Finally, 0.235 g of a solution of hydrofluoric acid (48% HF by weight) is added. The composition of the gel is:

SiO_2:0.098Al_2O_3:0.29[SDA-1]$(OH)_2$:0.59HF:2.4H_2O

[0074] where SDA-1 is the dication illustrated in FIG. 1.

[0075] The gel is statically heated for 14 days in steel autoclave with an internal Teflon cover at 150℃. The solid obtained after filtration, washing with distilled water and drying at 100℃. is ITQ-39.

[0076] D. 1.21 g of Al isopropoxide are added over 15.94 g of tetraethyl orthosilicate (TEOS). Then, 58.55 g of a solution of [SDA-1]$(OH)_2$ from Example 1 is added. The mixture is allowed to evaporate while stirring until complete elimination of the ethanol from the hydrolysis of the TEOS plus the quantity of water required in reaching the final composition indicated. Finally, 1.58 g of a solution of hydrofluoric acid (48% HF by weight) is added. The composition of the gel is:

SiO_2:0.039Al_2O_3:0.24[SDA-1]$(OH)_2$:0.50HF:1.62H_2O

[0077] where SDA-1 is the dication illustrated in FIG. 1.

[0078] The gel is statically heated for 11 days in steel autoclave with an internal Teflon cover at 150°C. The solid obtained after filtering, washing with distilled water and drying at 100°C. is ITQ-39 and its X-ray diffraction pattern is shown in FIG. 2. The solid after heating in air at 580°C. for six hours maintains the zeolite structure, as can be deduced from the X-ray diffraction pattern shown in FIG. 3.

[0079] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0080] The terms "a," "an," "the" and similar referents used in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[0081] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member may be referred to and claimed individually or in any combination with other members of the group or other elements found herein. It is anticipated that one or more members of a group may be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is deemed to contain the group as modified thus fulfilling the written description of all Markush groups used in the appended claims.

[0082] Certain embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations on these described embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0083] In closing, it is to be understood that the embodiments of the invention disclosed herein are illustrative of the principles of the present invention. Other modifications that may be employed are within the scope of the invention. Thus, by way of example, but not of limitation, alternative configurations of the present invention may be utilized in accordance with the teachings herein. Accordingly, the present invention is not limited to that precisely as shown and described.

CLAIMS

1. A process for the conversion of methanol to hydrocarbons within the C_5 to C_{17} range, which process comprises contact of a feed comprising methanol with a zeolite microporous crystalline material having an empirical formula:

$$x(M_{1/n}XO_2):yYO_2:SiO_2$$

wherein M is selected from H^+, an inorganic cation of charge +n, and mixtures thereof, X is at least one chemical element having an oxidation state of +3, Y is at least one second chemical element other than Si having an oxidation state +4, x has a value between 0 and about 0.3, y has a value between 0 and about 0.1, and wherein the synthesized material has an X-ray diffraction pattern having at least values of angle 2θ(degrees) and relative intensities (I/I_0) shown in Table II.

TABLE II	
2θ(degrees) ±0.5	Intensity (I/I_0)
7.8	mf
8.6	d(h)
14.8	d
15.8	d
19.4	d
21.4	m
22.1	f
23.0	mf
26.3	m
27.6	d
32.0	d
43.9	d

and recovery of hydrocarbons within the C_5 to C_{17} range from the conversion product.

2. A process according to claim 1 wherein, in the zeolite microporous crystalline material, X is selected from the group consisting of Al, Ga, B, Fe, Cr and mixtures thereof.

3. A process according to claim 1 wherein, in the zeolite microporous crystalline material, Y is selected from the group consisting of Ge, Ti, Sn, V and a mixture thereof.

4. A process according to claim 1 wherein, in the zeolite microporous crystalline material, x is less than 0.2.

5. A process according to claim 1 wherein, in the zeolite microporous crystalline material, y is less than 0.05.

6. A process according to any one of claims 1 to 5 wherein the zeolite microporous crystalline material has an X-ray diffraction pattern with at least the angle 2θ (degrees) and the relative intensities values as defined in Table 1.

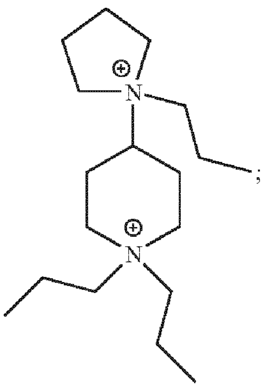


FIGURE 1

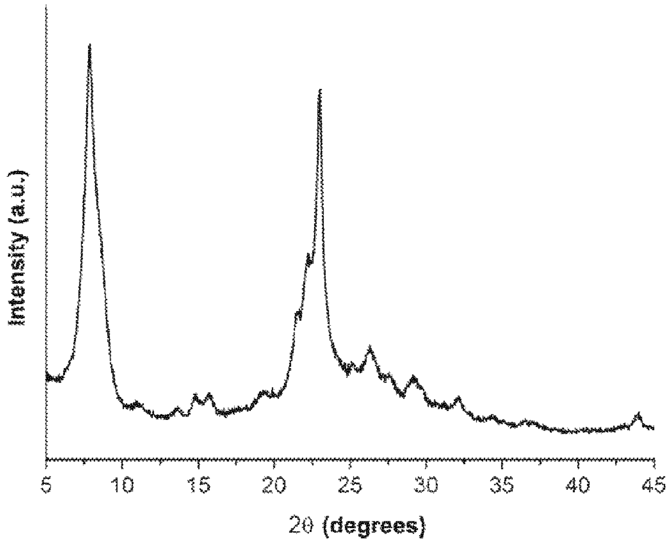


FIGURE 2

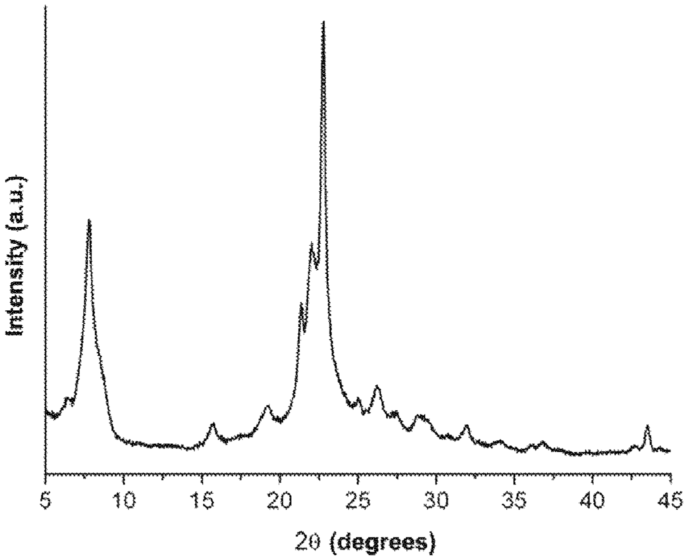


FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/060812

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C1/20 C07C11/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2 119 669 A1 (CONSEJO SUPERIOR INVESTIGACIONES CIENTIFICASES) 18 November 2009 (2009-11-18) paragraphs [0005] - [0015]; claim 16; examples 2-5 -----	1-6
Y	US 4 035 430 A (F.G. DWYER, ET AL.) 12 July 1977 (1977-07-12) cited in the application claim 1 -----	1-6
Y	US 4 138 440 A (C.D. CHANG, ET AL.) 6 February 1979 (1979-02-06) cited in the application claim 1 ----- -/--	1-6

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 30 October 2013	Date of mailing of the international search report 08/11/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer English, Russell

1

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International application No
PCT/EP2013/060812

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	D.H. OLSON, ET AL.: "CHEMICAL AND PHYSICAL PROPERTIES OF THE ZSM-5 SUBSTITUTIONAL SERIES", JOURNAL OF CATALYSIS, vol. 61, no. 2, February 1980 (1980-02), pages 390-396, XP000856253, Academic Press, Duluth, MN, US ISSN: 0021-9517, DOI: 10.1016/0021-9517(80)90386-3 figure 5 -----	
A	M. STOCKER: "Methanol-to-hydrocarbons: catalytic materials and their behaviour", MICROPOROUS AND MESOPOROUS MATERIALS, vol. 29, no. 1-2, June 1999 (1999-06), pages 3-48, XP004167548, Elsevier Science, Amsterdam, NL ISSN: 1387-1811, DOI: 10.1016/S1387-1811(98)00319-9 pages 15-33 -----	1-6

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/060812

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