(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 January 2016 (14.01.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/005472 A1

(51) International Patent Classification:
C01B 39/02 (2006.01)

(21) International Application Number:
PCT/EP2015/065641

(22) International Filing Date:
8 July 2015 (08.07.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PCT/IB2014/001490 9 July 2014 (09.07.2014) IB

(71) Applicant: **CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE** [FR/FR]; 3, rue Michel-Ange, 75016 Paris (FR).

(72) Inventors: **VALTCHEV, Valentin**; 7 rue des Aubépines, F-14610 Basly (FR). **GILSON, Jean-Pierre**; 5 rue de la Grande Mare, F-14610 Cairon (FR). **QIN, Zhengxing**; Appt. 205, 1015 Belles Portes, F-14200 Herouville Saint Clair (FR).

(74) Agents: **GOULARD, Sophie** et al.; Ipsilon Brema-loyer, Le Centralis, 63 avenue du Général Leclerc, 92340 Bourg-la-reine (FR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

[Continued on next page]

(54) Title: METHOD FOR THE PREPARATION OF SYNTHETIC CRYSTALLINE ZEOLITE MATERIALS WITH ENHANCED PORE VOLUME

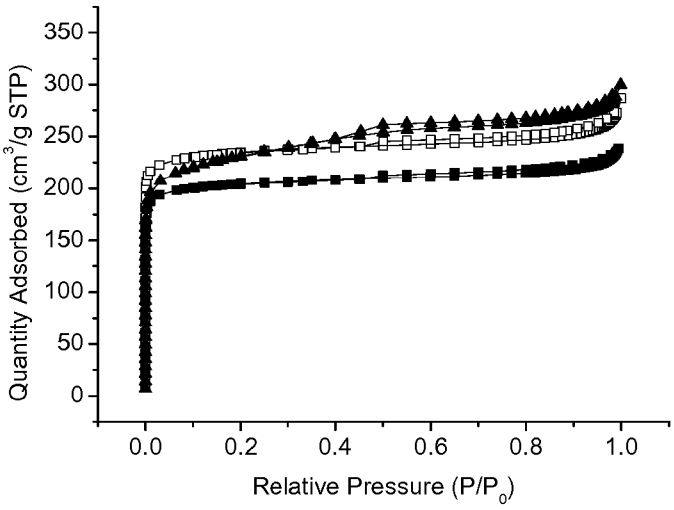

FIG.2

(57) Abstract: The present invention relates to a method for the preparation of a synthetic crystalline zeolite material with increased pore volume comprising micropores and mesopores, to said synthetic crystalline zeolite material, and to the uses of said method and said synthetic crystalline zeolite material in various applications.

WO 2016/005472 A1

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

METHOD FOR THE PREPARATION OF SYNTHETIC CRYSTALLINE ZEOLITE MATERIALS WITH ENHANCED PORE VOLUME

The present invention relates to a method for the preparation of a synthetic crystalline zeolite material, to said synthetic crystalline zeolite material, and to the uses of said method and said synthetic crystalline zeolite material in various applications.

Zeolites are hydrated metal aluminum silicates basically comprising a three-dimensional framework of SiO_4 and AlO_4 tetrahedra. The electroneutrality of each tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, for example a sodium ion. The micropore spaces (channels and cavities) are occupied by water molecules prior to dehydration. Zeolites are characterized by their high specific surface areas, high micropore volume (i.e. pores with a size of below 2 nm), and capacity to undergo cation exchange. Zeolites as microporous inorganic materials have different applications, such as catalysts (e.g. use in heterogeneous catalysis), absorbents, ion-exchangers, and membranes in many chemical and petrochemical processes (e.g. in oil refining, fine- and petro-chemistry) due to their superior properties including mechanical strength, acidity, size or shape selectivity, thermal and chemical stability, and large ion-exchange capacity. The number of established framework or structure types has increased progressively in the last 4 to 5 decades of highly active research in the field of zeolites. Currently, the number of established structure types is clearly in excess of 210. All zeolite structure types are referenced with three capital letter codes. They have different framework densities, chemical compositions, dimensional channel systems and thus, different properties. Examples of frequently encountered framework type zeolites are FAU-type zeolites which can be subdivided into FAU-X zeolite (Si/Al molar ratio = 1-1.5) and FAU-Y zeolite (Si/Al molar ratio > 1.5); MOR-type zeolites; LTL-type zeolites; and MFI-type zeolites which includes ZSM-5 zeolites. While the chemical composition, the framework density, and the type (one, two, or three dimensional) and size of the channel system of zeolites are important, a precise control of their porous network (i.e. pore architecture) can

dramatically influence their properties for example, in catalysis and adsorption. For example, in catalysis and adsorption, one of the drawbacks of zeolites is the occurrence of restricted diffusion due to their microporous network and pore blocking by coke formation, impeding the full use of their potential. Indeed, zeolite materials such as FAU-Y-type and ZSM-5-type zeolites have very small micropores (i.e. micropores having a size of less than 1.5 nm).

In order to circumvent the inherent diffusion limitations of microporous zeolite-type materials, it is known to introduce a secondary porosity consisting of larger pores, i.e. macropores and/or mesopores through the removal of a fraction of framework atoms.

As an example, van Donk *et al.* [*Catal. Rev. Sci. Eng.*, **2003**, *45*, 297-319] described the production of mesoporosity in a zeolite material by a dealumination method including steaming and acid leaching. However, the production of mesoporosity strongly depends on the chemical composition of the starting zeolite material since both mesopores size and volume decrease with the aluminum content. Thus, this method only applies to starting zeolite materials displaying a low Si/Al molar ratio of between 2.5 and 5. In addition, the obtained mesopores are irregular and are not homogeneously distributed within the zeolite material. Furthermore, since this method tends to selectively remove the aluminum framework, it changes the distribution of silicon and aluminum of the starting zeolite material and therefore, its acidic properties. Thus, an irreconcilable conflict exists between mesopores formation and acidity preservation, since the mesopores forms at the expense of framework aluminum.

Another approach described by Perez-Ramirez *et al.* [*Chem. Soc. Rev.*, **2008**, *37*, 2530-2542] to create mesoporosity is alkaline treatment, which tends to selectively remove the silicon framework and does not suffer as much from the above-mentioned dilemma between mesopore formation and acidity preservation. This approach has been widely used in recent years for the preparation of various mesoporous zeolite materials. However, low silica initial zeolite materials are excluded because starting from an initial zeolite material

having a high aluminum content leads to restricted silicon extraction, and thus minor mesopores formation. Thus, this approach is more applicable to zeolite materials displaying a high Si/Al molar ratio of between 30 and 50. In addition, like the dealumination method, the desilication approach changes substantially the chemical composition of the starting zeolite (i.e. its Si/Al initial molar ratio) and therefore, its acidic properties. Both methods, dealumination and desilication, are cation-selective approaches and are characterized by a surface reaction rather than a volume reaction. Thus, the volume of the starting zeolite material remains almost intact.

Other methods consist of using a sacrificial porogen such as carbon black, to produce mesoporosity in a zeolite material [*J. Am. Chem. Soc.*, **2000**, *122,* 7116-7117]. Then, the sacrificial porogen is eliminated after the synthesis by high temperature combustion (e.g. calcination). However, sacrificial porogens are generally not environmentally friendly (e.g. water and air pollution arising from their thermal decomposition), non-recyclable and expensive. Moreover, the high temperature combustion can lead to an irreversible aggregation of the nanocrystals of the zeolite material into larger solid particles, thus diminishing their expected advantages. Moreover, very small crystalline yields are obtained (i.e. yield of about 10%). In addition, partial distortion (collapse) of the crystalline structure of zeolite materials under calcination is observed. Finally, these methods can't be applied on a large scale.

Qin *et al.* [*Chem. Mater.*, **2013**, *25*, 2759-2766] have recently described a process for preparing MFI-type zeolite materials (e.g. ZSM-5 zeolites) displaying a secondary porosity consisting of macropores and/or large mesopores, by using buffering aqueous hydrofluoric acid (HF) solutions with ammonium fluoride (NH_4F) (i.e. HF-NH_4F solutions). However, the use of HF-NH_4F solutions does not lead to a substantial increase in the total pore volume since the micropore volume and the secondary pore volume (mesopore volume and/or macropore volume) remain almost constant, thus leading to zeolite materials with catalytic performances which are not optimized. Moreover, the kinetics of the HF-NH_4F is very fast, which makes a

precise control of the treatment almost impossible. In addition, aqueous HF solution is a contact-poison involving tissue death, thus preventing its use on a large scale without providing expensive equipment and downstream processing of the effluents.

By contrast, the use of low concentrated aqueous or non-aqueous NH_4F solutions (e.g. solutions having a NH_4F mass concentration lower than 5-10%) or the use of low amounts of NH_4F with respect to the mass of starting zeolite material (e.g. use of less than 0.5 g of NH_4F for 1 g of starting zeolite material) for the fluorination of zeolite materials has been extensively described. As an example, Le Van Mao *et al.* [*Appl*. Cat. *A*: General, **1999**, *185*, 41-52] described a process comprising: a step of fluorination of a zeolite material (H-ZSM-5) by impregnating said zeolite material with an aqueous solution of NH_4F, and a step of calcination of the resulting solid phase at elevated temperatures (e.g. 300 to 500°C). This process leads to the replacement of the oxygen atoms at the surface of the zeolite material with F atoms (formation of surface Si-F groups instead of surface Si-OH groups), thus tuning the acidic properties of the starting zeolite material and its hydrophobic properties. Although the resulting zeolite material shows higher catalytic activity, this process requires a high temperature activation step (i.e. calcination step) after the fluorination step. Such a calcination step can lead to the decomposition of NH_4F and the following attack of the zeolite material crystalline structure by the chemisorbed H^+F^- ion pairs. In addition, it is clearly shown that when the initial NH_4F loading is low, there is no significant change in zeolite framework, whereas by increasing it, a significant loss of micropore volume is observed which is due to the amorphisation of zeolite framework.

Consequently, an alternative method of synthesis that provides a synthetic crystalline zeolite material with increased total pore volume but without the above disadvantages is highly desirable, in particular for applications such as adsorption and heterogeneous phase catalysis.

More particularly, the aim of the present invention is to provide a preparation method which either increases the micropore volume or introduces

a secondary porosity comprising mesopores while maintaining or increasing the starting (i.e. initial) micropore volume, thus expanding the channels/cavities dimensions in any framework type of crystalline zeolite material, without any substantial change in its chemical composition (e.g. Si/Al molar ratio), its surface chemical composition, its acidic properties, and its hydrophilic/hydrophobic properties.

A first object of the present invention is a method for the preparation of a synthetic crystalline zeolite material comprising micropores and eventually mesopores, said synthetic crystalline zeolite material having a silicon to aluminum molar ratio Si/Al ≥ 1 and, wherein said method comprises at least the following steps:

1) a step of contacting a NH_4F solution with a starting crystalline zeolite material at a temperature ranging from about 0°C to about 100°C, said NH_4F solution having a NH_4F mass concentration of at least about 15 wt% and said starting crystalline zeolite material being essentially microporous and having a silicon to aluminum molar ratio Si/Al ≥ 1;

2) a washing step;

3) a drying step at a temperature ranging from about 25°C to about 120°C, for about 1h to about 24h, to recover said synthetic crystalline zeolite material.

The method of the present invention is neither Si nor Al selective, and thus etches the zeolite material without altering its framework composition. In addition, said method is very simple and safe, does not require any specific equipment and leads to synthetic crystalline zeolite materials having improved diffusion and/or controlled acidity, and therefore, better overall catalytic performances. In addition, the method does not consume much energy in contrast to high temperature steaming processes presently used in the industry (i.e. steaming with 100% H_2O vapors at a temperature of 700-850°C to obtain the zeolite Y commercialized under the brand name "Ultra Stable Zeolite Y" or USY), and generates less toxic waste.

Thanks to the use of concentrated NH_4F aqueous or non-aqueous solutions as a mild etchant, the chemical etching of the zeolite material framework is performed while increasing its total pore volume by either increasing its micropore volume without generating an additional mesoporosity, or creating uniform mesoporosity while maintaining or increasing its microporosity and thus, creating a uniform connection between the native micropores and the newly created mesopores. Thus, the method improves access to the micropore volume of the starting crystalline zeolite material.

Indeed, contrary to the previously described HF-NH_4F solution which only dissolves the defect parts of the zeolite material, the NH_4F solution used in the method of the present invention slowly and uniformly attacks the entire structure of the zeolite material leading to the increase of the pore volume. The dissolution process does not start from the surface of the zeolite material but is based on the saturation of the zeolite micropores with the concentrated NH_4F solution that regularly dissolves spaced zeolite material walls in the volume of the crystals, thus first expanding the micropore volume, and then creating small mesocavities or mesopores. The process can be controlled by a number of parameters including NH_4F concentration, zeolite/NH_4F ratio, time and temperature of treatment.

Zeolite materials obtained by the method of the present invention combine the intrinsic zeolite materials characteristics with mesopore size cavities distributed uniformly in said zeolite materials, leading to substantial improvement of their current commercial applications (e.g. fluid catalytic cracking (FCC), hydrocracking, catalytic dewaxing, olefins processing, aromatics production and processing, etc…). In addition, they can be prepared on a large scale.

Depending on the type of starting crystalline zeolite material and the reaction conditions, the method of the present invention increases the micropore volume (i.e. the size and/or the number of the micropores increases), or adds a mesoporous network to the starting crystalline zeolite material while maintaining or increasing the micropore volume. Thus, the total

pore volume is increased through the non-selective removal of a fraction of framework atoms.

Within the meaning of the present invention and unless noted otherwise, the term "micropores" is understood to mean pores having a mean dimension of less than 2 nm.

Within the meaning of the present invention and unless noted otherwise, the term "mesopores" is understood to mean pores having a mean dimension of about 2 to about 50 nm.

Within the meaning of the present invention and unless noted otherwise, the term "macropores" is understood to mean pores having a mean dimension of more than 50 nm.

Within the meaning of the present invention, the term "a zeolite material essentially microporous" is understood to mean a zeolite material in which the micropore volume represents more than about 70%, preferably more than about 80%, and more preferably more than about 90% of the total pore volume.

Within the meaning of the present invention and unless noted otherwise, the term "crystalline starting zeolite material" is understood to mean a starting zeolite material having a powder X-ray diffraction pattern approved by the Structure Commission of the International Zeolite Association (IZA-SC)(http://www.iza-structure.org/databases/).

Within the meaning of the present invention and unless noted otherwise, the term "crystalline synthetic zeolite material" is understood to mean a synthetic zeolite material having a powder X-ray diffraction pattern similar to the starting zeolite material used in the method of the invention. In other words, the level of crystallinity does not change more than 50%, preferably does not change more than 30%, and more preferably does not change more than 10%, by measuring the total areas under all the peaks in the XRD diffraction pattern.

According to the method of the invention, step 1) aims at contacting a starting crystalline zeolite material with an NH_4F solution having a NH_4F mass

concentration of at least about 15 wt%. Thus, the starting crystalline zeolite material used in step 1) is a dry starting crystalline zeolite material. In other words, step 1) is carried out on a dry starting crystalline zeolite material. The starting crystalline zeolite material is not mixed with an aqueous or organic solvent to form a suspension or a solution of said starting crystalline zeolite material before the contacting step 1). The starting crystalline zeolite material used in step 1) is in the form of a dry compound. The starting crystalline zeolite material of step 1) is therefore not used in the form of a suspension or a solution.

A NH_4F mass concentration of at least about 15 wt% corresponds to a NH_4F molar concentration of at least about 4.0 mol/l.

It is noted that since the starting crystalline zeolite material is used as a dry compound in step 1), the contacting step 1) leads to a resulting mixture composed of the starting crystalline zeolite material impregnated by the NH_4F solution or immersed in the NH_4F solution.

The NH_4F solution is preferably a NH_4F aqueous solution.

The NH_4F mass concentration in the solution is at least about 15 wt% at the beginning of step 1) and progressively decreases with time due to the reaction between NH_4F and the starting crystalline zeolite material.

In a preferred embodiment, the starting crystalline zeolite material of step 1) does not comprise mesopores.

Said starting crystalline zeolite material has preferably a mesopore volume of less than about 0.08 cm^3/g, and more preferably of less than about 0.04 cm^3/g.

The starting crystalline zeolite material of step 1) can have a Si/Al equal or greater than about 1.0, preferably equal or greater than about 1.6, more preferably of between about 1.6 and about 1000, and more preferably of between about 1.6 and about 100.

The starting crystalline zeolite material of step 1) can further comprise monovalent or divalent cations M, preferably selected from Na^+, K^+, Mg^{2+},

Ca^{2+}, NH_4^+ and H^+. The cations M compensate the negative charges of the starting crystalline zeolite material framework.

NH_4^+ and H^+ cations are preferred since they are inert with regards to the NH_4F species during the contacting step 1).

The starting crystalline zeolite material of step 1) can be chosen from FAU-type zeolite materials (FAU-Y), MFI-type zeolite materials (ZSM-5 or silicalite-1), MOR-type zeolite materials, LTL-type zeolite materials, and any other type of zeolite materials which contains silicon and aluminum in its framework such as Beta zeolite materials.

FAU-Y, ZSM-5, MOR-type, LTL-type, and Beta zeolite materials are preferred.

FAU-Y, LTL-type and MOR-type zeolite materials are more preferred.

Step 1) can be performed in a closed or open vessel. Open vessel is preferred so as to evacuate safely the ammonia released during the method.

Step 1) is preferably performed at a temperature ranging from about 0°C to about 60°C, more preferably at a temperature ranging from about 0°C to about 50°C, more preferably at a temperature ranging from about 20°C to about 60°C, and more preferably at a temperature ranging from about 20°C to about 50°C.

Step 1) can be carried out for a time ranging from about 5 to about 180 minutes, preferably from about 15 to about 120 minutes, and more preferably from about 15 to about 60 minutes.

During step 1), the NH_4 solution incorporates into the pores of the starting crystalline zeolite material.

Step 1) can be conducted thanks to an ultrasonic bath. Ultrasounds substantially accelerate the kinetics of the reaction and can therefore reduce the time of contacting the crystalline zeolite material with the NH_4F solution to several minutes.

The NH_4F solution used in step 1) can be previously prepared by dissolving solid NH_4F in a solvent according to a step 1_0).

The pH of the NH_4F solution prepared before step 1) (i.e. after step 1_0)) is preferably about 7.

The solvent can be selected from water, methanol, ethanol, acetone, and mixtures thereof. Water is preferred so as to form a NH_4F aqueous solution.

During the contacting step 1), the pH of the resulting mixture is about 8.0 or greater than about 8.0.

The NH_4F solution used in step 1) has preferably a NH_4F mass concentration of at least about 20 wt%.

In one preferred embodiment, the NH_4F solution has a NH_4F mass concentration from about 15 wt% to about 50 wt%, and preferably from about 20 wt% to about 40 wt%.

In one preferred embodiment, the mass ratio of solid NH_4F/starting crystalline zeolite material used in step 1) ranges from about 0.5 to about 25, preferably from about 1 to about 10, and more preferably from about 1.2 to 10.

Since the starting crystalline zeolite material is used as a dry compound, step 1) is preferably carried out by contacting the starting crystalline zeolite material with the whole NH_4F solution in only one go and/or rapidly. Thus, the starting crystalline zeolite material and the NH_4F solution are mixed instantly during step 1). In other words, step 1) is not carried out by adding dropwise and/or slowly the NH_4F solution on the starting crystalline zeolite material. This only one go and/or rapid contacting step 1) favors the saturation of the starting crystalline zeolite pores with concentrated NH_4F solution.

More particularly, step 1) can be performed by:

- immersing the starting crystalline zeolite material (in the form of a dry compound) in the NH_4F solution to form a heterogeneous mixture (i.e. immersed mixture), and then by stirring said heterogeneous mixture (i.e. immersed mixture); or

- pouring the NH_4F solution on the starting crystalline zeolite material (in the form of a dry compound) so as to saturate its micropore volume, and then by filtrating it so as to remove the excess of NH_4F solution and to form an impregnated solid.

Thus, the resulting mixture formed in step 1) can be either a heterogeneous mixture (i.e. immersed mixture) or an impregnated solid.

If step 1) is performed by immersing the starting crystalline zeolite material in the NH_4F solution to form a heterogeneous mixture, and then by stirring said heterogeneous mixture, the starting crystalline zeolite material has a total pore volume V_m and the NH_4F solution has a volume V_{sol}, with V_{sol} being preferably much larger than V_m. As an example, $V_{sol}/V_m \geq 5$, and preferably $V_{sol}/V_m \geq 10$.

Then, after the contacting step 1), the method comprises before the washing step 2) a step of filtrating the heterogeneous mixture to obtain a solid.

If step 1) is performed by pouring the NH_4F solution on the starting crystalline zeolite material so as to saturate its micropore volume, and then by filtrating it so as to remove the excess of NH_4F solution and to form an impregnated solid, the crystalline zeolite material has a volume $V_{m'}$ and the NH_4F solution has a volume $V_{sol'}$, with $V_{sol'}$ being preferably approximately equal to $V_{m'}$.

The immersing method is preferred.

The washing step 2) is then performed either on the solid obtained according to the immersing method, or on the impregnated solid obtained according to the pouring method.

The washing step 2) can be carried out several times so as to remove all the fluoride species from the synthetic crystalline zeolite material.

The washing step 2) is preferably performed four or five times, in particular with water.

Step 3) can be performed at a temperature ranging from about 60°C to about 100°C, preferably in an oven with air flow.

After step 2) or step 3), the synthetic crystalline zeolite material prepared according to the method of the present invention already displays the desired microporosity and eventually desired mesoporosity.

Thus, the method of the present invention preferably does not comprise any step so as to increase the mesoporosity of the synthetic crystalline zeolite material obtained in step 2) or in step 3).

As an example, the method of the invention does not involve the use of one or more sacrificial templates (e.g. hydrocarbons or carbon particles) which are conventionally incorporated in a zeolite material during the synthesis and then burned out (i.e. calcined) to leave behind and create mesopores.

Once the synthetic crystalline zeolite material is recovered according to step 3), it may be ion exchanged according to a step 4).

Typical ion exchange techniques involve contacting the synthetic crystalline zeolite material obtained in step 3) with a solution containing a salt of the desired replacing cation or cations. As an example, alkali metal cations can be removed and replaced with a proton (H^+), ammonium (NH_4^+), or any desired metal or organic cation.

When the synthetic crystalline zeolite material is in the NH_4^+-form after step 3) or after the ion-exchange step 4), it can be calcined in air or inert gas according to a step 5), so as to remove ammonia and produce the synthetic crystalline zeolite material in the H^+-form (acidic form).

This acidic form is required when the material is used as a catalyst in acid-catalyzed reactions such as most of the oil refining and petrochemical reactions.

Step 5) can be performed at temperatures ranging from about 380°C to about 550°C, for periods of time ranging from about 1 to about 5 hours, to produce a synthetic crystalline zeolite material in acidic form.

After, this calcination step 5), the synthetic crystalline zeolite material can be directly used as a catalyst.

It is noted that the acidic form is not required when the material is used as a catalyst in base-catalyzed reactions such as side chain alkylation reactions of aromatic hydrocarbons.

According to a preferred embodiment of the invention, the method does not comprise any calcination step, except for removing ammonia when the synthetic crystalline zeolite material obtained in step 3) or 4) is in the NH_4^+-form (i.e. synthetic crystalline zeolite material comprising NH_4^+ cations).

Within the meaning of the present invention, the term "calcination" is understood to mean a heat treatment at a temperature going from 380°C to 700°C, during 1 to 10 hours, under an air, oxygen or inert (N_2) atmosphere.

The synthetic crystalline zeolite material prepared according to the method of the present invention can be functionalized according to a step 6) with active (metal or organic) compounds thanks to its newly created mesopores, thus allowing for the catalytic processing of bulky molecules that cannot be processed in untreated zeolites. Thus, the method can further comprise a step 6) of functionalizing said synthetic crystalline zeolite material with at least one active (metal or organic) compound.

Said active (metal, inorganic, or organic) compounds can be chosen from metals, metal oxides, metal sulphides, metal carbides, metal phosphides, large organic and organometallic molecules, zeolites different from said synthetic crystalline zeolite material, and re-crystallized synthetic crystalline zeolite material. The functionnalization opens the route to encapsulation of active species in the synthetic zeolite material crystal volume.

Said step 6) can be performed after step 3), step 4) or step 5).

The method of the invention does not comprise before the contacting step 1), any step of mixing the starting crystalline zeolite material with an aqueous or organic solvent to form a suspension or a solution of said starting crystalline zeolite material, since the starting crystalline zeolite material used in step 1) is in the form of a dry compound.

The synthetic crystalline zeolite material obtained by the method of the present invention can comprise micropores having a mean dimension of more than about 1 nm, preferably of more than about 1.5 nm.

The synthetic crystalline zeolite material obtained by the method of the present invention can further comprise mesopores having a mean dimension of about 2 to 25 nm, preferably of about 2 to 15 nm, and more preferably of about 2 to 6 nm.

The size of the mesopores and/or the micropores can be controlled by the NH_4F mass concentration of the NH_4F solution, the temperature and the time of the contacting step 1).

The synthetic crystalline zeolite material obtained by the method of the present invention preferably does not comprise macropores.

The method of the present invention can lead to a synthetic crystalline zeolite material having a Si/Al molar ratio equal or greater than 1.0, preferably more than 1.6, more preferably of between about 1.6 and 1000, and more preferably of between about 1.6 and 100.

The synthetic crystalline zeolite material obtained can be chosen from FAU-type zeolite materials (FAU-Y), MFI-type zeolite materials (ZSM-5 or silicalite-1), MOR-type zeolite materials, LTL-type zeolite materials, and any other type of zeolite materials which contains silicon and aluminum in its framework such as Beta zeolite materials.

FAU-Y, ZSM-5, MOR-type, LTL-type, and Beta zeolite materials are preferred.

FAU-Y, LTL-type and MOR-type zeolite materials are more preferred.

In a first embodiment, the synthetic crystalline zeolite material obtained by the method of the invention is a FAU-type zeolite material, and preferably a Y-type zeolite having a Si/Al molar ratio ranging from 2.5 to 30.

In a second embodiment, the synthetic crystalline zeolite material obtained by the method of the invention is a MFI-type zeolite material, and

preferably a ZSM-5-type zeolite, having a Si/Al molar ratio ranging from 15 to 100.

The method of the present invention does not substantially change the Si/Al molar ratio.

Within the meaning of the present invention, the term "the method of the present invention does not substantially change the Si/Al molar ratio means that the Si/Al molar ratio of the starting crystalline zeolite material cannot vary during the method of the present invention of more than about 2, and preferably of more than about 1, and more preferably of more than about 0.1.

The synthetic crystalline zeolite material obtained by the method of the present invention can further comprise monovalent or divalent cations M', preferably selected from Na^+, K^+, Mg^{2+}, Ca^{2+}, H^+, and NH_4^+.

The method of the present invention can lead to an increase of the total pore volume of at least about 15%, preferably of at least about 20%, preferably of at least about 30%, and more preferably of at least about 50%, with respect to the total pore volume of the starting crystalline zeolite material.

The method of the present invention can lead to an increase of the specific surface area of at least about 5%, preferably of at least about 7%, and more preferably of at least about 15%, with respect to the specific surface area of the starting crystalline zeolite material.

The method of the present invention can lead to an increase of the micropore volume of at least about 5% and preferably of at least about 10%, with respect to the micropore volume of the starting crystalline zeolite material.

The method of the present invention can lead to an increase of the mesopore volume of at least about 50%, preferably of at least about 80%, and more preferably of at least about 100%, with respect to the mesopore volume of the starting crystalline zeolite material, while at least maintaining the micropore volume of the starting crystalline zeolite material.

The synthetic crystalline zeolite material obtained by the method of the present invention can have a mesopore volume of at least about 0.05 cm^3/g, preferably of at least about 0.08 cm^3/g, preferably of at least about 0.15 cm^3/g, and more preferably of at least about 0.2 cm^3/g.

The synthetic crystalline zeolite material obtained by the method of the present invention can have a specific surface area of at least about 350 m^2/g, and preferably ranging from about 400 m^2/g to about 800 cm^2/g.

The synthetic crystalline zeolite material obtained by the method of the present invention can have a micropore volume of at least about 0.1 cm^3/g, preferably of at least about 0.15 cm^3/g, and more preferably of at least about 0.2 cm^3/g.

A second object of the present invention is a synthetic crystalline zeolite material prepared according to the method of the present invention, said synthetic crystalline zeolite material comprising micropores and eventually mesopores, and having a silicon to aluminum molar ratio Si/Al ≥ 1.

The synthetic crystalline zeolite material is as defined in the first object of the present invention.

The synthetic crystalline zeolite material prepared according to the method of the present invention has intra-particles porosity. Thus, the synthetic crystalline zeolite material differs from the zeolites of the prior art with textural meso-/macroporosity which is a consequence of agglomeration of single zeolite particles.

The enhancement of zeolite porosity in the method of the present invention is achieved by internal-surface dissolution through 1) saturation and 2) dissolution of zeolite pores with concentrated NH_4F solution, whereas in the methods of the prior art, it is achieved by outer-surface dissolution of zeolite crystals.

Indeed, the method of the present invention is based on the etching of zeolite crystals. Thus, the enhanced pore volume is namely due to the changes in the volume of the single crystal. The method of the present invention does not include the formation of inter-particles porosity since the main contribution

comes from the dissolution of individual zeolite particles so as to create intra-particles porosity. Intra-particles porosity can be observed by transmission electron microscopy and is characterized by the presence of pores with size larger than 2 nm in the volume of the single zeolite crystals. On the contrary, inter-particles porosity is characterized by the presence of single crystals aggregation. Indeed, the space (or the voids) among the obtained aggregated single zeolite crystals is taken as another type of mesopore or macropores depending on the size of the voids and is called inter-particles meso-/macroporosity.

A third object of the present invention is the use of the method of the present invention so as to increase the total pore volume of a crystalline zeolite material which is essentially microporous.

The total pore volume is increased by either an increase of the micropore volume only or an increase of the mesopore volume while maintaining or increasing the micropore volume.

A fourth object of the present invention is the use of the method of the present invention so as to introduce micropores having a mean dimension of more than about 1 nm, and preferably of more than about 1.5 nm and/or to introduce mesopores having a mean dimension of about 2 to about 25 nm, and preferably of about 2 to about 15 nm while maintaining or increasing the micropore volume, in a crystalline zeolite material which is essentially microporous.

A fifth object of the present invention is the use of the synthetic crystalline zeolite material prepared according to the method of the present invention, as a catalyst or adsorbent in gas-solid and liquid-solid reactions (e.g. heterogeneous catalytic reactions), as seed crystals for zeolite material synthesis, and for the preparation of membranes or layers (films).

In a preferred embodiment, the synthetic crystalline zeolite material prepared according to the method of the present invention is used as a catalyst to transform bulky molecules, for example in oil refining and petrochemistry (e.g. fluid catalytic cracking, hydrocracking, etc...).

Within the meaning of the present invention, the term "bulky molecule" is understood to mean an organic molecule having a kinetic diameter of more than 0.9 nm, such as 1, 3, 5-tri-*iso*-propylbenzene (TIPB), and preferably of more than 0.95 nm.

Examples of heterogeneous catalytic reactions are hydrocarbon conversion reactions which include isomerization of C_5 and C_6 compounds to increase the octane of gasoline, hydrocracking, fluid catalytic cracking, iso-butane alkylation for fuels, aromatics processing, olefins oligomerization, biomass (oxygenated hydrocarbons) upgrading.

Indeed, the large presence of these uniformly distributed mesopores in the volume of the synthetic crystalline zeolite material can serve as superior transfer stations between inner part and outside surface of the zeolite material, and between different microporous zones of the zeolite material volume. The system of mesopores can also serve as a trap for the bulky compounds and prevent from the blocking of pores.

A sixth object of the present invention is the use of the synthetic crystalline zeolite material prepared according to the method of the present invention, to incorporate active (metal, inorganic, or organic) compounds thanks to its newly created micro- and/or mesoporous network.

The obtained synthetic crystalline zeolite material (i.e. the functionalized synthetic crystalline zeolite material) can then be used as a catalyst or adsorbent in gas-solid and liquid-solid reactions (e.g. heterogeneous catalytic reactions), as seed crystals for zeolite material synthesis, and for the preparation of membranes or layers (films).

The synthetic crystalline zeolite material prepared according to the method of the present invention can also be used for medical, pharmaceutical and cosmetic purposes, environmental drug delivery, medical imaging, and other biomedical applications, as well as for chemical sensing and optical devices.

The synthetic crystalline zeolite material prepared according to the method of the present invention can also be incorporated in matrices such as

SiO_2, Al_2O_3, or amorphous silica-alumina matrices, so as to be shaped by known techniques such as spray drying, oil-drop, extrusion, pelletizing or tableting.

EXAMPLES

The starting materials used in the examples which follow, are listed below:

- solid NH_4F: ≥98.0% purity, Sigma Aldrich;

- Commercial zeolite Y produced by UOP under the commercial brand LZY-62 having a Si/Al molar ratio of 2.6 and a size of crystals of 0.5 to 1 µm was used as a starting crystalline zeolite material;

- Commercial zeolite ZSM-5 produced by Süd Chemie (Clariant) under the commercial brand MFI-55 (NH_4-form) having a Si/Al molar ratio of 21.3 and a size of crystals of 5 µm was used as a starting crystalline zeolite material;

- Commercial zeolite MOR produced by Zeolyst under the commercial brand CBV 10A having a Si/Al molar ratio of 6.7 and a size of crystals of 0.1~0.2 µm was used as a starting crystalline zeolite material;

- Commercial zeolite LTL produced by Zeolyst under the commercial brand Zeolite L (14/10436) having a Si/Al molar ratio of 3.3 and a size of crystals of 0.2~0.5 µm was used as a starting crystalline zeolite material.

Unless noted otherwise, these starting materials were used as received from the manufacturers, without additional purification.

The various zeolites obtained in the examples were characterized over various scales of sizes.

Powder X-ray diffraction (XRD) analysis:

Powder samples of the synthetic crystalline zeolite materials obtained after step 3) and starting crystalline zeolite materials were analyzed using a *PANalytical* X'Pert Pro diffractometer with CuKα monochromatized radiation (λ = 1.5418 Å). The samples were scanned in the range 5-50° 2θ with a step size of 0.02°.

N_2 sorption analysis:

Nitrogen adsorption/desorption isotherms were measured using Micrometrics ASAP 2020 volumetric adsorption analyzer. Samples of the synthetic crystalline zeolite materials obtained after step 3) and starting crystalline zeolite materials were degassed at 573 K under vacuum overnight prior to the measurement. The micropore volume was estimated by Nonlocal Density Functional Theory (NLDFT). The volume adsorbed at P/P_0 = 0.99 represents the total pore volume. The mesopore volume was estimated by the difference between the total pore volume and the micropore volume. The micropore and mesopore size distributions of solids were estimated by NLDFT and Barret-Joyner-Halenda (BJH) methods, respectively. The specific surface area was estimated by the Brunauer-Emmett-Teller (BET) method.

Chemical analysis:

The chemical compositions (e.g. Si/Al molar ratios) of the synthetic crystalline zeolite materials obtained after step 3) were determined by inductively coupled plasma (ICP) optical emission spectroscopy using a Varian ICP-OES 720-ES.

Transmission electron microscopy (TEM):

Ethanol suspensions of the synthetic crystalline zeolite materials obtained after step 3) were sonicated for 15 min and then 2-3 drops of said suspensions were dried on carbon-film-covered 300-mesh copper electron microscope grids. The crystal size, morphology and crystallinity of solids were determined by a transmission electron microscopy (TEM) using a JEOL100CX microscope operating at 200 kV.

Ammonium exchange and thermal treatment:

When the starting crystalline zeolite materials or the synthetic crystalline zeolite materials obtained after step 3) are not in the NH_4^+- or H^+-form, they were ion-exchanged with a solution of 0.2M of NH_4Cl (1 h, 25°C). The ion-exchange procedure was repeated 2 times. After the third ion exchange step, the crystalline zeolite materials were washed with distilled

water, and calcined (e.g. at 550°C) for elimination of the NH_3 and obtaining the crystalline zeolite materials in acidic form.

Scanning electron microscopy (SEM):

The surface features, morphology and size of zeolite materials were determined by a MIRA-LMH (TESCAN) scanning electron microscope (SEM) equipped with a field emission gun. The accelerating voltage was 30 kV. All samples prior the SEM characterization were covered with a Pt-Pd conductive layer.

Example 1

Preparation of synthetic crystalline zeolite materials Y_1 and Y_2 according to the method of the invention and characterization thereof

Example 1-1

Step 1):

A NH_4F solution was prepared by mixing 10 g of solid NH_4F with 30 g of distilled water. The NH_4F solution had a mass concentration of 25 wt%. Then, 7.5 g of starting crystalline zeolite material Y was immersed into the NH_4F solution described above to form a heterogeneous mixture. Then, the heterogeneous mixture was treated at 0°C for 30 minutes under stirring and ultrasounds, and was filtrated to obtain a solid.

Steps 2) and 3):

Then, the obtained solid was thoroughly washed with distilled water and dried at 100°C.

A synthetic crystalline zeolite material Y_1 with a Si/Al molar ratio of 2.6 was obtained.

The yield was 90%.

Example 1-2

The same method as the one described in example 1-1 was used except that in step 1), the treatment was performed at 0°C for 60 minutes.

A synthetic crystalline zeolite material Y_2 with a Si/Al molar ratio of 2.7 was obtained.

The yield was 85%.

The Si/Al molar ratio and porosity properties [the specific surface area (S_{BET}), the micropore volume (V_{micro}), the mesopore volume (V_{meso}), and the total pore volume (V_{total})] of the starting crystalline zeolite material Y and of the prepared synthetic crystalline zeolite materials Y_1 and Y_2 are given in Table 1 below:

The specific surface area and porosity properties of the crystalline zeolite materials were obtained by N_2 sorption measurements.

Table 1

crystalline zeolite material	Si/Al molar ratio	S_{BET} ($m^2.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)	V_{total} ($cm^3.g^{-1}$)
Y	2.6	652	0.29	0.07	0.36
Y_1	2.6	750	0.35	0.07	0.42
Y_2	2.7	755	0.31	0.13	0.44

Hence, Table 1 clearly shows that the method of the present invention leads to the increase of the micropore volume and optionally to the introduction of a secondary porosity, and therefore allows in both examples 1-1 and 1-2 the increase of the total pore volume of the starting crystalline zeolite material. Indeed, in Y_1, it is only observed an increase of the micropore volume, whereas in Y_2, both the micropore volume and the mesopore volume are increased. The chemical analyses revealed that the Si/Al ratio only slightly increased from 2.6 to 2.7 in example 1-2.

As it can be also seen in Table 1, the method of the present invention allows under certain conditions to increase the micropore volume without changing the mesopore volume of material (cf. synthetic crystalline zeolite

material Y_1). The formation of mesopores (2-10 nm) is only observed in synthetic crystalline zeolite materials Y_2.

In addition, Figure 1 represents the Powder X-ray diffraction (XRD) of the starting crystalline zeolite material Y (figure 1a), the synthetic crystalline zeolite material Y_1 (figure 1b) and the synthetic crystalline zeolite material Y_2 (figure 1c), and shows the intensity (in arbitrary units, a.u.) as a function of two theta (in degree). Figure 1 reveals high crystallinity and no indications of amorphous phase formation after the contacting step 1).

Figure 2 represents the nitrogen adsorption/desorption isotherms of the starting crystalline zeolite material Y (figure 2, solid squares), the synthetic crystalline zeolite material Y_1 (figure 2, open squares) and the synthetic crystalline zeolite material Y_2 (figure 2, solid triangles), and shows the volume adsorbed (in $cm^3.g^{-1}$) as a function of the relative pressure P/P_0 (in units).

Nitrogen adsorption characterizes the porosity of the crystalline zeolite materials. According to figure 2, it can be concluded that the prepared synthetic crystalline zeolite material Y_2 exhibits a hysteresis loop related with the formation mesopores. After the pronounced uptake at low relative pressure, crystalline zeolite materials Y and Y_1 exhibit almost horizontal adsorption and desorption branches that shows no presence of mesopores. The synthetic crystalline zeolite material Y_1 shows higher uptake at low relative pressure which is characteristic of microporous zeolite type materials. This uptake is more intense in respect to the starting crystalline zeolite material Y revealing larger micropore volume of the synthetic crystalline zeolite material Y_1.

Figure 3 represents the pore size distribution of the starting crystalline zeolite material Y (figure 3, solid squares), the synthetic crystalline zeolite material Y_1 (figure 3, open squares) and the synthetic crystalline zeolite material Y_2 (figure 3, solid triangles), and shows the pore volume calculated as dV/dlogD (in $cm^3.g^{-1}$) as a function of the pore diameter (in nm).

Figure 3 clearly reflects the production of additional mesoporosity. There is a right shift of the pore size distributions indicating that the synthetic crystalline zeolite material Y_2 comprises mesopores with a diameter ranging from 2 to 10 nm, and preferably from 2 to 4 nm.

Figure 4 shows representative electron micrograph of thin slices of the synthetic crystalline zeolite material Y_2 (figure 4) extracted from the electron tomography study. The set of experimental data obtained with complementary methods (TEM, TEM tomography, nitrogen adsorption, etc...) unambiguously shows that the mesopores are similar in size in the synthetic crystalline zeolite material, and they are uniformly distributed throughout the volume of the synthetic crystalline zeolite materials. In addition, figure 4 clearly shows intra-particles porosity induced by internal-surface dissolution.

Example 2

Catalytic activity of synthetic crystalline zeolite materials Y_1 and Y_2

A test was performed to evaluate the catalytic activity of the synthetic crystalline zeolite materials prepared according to the method of the invention.

The synthetic crystalline zeolite materials Y_1 and Y_2 prepared in example 1 and the starting crystalline zeolite material Y were further ion-exchanged with ammonium cations (step 4) and heated at 550°C to eliminate NH_3 (step 5) and obtain respectively the synthetic crystalline zeolite materials in acidic form Y'_1 and Y'_2 and the starting crystalline zeolite material in acidic form Y' (also called synthetic and starting crystalline zeolite catalysts).

Then, the conversion of a bulky molecule 1,3,5-triisopropylbenzene (TIPB) in the presence of crystalline zeolite catalyst Y'_1, Y'_2 or Y' was studied. The tests were performed under identical conditions [P_{Tot} = 101325 Pa, P_{TIPB} = 192 Pa, and weight/feed flow rate ($W/F°_{TIPB}$) = 1.27 x 10^3 g.min.mol^{-1}] in a downflow fixed bed gas phase reactor at a temperature of 225°C.

Figure 5 represents the conversion of TIPB (in %) as a function of time on stream (in minutes) for the synthetic crystalline zeolite catalyst Y'_1 (figure 5, open squares), the synthetic crystalline zeolite catalyst Y'_2 (figure 5,

solid triangles) and the starting crystalline zeolite catalyst Y' (figure 5, solid squares).

The kinetic diameter of TIPB is 0.95 nm, which is larger than the pore opening of the commercial crystalline zeolite material Y (i.e. 0.74 nm). The substantially higher activity of the synthetic crystalline zeolite catalysts Y'_1 and Y'_2 in comparison to the starting crystalline zeolite catalyst Y' is a strong evidence that the method of the present invention leads to the modification of the porous network of the starting crystalline zeolite material Y which is essentially microporous. The method obviously expands pore dimensions and thus bulkier molecules are able to reach more active sites of the crystalline zeolite material. The method would allow a more efficient use of currently used zeolite catalysts in, for instance, oil refining (in particular cracking reactions where the molecular mass of the reactant is drastically reduced) and petrochemistry. In addition, the method of the invention would also allow the preparation of new synthetic crystalline zeolite catalysts able to process much bulkier molecules than those currently used in the industry.

Example 3

Preparation of synthetic crystalline zeolite materials ZSM-5_a, ZSM-5_b, ZSM-5_c, ZSM-5_d, ZSM-5_e, ZSM-5_f, and ZSM-5_g according to the method of the invention and characterization thereof

Example 3-1

Step 1):

A NH_4F solution was prepared by mixing 80 g of solid NH_4F with 120 g of distilled water. The NH_4F solution had a mass concentration of 40 wt%. Then, 10 g of starting crystalline zeolite material ZSM-5 was immersed into the NH_4F solution described above to form a heterogeneous mixture. The heterogeneous mixture was treated at 50°C for 5 minutes under stirring and ultrasounds, and was filtrated to obtain a solid.

Steps 2) and 3):

Then, the obtained solid was thoroughly washed with distilled water and dried at 100°C for 10 h.

A synthetic crystalline zeolite material ZSM-5_a with a Si/Al molar ratio of 22.3 was obtained.

Example 3-2

The same method as the one described in example 3-1 was used except that in step 1), the treatment was performed at 50°C for 15 minutes. A synthetic crystalline zeolite material ZSM-5_b with a Si/Al molar ratio of 22.5 was obtained.

Example 3-3

The same method as the one described in example 3-1 was used except that in step 1), the treatment was performed at 50°C for 22.5 minutes. A synthetic crystalline zeolite material ZSM-5_c with a Si/Al molar ratio of 22.0 was obtained.

Example 3-4

The same method as the one described in example 3-1 was used except that in step 1), the treatment was performed at 50°C for 30 minutes. A synthetic crystalline zeolite material ZSM-5_d with a Si/Al molar ratio of 22.1 was obtained.

Example 3-5

The same method as the one described in example 3-1 was used except that in step 1), the treatment was performed at 50°C for 45 minutes. A synthetic crystalline zeolite material ZSM-5_e with a Si/Al molar ratio of 22.8 was obtained.

Example 3-6

The same method as the one described in example 3-1 was used except that in step 1), the treatment was performed at 50°C for 60 minutes. A

synthetic crystalline zeolite material ZSM-5_f with a Si/Al molar ratio of 23.2 was obtained.

Example 3-7

The same method as the one described in example 3-1 was used except that in step 1), the treatment was performed at 50°C for 120 minutes. A synthetic crystalline zeolite material ZSM-5_g with a Si/Al molar ratio of 23.4 was obtained.

The Si/Al molar ratio and porosity properties [the specific surface area (S_{BET}), the micropore volume (V_{micro}), the mesopore volume (V_{meso}), and the total pore volume (V_{total})] of the starting crystalline zeolite material ZSM-5 and of the prepared synthetic crystalline zeolite materials ZSM-5_a, ZSM-5_b, ZSM-5_c, ZSM-5_d, ZSM-5_e, ZSM-5_f and ZSM-5_g are given in Table 2 below:

The specific surface area and porosity properties of the crystalline zeolite materials were obtained by N_2 sorption measurements.

Table 2

crystalline zeolite material	Si/Al molar ratio	S_{BET} ($m^2.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)	V_{total} ($cm^3.g^{-1}$)
ZSM-5	21.3	377	0.18	0.02	0.20
ZSM-5_a	22.3	368	0.18	0.07	0.25
ZSM-5_b	22.5	391	0.17	0.09	0.26
ZSM-5_c	22.0	394	0.17	0.12	0.29
ZSM-5_d	22.1	NA	NA	NA	NA
ZSM-5_e	22.8	405	0.17	0.22	0.39
ZSM-5_f	23.2	395	0.17	0.28	0.45
ZSM-5_g	23.3	NA	NA	NA	NA

NA: not analyzed

Table 2 clearly shows that the method of the present invention leads to the introduction of a secondary porosity while maintaining the starting

micropore volume, and allows the increase of the total pore volume of the starting crystalline zeolite material (increase of 125% with respect to the starting total pore volume in example 3-6). The chemical analyses revealed that the Si/Al ratio only slightly increased from 21.3 to 23.3. These results are in sharp contrast to the conventional desilication or steaming dealumination approaches currently used for the creation of mesopores in zeolite framework, which change substantially the Si/Al ratio of the starting zeolite materials.

In addition, Figure 6 represents the Powder X-ray diffraction (XRD) of the starting crystalline zeolite material ZSM-5 (figure 6a), the synthetic crystalline zeolite material ZSM-5_a (figure 6b), the synthetic crystalline zeolite material ZSM-5_b (figure 6c), the synthetic crystalline zeolite material ZSM-5_c (figure 6d), the synthetic crystalline zeolite material ZSM-5_e (figure 6e) and the synthetic crystalline zeolite material ZSM-5_f (figure 6f), and shows the intensity (in arbitrary units, a.u.) as a function of two theta (in degree). Figure 6 reveals high crystallinity and no indications of amorphous phase formation after step 1).

Figure 7 represents the nitrogen adsorption/desorption isotherms of the starting crystalline zeolite material (figure 7, solid squares), the synthetic crystalline zeolite material ZSM-5_a (figure 7, open squares), the synthetic crystalline zeolite material ZSM-5_b (figure 7, solid triangles), the synthetic crystalline zeolite material ZSM-5_c (figure 7, open triangles) the synthetic crystalline zeolite material ZSM-5_e (figure 7, solid circles) and the synthetic crystalline zeolite material ZSM-5_f (figure 7, open circles), and shows the volume adsorbed (in $cm^3.g^{-1}$) as a function of the relative pressure P/P_0 (in units). For clarity reasons, the isotherms are shifted in Y direction (i.e. ordinate direction) by +20, +40, +60, +80, +100 $cm^3\ g^{-1}$, for the synthetic crystalline zeolite materials ZSM-5_a, ZSM-5_b, ZSM-5_c, ZSM-5_e, ZSM-5_f, respectively.

Figure 7 shows that the starting crystalline zeolite material exhibits a typical Type I adsorption-desorption isotherm usually obtained for a microporous type material. Depending on the step 1) conditions, the synthetic crystalline zeolite materials change their surface/porous characteristics. More

deeply treated crystalline zeolite materials (e.g. ZSM-5_e and ZSM-5_f) exhibit a combination of Type I and Type IV adsorption-desorption isotherms. In other words, besides the sharp uptake at low relative pressure which is characteristic of zeolite type materials, a second uptake with hysteresis loop is observed at high relative pressure. The hysteresis loop is characteristic of the formation of pores or cavities with mesoporous dimensions.

The analysis of pore size distribution of the starting crystalline zeolite material ZSM-5 and the synthetic crystalline zeolite materials ZSM-5_a, ZSM-5_b, ZSM-5_c, ZSM-5_e and ZSM-5_f showed the progressive formation of larger pores. The secondary porosity ranges from 4 to 100 nm depending on the contacting time of step 1).

Figures 8, 9 and 10 represent the genesis and propagation of mesopores in the framework of the crystalline zeolite materials.

Figures 8, 9a, 9b, 9c and 9d represent scanning electron microscopy (SEM) images of the starting crystalline zeolite material ZSM-5 and the synthetic crystalline zeolite materials ZSM-5_a, ZSM-5_c, ZSM-5_e, ZSM-5_f, respectively. Figures 10a and 10b represent respectively transmission electron microscopy (TEM) images of the crystalline zeolite materials ZSM-5_d and ZSM-5_g.

As it can be seen in figure 8 the starting crystalline zeolite material ZSM-5 has a flat surface. After 5 min of contacting time (cf. step 1)), figure 9a reveals the first traces of dissolution and the disappearance of the small intergrown domain. At the very early stages of zeolite dissolution, the more energetic defect zones are attacked. These are namely defect zones and intergrowth zones between well crystallized zeolite domains. Then, with the increase of contacting time, the crystals of the zeolite material become progressively dissolved. Defects, small intergrown crystals are progressively removed in the whole volume of zeolite crystals (figure 10a). Further dissolution leads to increase of the size of holes remaining after dissolution of intergrown crystallites. In the first stages, the dissolution process follows the form of removed particles and thus cavities and channels with rectangular

shape can be seen. This dissolution mechanism leads to the mosaic structure shown in figure 10b.The fact that the NH_4F concentrated solution attacks first the defect parts of the crystals and thus, purifies the crystals from defects and intergrowth that have negative impact on the diffusion thorough zeolite channels, is another advantage of the present invention. Figure 10 clearly shows intra-particles porosity induced by internal-surface dissolution.

An important consequence is the generation of secondary porosity as a function of crystal growth process. Hence, by controlling the nucleation and growth of zeolite material, the genesis and propagation of secondary pore structure can be controlled, while maintaining the micropore volume of the starting crystalline zeolite material.

Example 4

Catalytic activity of synthetic crystalline zeolite materials ZSM-5_a, ZSM-5_c, ZSM-5_d and ZSM-5_e

Tests were performed to evaluate the catalytic activity of the synthetic crystalline zeolite materials prepared according to the method of the invention.

The synthetic crystalline zeolite materials ZSM-5_a, ZSM-5_c, ZSM-5_d and ZSM-5_e prepared in example 3 and the starting crystalline zeolite material ZSM-5 were heat treated at 550°C to eliminate NH_3 (step 5) and obtain respectively the synthetic crystalline zeolite materials in acidic form ZSM-$5'_a$, ZSM-$5'_c$, ZSM-$5'_d$ and ZSM-$5'_e$ and the starting crystalline zeolite material in acidic form ZSM-5 (also called synthetic and starting crystalline zeolite catalysts).

Then, the conversion of *m*-xylene in the presence of the crystalline zeolite catalysts ZSM-5', ZSM-$5'_a$, ZSM-$5'_c$, ZSM-$5'_e$ and ZSM-$5'_f$ and the conversion of 1,3,5-triisopropylbenzene (TIPB) in the presence of the crystalline zeolite catalysts ZSM-5', ZSM-$5'_a$, and ZSM-$5'_e$ were studied.

The tests to convert *m*-xylene were performed under identical conditions [P_{Tot} = 101325 Pa, $P_{m\text{-xylene}}$ = 2500 Pa, and $W/F°_{m\text{-xylene}}$ = 7-87 $g.h.mol^{-1}$] in a downflow fixed bed gas phase reactor at a temperature of 350°C.

The tests to convert TIPB were performed under identical conditions [P_{Tot} = 101325 Pa, $P_{m\text{-xylene}}$ = 192 Pa, and $W/F°_{TIPB}$ = 6.3727 x 10^3 g.min.mol^{-1}] in a downflow fixed bed gas phase reactor at a temperature of 300°C.

Figure 11 represents the conversion of *m*-xylene (in %) as a function of the weight/feed flow rate (in $W/F°_{m\text{-xylene}}$) for the crystalline zeolite catalysts ZSM-5' (figure 11, solid squares), ZSM-5'$_a$ (figure 11, open squares), ZSM-5'$_c$ (figure 11, solid triangles), ZSM-5'$_e$ (figure 11, open triangles) and ZSM-5'$_f$ (figure 11, open circles).

Figure 12 represents the conversion of TIPB (in %) as a function of time on stream (in minutes) for the crystalline zeolite catalysts ZSM-5' (figure 12, solid squares), ZSM-5'$_a$ (figure 12, solid circles), and ZSM-5'$_e$ (figure 12, solid triangles).

Figures 11 and 12 show that the synthetic crystalline zeolite catalysts prepared according the method of the invention exhibit substantially improved catalytic performances in both *m*-xylene and TIPB.

Example 5

Preparation of synthetic crystalline zeolite materials MOR_1 according to the method of the invention and characterization thereof

Step 1):

A NH_4F solution was prepared by mixing 8 g of solid NH_4F with 32 g of distilled water. The NH_4F solution had a mass concentration of 20 wt%. Then, 5 g of starting crystalline zeolite material MOR was immersed into the NH_4F solution described above to form a heterogeneous mixture. Then, the heterogeneous mixture was stirred at 50°C for 45 minutes and was filtrated to obtain a solid.

Steps 2) and 3):

Then, the obtained solid was thoroughly washed with distilled water and dried at 30°C.

A synthetic crystalline zeolite material MOR_1 with a Si/Al molar ratio of 6.7 was obtained. The Si/Al molar ratio and porosity properties [the specific

surface area (S_{BET}), the micropore volume (V_{micro}), the mesopore volume (V_{meso}), and the total pore volume (V_{total})] of the starting crystalline zeolite material MOR and of the prepared synthetic crystalline zeolite material MOR_1 are given in Table 3 below.

The specific surface area and porosity properties of the crystalline zeolite materials were obtained by N_2 sorption measurements.

Table 3

crystalline zeolite material	Si/Al molar ratio	S_{BET} ($m^2.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)	V_{total} ($cm^3.g^{-1}$)
MOR	6.7	379	0.17	0.06	0.23
MOR_1	6.7	441	0.19	0.09	0.28

Table 3 clearly shows that the method of the present invention leads to the introduction of a secondary porosity and the increase of the micropore volume, thus involving the increasing of the total pore volume of the starting crystalline zeolite material. The chemical analyses revealed that the Si/Al ratio remains constant.

Figure 13 represents the nitrogen adsorption/desorption isotherms of the starting crystalline zeolite material MOR (figure 13, solid squares) and the synthetic crystalline zeolite material MOR_1 (figure 13, open squares), and shows the volume adsorbed (in $cm^3.g^{-1}$) as a function of the relative pressure P/P_0 (in units).

Example 6

Preparation of synthetic crystalline zeolite materials LTL_1 according to the method of the invention and characterization thereof

Step 1):

A NH_4F solution was prepared by mixing 8 g of solid NH_4F with 32 g of distilled water. The NH_4F solution had a mass concentration of 20 wt%. Then, 5 g of starting crystalline zeolite material LTL was immersed into the NH_4F

solution described above to form a heterogeneous mixture. Then, the heterogeneous mixture was stirred at 35°C for 60 minutes, and was filtrated to obtain a solid.

Steps 2) and 3):

Then, the obtained solid was thoroughly washed with distilled water and dried at 30°C.

A synthetic crystalline zeolite material LTL_1 with a Si/Al molar ratio of 3.3 was obtained.

The Si/Al molar ratio and porosity properties [the specific surface area (S_{BET}), the micropore volume (V_{micro}), the mesopore volume (V_{meso}), and the total pore volume (V_{total})] of the starting crystalline zeolite material LTL and of the prepared synthetic crystalline zeolite material LTL_1 are given in Table 4 below:

The specific surface area and porosity properties of the crystalline zeolite materials were obtained by N_2 sorption measurements.

Table 4

crystalline zeolite material	Si/Al molar ratio	S_{BET} ($m^2.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)	V_{total} ($cm^3.g^{-1}$)
LTL	3.3	338	0.15	0.04	0.19
LTL_1	3.3	431	0.17	0.08	0.25

Table 4 clearly shows that the method of the present invention leads to the increase of the total pore volume of the starting crystalline zeolite material. The increase of total pore is namely due to the increase of both the micropore and mesopore volumes. The chemical analyses revealed that the Si/Al ratio remains constant.

Figure 14 represents the nitrogen adsorption/desorption isotherms of the starting crystalline zeolite material LTL (figure 14, solid squares) and the synthetic crystalline zeolite material LTL_1 (figure 14, open squares), and shows

the volume adsorbed (in $cm^3.g^{-1}$) as a function of the relative pressure P/P_0 (in units).

Comparative example 7

Preparation of synthetic crystalline zeolite materials Y_A and Y_B which are not part of the invention

Synthetic zeolites Y_A and Y_B were prepared according the method described in US 5,100,644 and with the conditions used in examples 9 and 10 of US 5,100,644, respectively.

A NH_4F solution was prepared by mixing 3.9 g of solid NH_4F with 4.96 g of distilled water. The NH_4F solution had a mass concentration of 44 wt%. Then, separately, 7.39 g of commercial zeolite Y was mixed with 29.19 g of distilled water to form a zeolite suspension having a zeolite mass concentration of 20.2 wt%.

Then, the NH_4F solution was added slowly over a period of 90 minutes at 75°C on the zeolite suspension, the NH_4F solution and the zeolite suspension being maintained at 75°C during the slow addition. After the addition, the resulting mixture was maintained for a further 3 hours at 75°C.

The solid synthetic zeolite material was separated by filtration, washed with water and dried in air at room temperature.

A synthetic crystalline zeolite material Y_A with a Si/Al molar ratio of 3.5 was obtained. Y_A is not part of the invention since it was not prepared according to the method of the invention.

The same method was repeated with a NH_4F solution prepared by mixing 4.95 g of solid NH_4F with 4.95 g of distilled water. The NH_4F solution had a mass concentration of 50 wt%. Then, separately, 7.39 g of commercial zeolite Y was mixed with 23.4 g of distilled water to form a zeolite suspension having a zeolite mass concentration of 24 wt%.

A synthetic crystalline zeolite material Y_B with a Si/Al molar ratio of 4.2 was obtained. Y_B is not part of the invention since it was not prepared according to the method of the invention.

Figure 15 represents the Powder X-ray diffraction (XRD) of the starting crystalline zeolite material Y (figure 15a), the synthetic crystalline zeolite material Y_A (figure 15b) and the synthetic crystalline zeolite material Y_B (figure 15c), and shows the intensity (in arbitrary units, a.u.) as a function of two theta (in degree). Figure 15 reveals high crystallinity of the starting crystalline zeolite material. However, a substantial loose of crystallinity can be observed for Y_A and Y_B zeolite materials.

Figure 16 represents the nitrogen adsorption/desorption isotherms of the starting crystalline zeolite material Y (figure 16, solid squares), the synthetic zeolite material Y_B (figure 16, open squares) and the synthetic zeolite material Y_C (figure 16, open circles), and shows the volume adsorbed (in $cm^3.g^{-1}$) as a function of the relative pressure P/P_0 (in units).

Nitrogen adsorption characterizes the porosity of the zeolite materials. According to figure 16 and by comparison with figure 2, it can be concluded that the prepared synthetic zeolite materials Y_A and Y_B which are not part of the invention, show much lower microporosity level and much larger mesopore size compared with Y_1 and Y_2 which are part of the invention and prepared in example 1. Such obvious difference in nitrogen adsorption performance reflects the substantial difference in the porosity of zeolites prepared in different ways, and hence reflects the substantial different interaction between zeolite and NH_4F solutions in the method of the invention compared to the methods of the prior art.

The Si/Al molar ratio and porosity properties [the specific surface area (S_{BET}), the micropore volume (V_{micro}), the mesopore volume (V_{meso}), and the total pore volume (V_{total})] of the starting crystalline zeolite material Y and of the prepared synthetic crystalline zeolite material Y_A and Y_B are given in Table 5 below:

The specific surface area and porosity properties of the zeolite materials Y_A and Y_B were obtained by N_2 sorption measurements.

Table 5

crystalline zeolite material	Si/Al molar ratio	S_{BET} ($m^2.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)	V_{total} ($cm^3.g^{-1}$)
Y	2.6	652	0.29	0.07	0.36
Y_A	3.5	563	0.26	0.17	0.43
Y_B	4.2	409	0.18	0.16	0.34

The method of the prior art clearly results in a decrease of the micropore volume and in substantial increase of mesopore volume. Thus, the mesopore volume is not increased while maintaining or increasing the starting micropore volume like in the method of the present invention. Indeed, the decrease of the micropore volume results in a deterioration of the adsorption capacity of the zeolite material and in a decrease of its separation capacity.

There is also a substantial decrease of the specific surface area and the Si/Al molar ratio does not remain constant. The decrease of the specific surface area is related with lower crystallinity and induces a decrease of the availability of active sites and thus a dropping of the catalytic activity.

CLAIMS

1. A method for the preparation of a synthetic crystalline zeolite material comprising micropores and eventually mesopores, said synthetic crystalline zeolite material having a silicon to aluminum molar ratio Si/Al ≥ 1 and, wherein said method comprises at least the following steps:

1) a step of contacting a NH_4F solution with a dry starting crystalline zeolite material at a temperature ranging from 0°C to 100°C, said NH_4F solution having a NH_4F mass concentration of at least 15 wt% and said starting crystalline zeolite material being essentially microporous and having a silicon to aluminum molar ratio Si/Al ≥ 1;

2) a washing step;

3) a drying step at a temperature ranging from 25°C to 120°C, for 1h to 24h, to recover said synthetic crystalline zeolite material.

2. The method according to claim 1, wherein step 1) is carried out for a time ranging from 5 to 180 minutes.

3. The method according to claim 1 or claim 2, wherein the pH of the NH_4F solution before step 1) is 7.

4. The method according to anyone of claims 1 to 3, wherein the mass ratio of solid NH_4F/starting crystalline zeolite material used in step 1) ranges from 0.5 to 25.

5. The method according to anyone of claims 1 to 4, wherein it further comprises a step 4) of ion exchanging.

6. The method according to anyone of claims 1 to 5, wherein the NH_4F solution used in step 1) has a NH_4F mass concentration of at least 20 wt%.

7. The method according to anyone of claims 1 to 6, wherein it leads to an increase of the total pore volume of at least 15%, with respect to the total pore volume of the starting crystalline zeolite material.

8. The method according to anyone of claims 1 to 7, wherein step 1) is carried out by contacting the starting crystalline zeolite material with the whole NH_4F solution in only one go and/or rapidly.

9. The method according to anyone of claims 1 to 8, wherein step 1) is performed by:

- immersing the dry starting crystalline zeolite material in the NH_4F solution to form a heterogeneous mixture, and then by stirring said heterogeneous mixture; or

- pouring the NH_4F solution on the dry starting crystalline zeolite material so as to saturate its micropore volume, and then by filtrating it so as to remove the excess of NH_4F solution and to form an impregnated solid.

10. The method according to anyone of claims 1 to 9, wherein it further comprises a step 6) of functionalizing said synthetic crystalline zeolite material with at least one active compound.

11. A synthetic crystalline zeolite material prepared according to the method as defined in anyone of claims 1 to 10, wherein said synthetic crystalline zeolite material comprises micropores having a mean dimension of more than 1 nm, and eventually mesopores and has a silicon to aluminum molar ratio $Si/Al \geq 1$.

12. A synthetic crystalline zeolite material according to claim 11, wherein it further comprises mesopores having a mean dimension of 2 to 25 nm.

13. A synthetic crystalline zeolite material according to claim 11 or 12, wherein it has a mesopore volume of at least 0.05 cm^3/g.

14. A synthetic crystalline zeolite material according to anyone of claims 11 to 13, wherein it has a micropore volume of at least 0.1 cm^3/g.

15. The use of the method as defined in anyone of claims 1 to 10, so as to increase the total pore volume of a crystalline zeolite material which is essentially microporous.

16. The use of the method as defined in anyone of claims 1 to 10, so as to introduce micropores having a mean dimension of more than 1 nm and/or to introduce mesopores having a mean dimension of 2 to 25 nm while maintaining or increasing the micropore volume, in a crystalline zeolite material which is essentially microporous.

17. The use of the synthetic crystalline zeolite material prepared according to the method as defined in anyone of claims 1 to 10, so as to incorporate active compounds thanks to its newly created micro- and/or mesoporous network.

18. The use of the synthetic crystalline zeolite material prepared according to the method as defined in anyone of claims 1 to 10, as a catalyst or adsorbent in gas-solid and liquid-solid reactions, as seed crystals for zeolite material synthesis, and for the preparation of membranes or layers.

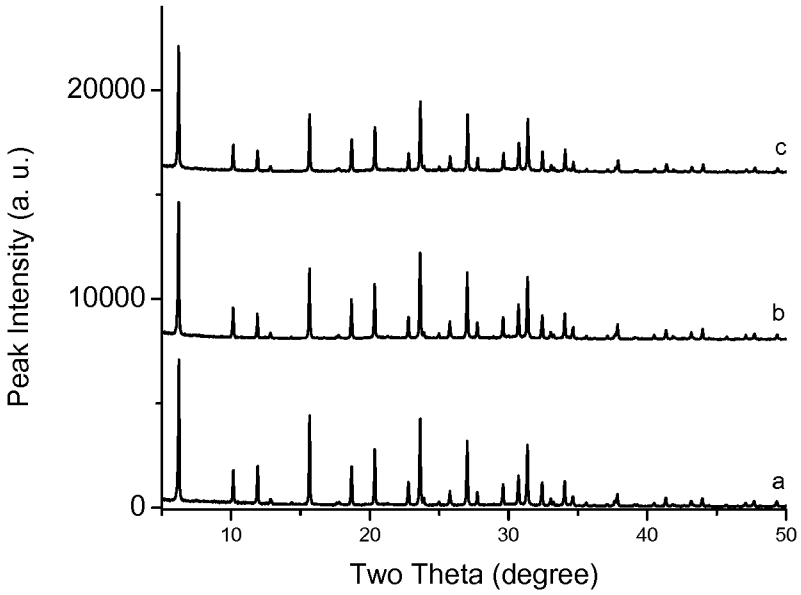
Peak Intensity (a. u.)
20000
10000
0
c
b
a
10
20
30
40
50
Two Theta (degree)

FIG.1

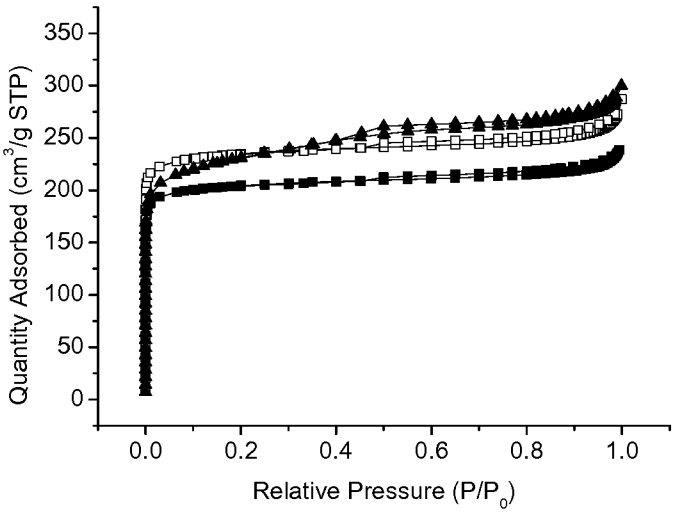
Quantity Adsorbed (cm3/g STP)
350
300
250
200
150
100
50
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/P0)

FIG.2

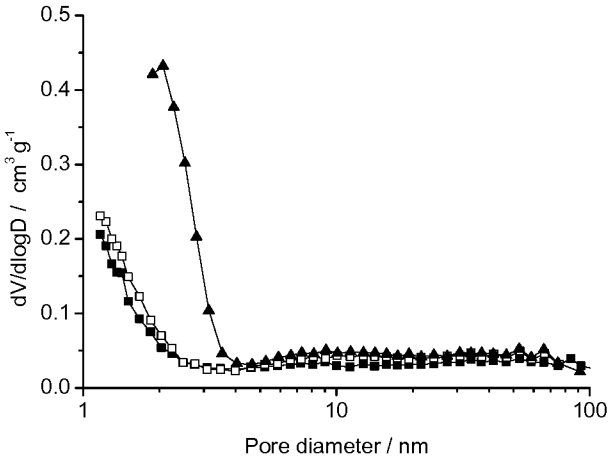

FIG.3

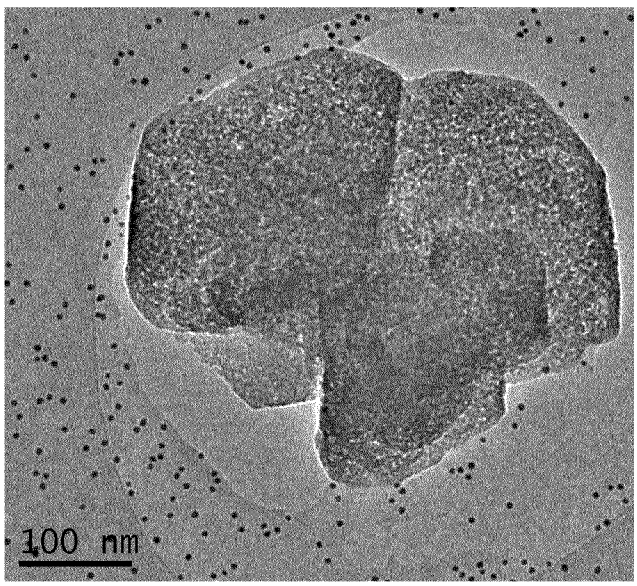

FIG.4

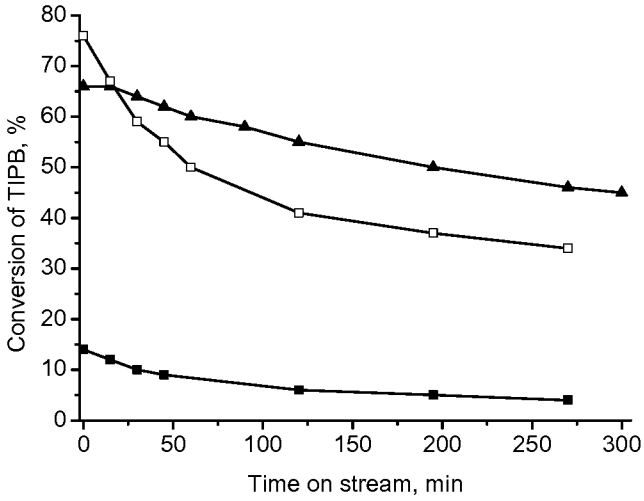
Conversion of TIPB, %
Time on stream, min
0
10
20
30
40
50
60
70
80
0
50
100
150
200
250
300

FIG.5

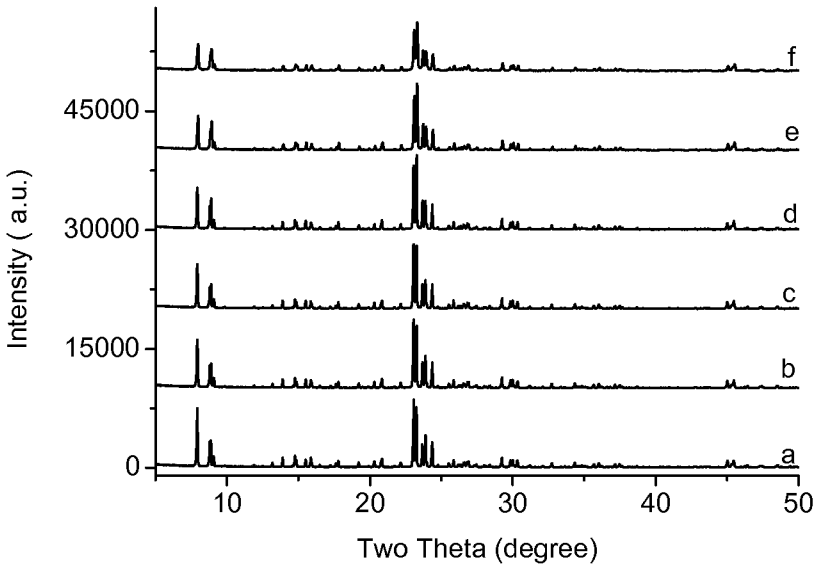
Intensity (a.u.)
Two Theta (degree)
0
15000
30000
45000
10
20
30
40
50
a
b
c
d
e
f

FIG.6

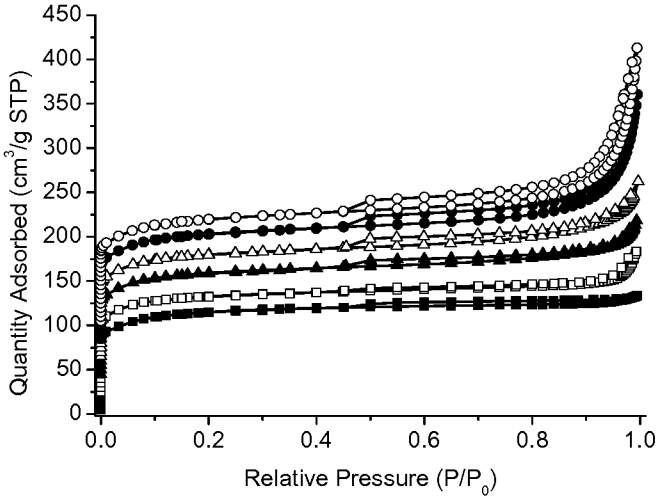
Quantity Adsorbed (cm3/g STP)
450
400
350
300
250
200
150
100
50
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/P0)

FIG.7

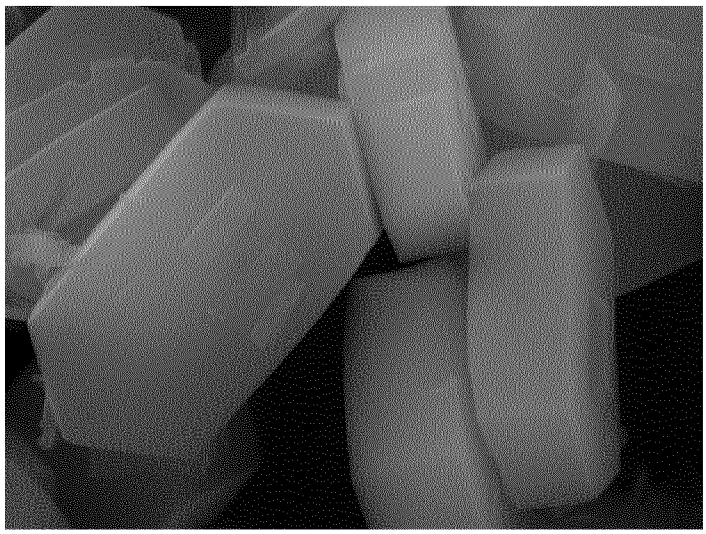

FIG.8

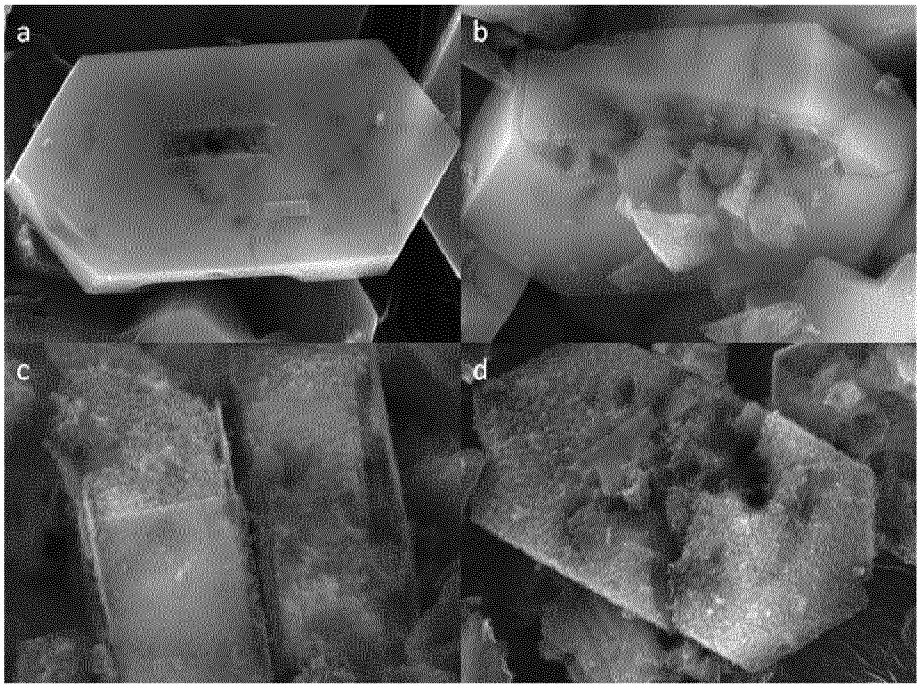

FIG.9

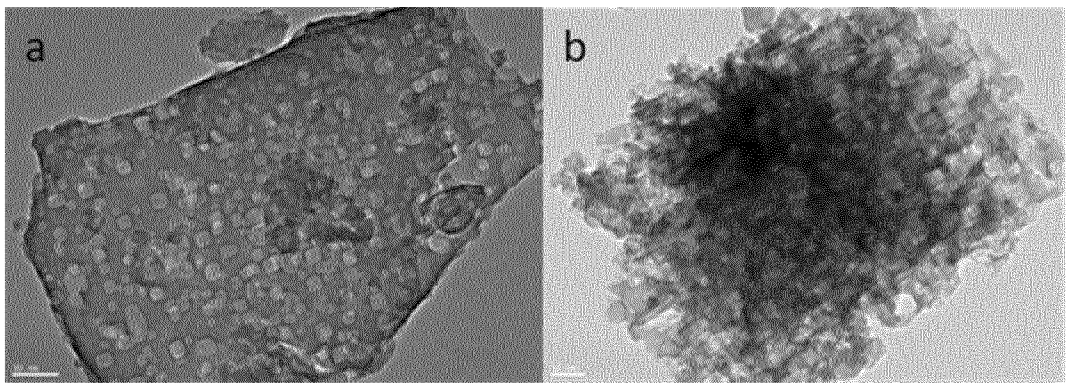

FIG.10

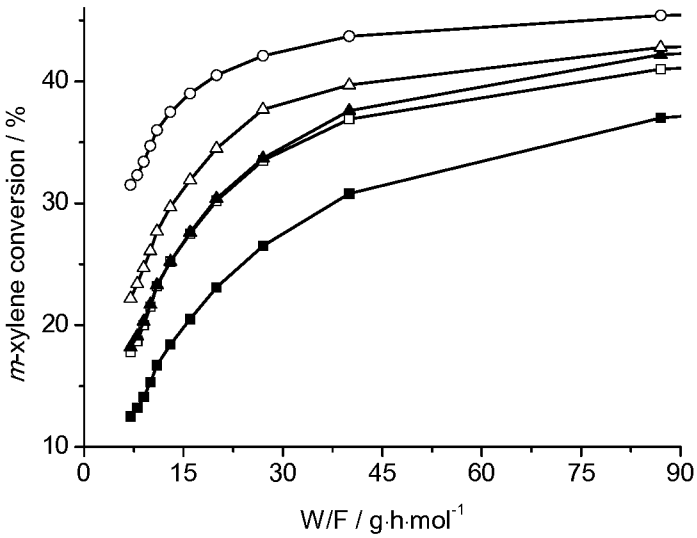
m-xylene conversion / %
10
20
30
40
0
15
30
45
60
75
90
W/F / g·h·mol-1

FIG.11

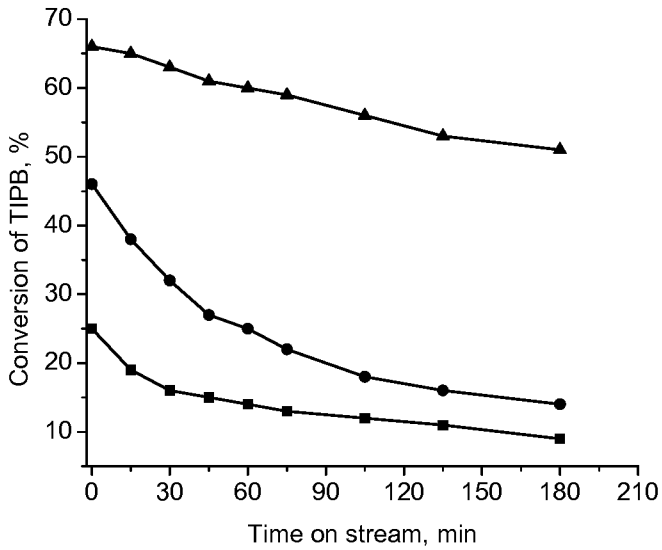
Conversion of TIPB, %
10
20
30
40
50
60
70
0
30
60
90
120
150
180
210
Time on stream, min

FIG.12

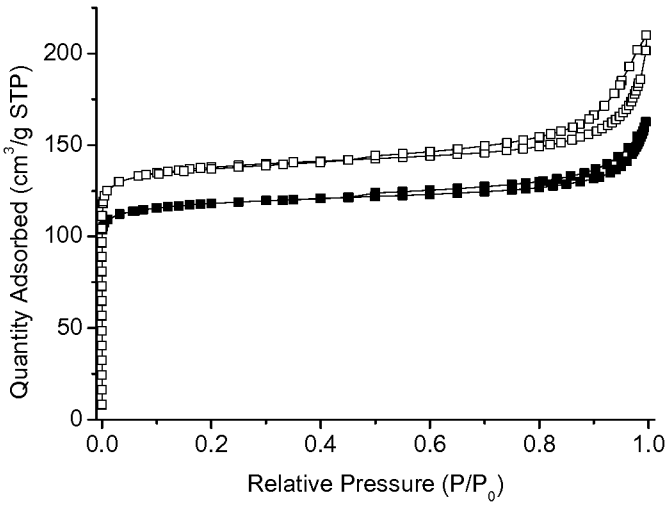
Quantity Adsorbed (cm3/g STP)
200
150
100
50
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/P0)

FIG.13

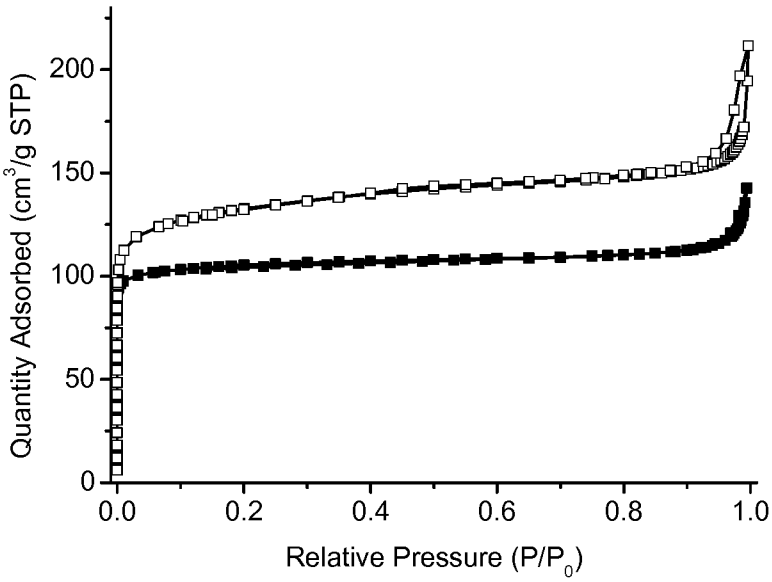
Quantity Adsorbed (cm3/g STP)
200
150
100
50
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/P0)

FIG.14

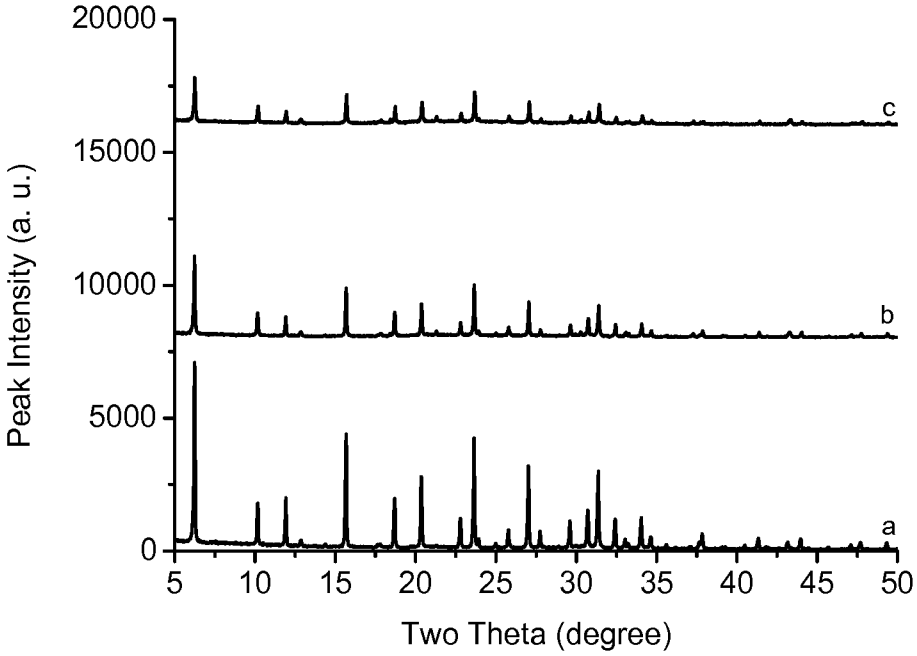
20000
15000
10000
5000
0
Peak Intensity (a. u.)
c
b
a
5
10
15
20
25
30
35
40
45
50
Two Theta (degree)

FIG.15

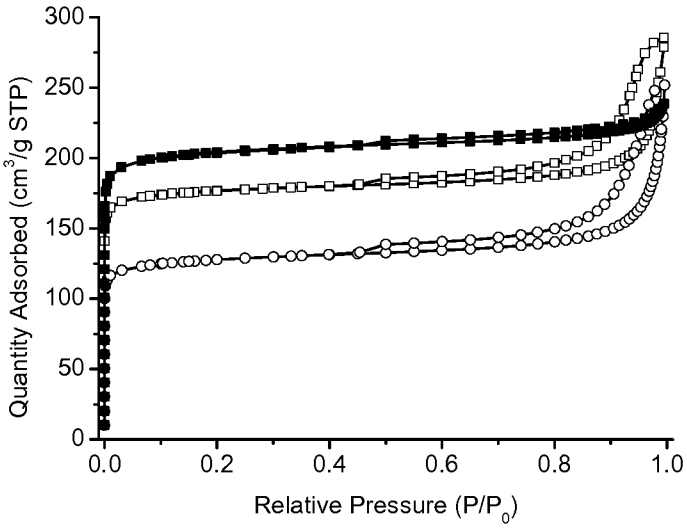
300
250
200
150
100
50
0
Quantity Adsorbed (cm3/g STP)
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/P0)

FIG.16

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/065641

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B39/02
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)
C01B

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, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/085311 A1 (YOUN MINHYE [KR] ET AL) 4 April 2013 (2013-04-04) figure 12B paragraphs [0037], [0077], [0176] table 1 -----	11-14, 17,18
X	EP 1 882 676 A2 (TOPSOE HALDOR AS [DK]) 30 January 2008 (2008-01-30) paragraph [0017]; claims 1,2,7-11; tables 1,2 the whole document -----	11-14, 17,18
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] 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	Date of mailing of the international search report
23 October 2015	09/11/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Rigondaud, Bernard

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 100 644 A (SKEELS GARY W [US] ET AL) 31 March 1992 (1992-03-31) column 4, lines 30-37 column 5, lines 9-25, 35-40 column 6, lines 6-44 column 7, line 3 - column 8, line 67 column 9, lines 16-21 examples 7-10 column 9, lines 40-53; tables 3-4 column 15, lines 14-19 the whole document	1-18
A	US 2012/027673 A1 (LARSEN SARAH [US] ET AL) 2 February 2012 (2012-02-02) paragraphs [0047] - [0048]; examples 1,2; table I and III the whole document	11-18
A	ZHEN TIAN ET AL: "Characterization of Fluorinated H[beta] Zeolite with NH₄F", ADVANCED MATERIALS RESEARCH, vol. 160-162, 11 November 2010 (2010-11-11), pages 524-528, XP055181177, DOI: 10.4028/www.scientific.net/AMR.160-162.524 Experimental - Catalyst preparation; page 524 page 525, paragraph 4 table 1 the whole document	1-18
A	EP 0 244 056 A2 (MOBIL OIL CORP [US]) 4 November 1987 (1987-11-04) Example; page 7 - page 8 the whole document	1-18
A	Z. QIN ET AL: "Chemical Equilibrium Controlled Etching of MFI-Type Zeolite and Its Influence on Zeolite Structure, Acidity, and Catalytic Activity", CHEMISTRY OF MATERIALS, vol. 25, no. 14, 21 June 2013 (2013-06-21) , pages 2759-2766, XP055181150, ISSN: 0897-4756, DOI: 10.1021/cm400719z cited in the application 2. Experimental section; page 2760, left-hand column; tables 1,2 the whole document	1-18

-/--

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LI ET AL: "Enhanced performance of methane dehydro-aromatization on Mo-based HZSM-5 zeolite pretreated by NH4F", CATALYSIS COMMUNICATIONS, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 8, no. 11, 18 January 2007 (2007-01-18), pages 1567-1572, XP022262185, ISSN: 1566-7367, DOI: 10.1016/J.CATCOM.2007.01.013 2.1 Sample preparation; page 1568, left-hand column the whole document -----	1-18
A	MAO R L V ET AL: "ZSM-5 zeolite with enhanced acidic properties", APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 185, no. 1, 6 September 1999 (1999-09-06), pages 41-52, XP004271906, ISSN: 0926-860X, DOI: 10.1016/S0926-860X(99)00132-5 2.1 Catalyst preparation (ii); page 42, right-hand column; table 2 the whole document -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/065641

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013085311 A1	04-04-2013	NONE	
EP 1882676 A2	30-01-2008	CN 101130434 A	27-02-2008
		EP 1882676 A2	30-01-2008
		JP 5579960 B2	27-08-2014
		JP 2008019161 A	31-01-2008
		US 2008014140 A1	17-01-2008
US 5100644 A	31-03-1992	NONE	
US 2012027673 A1	02-02-2012	NONE	
EP 0244056 A2	04-11-1987	CA 1288086 C	27-08-1991
		DK 111287 A	06-09-1987
		EP 0244056 A2	04-11-1987
		JP S62216913 A	24-09-1987
		NZ 219327 A	24-02-1989
		ZA 8701594 A	26-10-1988