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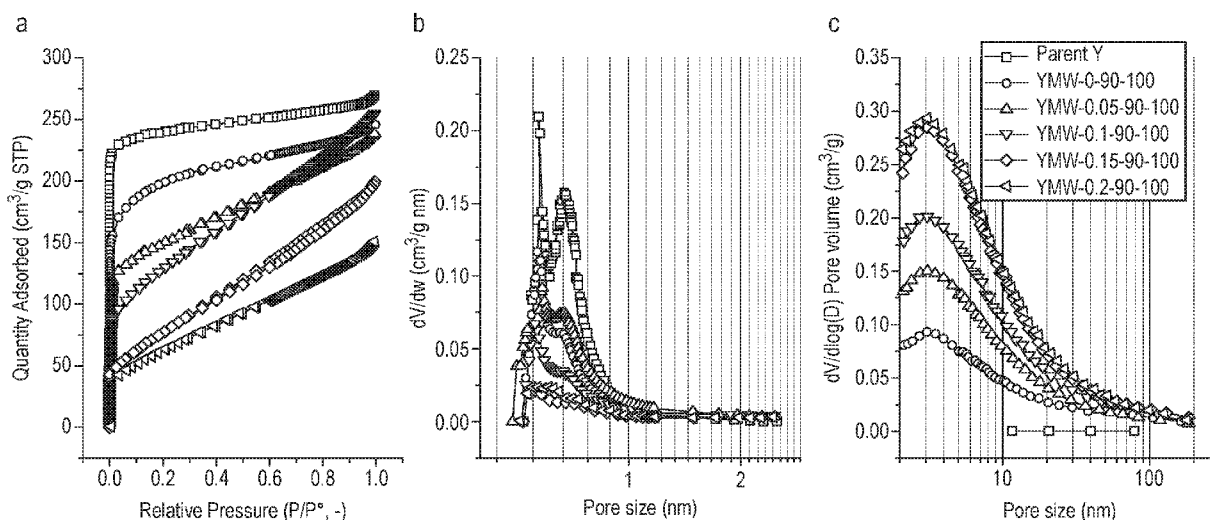
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(54) Title: ZEOLITE MODIFICATION PROCESS AND PRODUCT THEREOF

**FIG. 1**

(57) **Abstract:** A process for modifying zeolites is described, as well as the modified zeolites resulting from such a process and their use in various applications, including catalysis. The zeolite modification process comprises a step of contacting a zeolite with an aqueous mixture comprising at least one chelating agent, and subjecting the resulting mixture to microwave radiation. When compared with conventional hydrothermal zeolite modification techniques, the microwave-assisted chelation process allows the mesoporosity of zeolites to be increased in a considerably shortened period of time. The resulting highly mesoporous modified zeolites have improved catalytic properties, notably in fluid catalytic cracking.



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ZEOLITE MODIFICATION PROCESS AND PRODUCT THEREOF

INTRODUCTION

[0001] The present invention relates to a process for the modification of a zeolite, as well as to modified zeolites themselves and uses of the modified zeolites. More particularly, the present invention relates to a zeolite modification process for creating mesoporosity within the zeolite. The resulting zeolites, having significantly developed mesoporosity, are particularly suitable for use as catalysts in catalytic conversions such as the catalytic cracking of hydrocarbons.

BACKGROUND OF THE INVENTION

[0002] Synthetic zeolites are a class of microporous crystalline materials (silica-alumina frameworks with intrinsic pores of <1 nm, or specifically between 0.41 nm for zeolite A and 0.74 nm for zeolite Y) produced synthetically, which are industrially important materials and have been widely used as heterogeneous catalysts and absorbents for commercial purpose since the 1950s¹. For example, zeolite Y with the faujasite (FAU) topology is the most important active component in the current industrial standard catalysts for catalytic cracking and hydrocracking processes.

[0003] Indeed various processes such as catalytic shape-/size-selective hydrocarbon conversion reactions¹ benefit from the intrinsic micropores of synthetic zeolites, however, micropores of zeolites also cause accessibility and diffusion issues during their applications. For example, the reduced accessibility of the reactants from the reactor stream to the active sites within the microporous framework leads to low reaction rates. Additionally, reduced diffusion of the reaction intermediates/products from the framework to the bulk reactor media can also give rise to catalyst deactivation by coking. For these reasons, the practical solutions addressing accessibility and diffusion limitations in microporous zeolites are of great interest to both industry and academia due to their direct industrial relevance.

[0004] To date, various strategies have been explored to enhance the molecular transport in zeolites, exemplified by (i) the design of zeolites with either intrinsic large pores² or nanosized crystals (nanozeolites)^{2,3}; (ii) the hard-/soft-templating methods to prepare zeolite structures with secondary mesopores ; and (iii) the post-synthetic modifications of microporous zeolites to introduce hierarchical intracrystalline mesopores^{4,5}. Among these methods, the post-synthetic methods (such as dealumination and desilication)^{4,6,7} are far more attractive than others due to the use of commercial zeolites, entailing low production costs with respect to materials⁶.

[0005] Conventional post-synthetic modifications by dealumination and desilication (one-step or combinations of the two) are performed primarily by steaming and hydrothermal (HT) treatments in the presence of acids, bases or chelating agents^{6,7}. Despite their effectiveness, conventional post-synthetic methods for the modification of zeolites to introduce mesoporosity are particularly lengthy and energy-intensive, and are therefore unlikely to leapfrog the current industrial standard⁶.

[0006] Natural organic acids have been shown to dealuminate zeolites (via a stepwise hydrolysis/chelation mechanism⁸) with little loss in crystallinity (known as chemical treatment)^{4,5,8,9}. However, the chelation process under HT conditions proceeds very slowly (a timescale of hours^{8,10}) because the framework aluminium (Al) first needs to be hydrolysed under the acidic HT conditions before being complexed by a chelating agent to form solvable Al-chelate complexes⁹ for eventual extraction from the porous network.

[0007] Owing to the shortcomings of conventional routes, there remains a need for further effective and efficient means of enhancing the molecular transport in zeolites.

[0008] The present invention was devised with the foregoing in mind.

SUMMARY OF THE INVENTION

[0009] According to a first aspect of the present invention there is provided a process for the modification of a zeolite, the process comprising / consisting essentially of / consisting of the steps of:

- a) providing a zeolite;
- b) modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent, and subjecting the resulting mixture to microwave radiation; and
- c) isolating the modified zeolite.

[0010] According to a second aspect of the present invention there is provided a modified zeolite obtained, directly obtained or obtainable by the process of the first aspect.

[0011] According to a third aspect of the present invention there is provided a zeolite Y having a specific mesopore volume (i.e. the total pore volume minus the micropore volume) of at least $0.470 \text{ cm}^3 \text{ g}^{-1}$.

[0012] According to a fourth aspect of the present invention there is provided a use of a zeolite according to the second or third aspect in one or more applications selected from catalysis, sorption, ion exchange, molecular sieving, water purification, odour control and desiccation.

[0013] According to a fifth aspect of the present invention there is provided a catalytic cracking process comprising the step of:

- a) cracking a hydrocarbon feed stream in the presence of a zeolite according to the second or third aspect.

DETAILED DESCRIPTION OF THE INVENTION

Zeolite modification process

[0014] As described hereinbefore, the first aspect of the invention provides a process for the modification of a zeolite, the process comprising the steps of:

- a) providing a zeolite;
- b) modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent, and subjecting the resulting mixture to microwave radiation; and
- c) isolating the modified zeolite.

[0015] Although microwave heating of synthesized zeolites has been studied for over 30 years^{11,12}, it has primarily been employed under dry conditions (i.e. the zeolite being exposed to microwaves is not in contact with a solvent) to desorb adsorbates that have been adsorbed during use of the zeolite as an adsorbent^{11,12,13,14}.

[0016] Whilst there exist a few reports on the use of microwaves in the liquid-phase modification of zeolites for tuning the acidity (*via* dealumination)^{15,16,17,18} and porosity (*via* desilication or detitanation)^{19,20,21,22} of the zeolite, such reports suggest that the microwaves only serve the purpose of intensifying heat transfer within the systems *via* effective and rapid volumetric heating. The resulting zeolites offer mesoporous characteristics that are only comparable to the analogues produced by the conventional HT methods.

[0017] Through meticulous consideration of the mechanism involved in microwave-assisted processes, the inventors have now devised the present invention. Without wishing to be bound by theory, the inventors have reasoned that, in an aqueous solution, polar water molecules are polarised and relaxed instantaneously in relation to the alternating electric field under microwave irradiation (rotational polarisation²³), absorbing and converting electromagnetic energy into heat. FAU zeolites with low Si/Al ratios are universally known as hydrophilic zeolites, in which the presence of aluminium associated hydroxyl groups contributes to the preferential binding of water molecules (*via* hydrogen bonding) on the Brønsted acid sites²⁴, leading to the formation of the condensed water phase adjacent to the framework Al. Therefore, under the MW irradiation, the inventors reasoned that the rotational polarisation of the water molecules in the condensed layer

on the pore surface must also occur, and that since the water molecules are bonded to the zeolite framework, their free oscillation should benefit the formation of extra-framework aluminium (EFAL).

[0018] As a result of these detailed mechanistic studies, the inventors have now surprisingly determined that when microwave irradiation is conducted in the presence of a chelating agent, the hydrolysis step (essential to HT techniques) can be skipped altogether, thereby enabling the direct complexation of Al species by chelating agents under the microwave irradiation and significantly reducing the overall treatment time. The considerably shortened process allows for the preparation of hierarchical meso- and microporous and ordered mesoporous silica-alumina materials rapidly and effectively in a controlled manner.

[0019] In an embodiment, the zeolite provided in step a) has a framework type selected from the group consisting of FAU (faujasite), BEA (beta) and MFI (ZSM-5). Suitably, the zeolite provided in step a) has a FAU framework type.

[0020] In an embodiment, the zeolite provided in step a) is selected from the group consisting of Zeolite Y and Zeolite X. Suitably, the zeolite provided in step a) is Zeolite Y.

[0021] In an embodiment, the at least one chelating agent is capable of sequestering aluminium ions. Suitably, the at least one chelating agent is an organic acid.

[0022] In an embodiment, the at least one chelating agent is bi-, tri-, tetra- or multidentate, having at least 2 (e.g. 2 – 8) donor groups. Suitably, the at least one chelating agent has at least 4 (e.g. 4 – 8) donor groups. More suitably, the at least one chelating agent has at least 6 (e.g. 6 – 8) donor groups.

[0023] In an embodiment, the at least one chelating agent comprises at least one carboxyl or carboxylate donor group. Suitably, the at least one chelating agent comprises at least two carboxyl or carboxylate donor groups. More suitably, the at least one chelating agent comprises at least three carboxyl or carboxylate donor groups. Most suitably, the at least one chelating agent comprises at least four carboxyl or carboxylate donor groups. The at least one chelating agent may also comprise one or more amino donor groups.

[0024] In a particularly suitable embodiment, the at least one chelating agent is a clathrochelate (e.g. sepulchrate).

[0025] In an embodiment, the at least one chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid (EDTA), citric acid, oxalic acid, tartaric acid and pentetic acid. Suitably, the at least one chelating agent is selected from the group consisting of EDTA and pentetic acid. Most suitably, the at least one chelating agent is EDTA.

[0026] Suitably, the chelating agent is a mono carboxylic, dicarboxylic or polycarboxylic acids, including saturated and unsaturated, substituted and unsubstituted acids (e.g. amino carboxylic acids) can find utility in the practice of the invention. Examples of such acids include, in addition to EDTA, organic chelating agents such as citric acid (CA), oxalic acid (OA), tartaric acid (TA) and pentetic acid (DA) are effective using to produce mesopores using the MWAC method. In an embodiment, the at least one chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid (EDTA), oxalic acid, tartaric acid and pentetic acid.

[0027] In an embodiment, the concentration of the at least one chelating agent in the aqueous mixture is 0.02 M to 0.25 M. Suitably, the concentration of the at least one chelating agent in the aqueous mixture is 0.03 M to 0.24 M. More suitably, the concentration of the at least one chelating agent in the aqueous mixture is 0.04 M to 0.23 M. Even more suitably, the concentration of the at least one chelating agent in the aqueous mixture is 0.05 M to 0.22 M. Yet more suitably, the concentration of the at least one chelating agent in the aqueous mixture is 0.075 M to 0.22 M. Yet even more suitably, the concentration of the at least one chelating agent in the aqueous mixture is 0.09 M to 0.21 M.

[0028] In a particularly suitable embodiment, the concentration of the at least one chelating agent in the aqueous mixture is 0.08 – 0.12 M or 0.18 – 0.22 M.

[0029] In an embodiment, step b) is performed at a temperature of 25 – 125°C. Suitably, step b) is performed at a temperature of 40 – 110°C. More suitably, step b) is performed at a temperature of 75 – 110°C. Most suitably, step b) is performed at a temperature of 90 – 110°C.

[0030] In an embodiment, step b) is performed with agitation (e.g. stirring).

[0031] The frequency of the microwave radiation used in step b) is suitably 2000 – 3000 MHz. More suitably, the frequency of the microwave radiation used in step b) is 2250 – 2750 MHz. Most suitably, the frequency of the microwave radiation used in step b) is 2350 – 2550 MHz.

[0032] The power output of the microwave radiation source is not particularly limited. Suitably, the power output of the microwave radiation source is up to 300 W (e.g. 100, 150, 200 or 300 W).

[0033] In an embodiment, the aqueous mixture that is contacted with the zeolite in step b) is basic (e.g. it has a pH of 11 – 14, or more suitably 12 – 14). In such embodiments, the base washing step discussed below in respect of step c) may be bypassed.

[0034] In an embodiment, the reaction conducted in step b) is quenched. The reaction may be quenched by a variety of means. For example, the reaction may be quenched by cooling the reaction mixture (e.g. using an ice bath).

[0035] In an embodiment, step c) comprises isolating the modified zeolite from:

- i) the aqueous mixture of at least one chelating agent, and/or
- ii) one or more reaction by-products formed during step b).

It will be understood that reaction by-products include extra-framework aluminium formed during application of the microwave radiation. The extra-framework aluminium may be in a chelated or non-chelated form.

[0036] Isolation step c) may involve one or more techniques, which may be conducted in sequence or simultaneously.

[0037] In an embodiment, the modified zeolite is isolated by centrifugation. For example, the reaction mixture resulting from step b) may be centrifuged at a suitable speed (e.g. 3000 – 5000 rpm) to isolate the solid modified zeolite from the aqueous mixture.

[0038] In an embodiment, the modified zeolite is isolated by filtration. For example, the reaction mixture resulting from step b) may be filtered to isolate the solid modified zeolite from the aqueous mixture.

[0039] In an embodiment, the modified zeolite is isolated by washing the modified zeolite with a basic solution. The basic solution suitably has a pH of 11 – 14, more suitably 12 – 14. An exemplary basic solution is an aqueous NaOH solution having a concentration of 0.1 – 0.4 M (e.g. 0.15 – 0.25 M). Suitably, the modified zeolite is washed with 10 – 50 cm³ of the basic solution per 1 g of zeolite that is provided in step a) and used in step b). More suitably, the modified zeolite is washed with 20 – 40 cm³ of the basic solution per 1 g of zeolite that is provided in step a) and used in step b).

[0040] The base washing step can be conducted by several means. For example, the solid modified zeolite resulting from step b) (i.e. that which has been isolated by centrifugation, filtration, or another means) may be rinsed with the basic solution, or may be dispersed in the basic solution (e.g. with agitation) for an extended period of time. Alternatively, the basic solution may be added directly to the reaction mixture resulting from step b) once the microwave radiation step is complete (e.g. after the reaction mixture has been quenched), suitably with stirring. The resulting mixture may then be subjected to one or more isolation steps (e.g. centrifugation or filtration) to separate the solid modified zeolite from the aqueous mixture. Irrespective of which technique is used, the base washing step is suitably carried out at a temperature of 20 – 80°C (e.g. 50 – 75°C) for a period of 30 seconds to 2 hours (e.g. 1 minute, 30 minutes or 1 hour).

[0041] In an embodiment, the modified zeolite is isolated by subjecting the modified zeolite to ultrasonic treatment. For example, the reaction vessel in which step b) is conducted may be sonicated in a sonication bath. A basic solution (as described above) may be added into the reaction vessel before, during or after sonication. Once sonication is complete, the resulting

mixture may be subjected to one or more isolation step (e.g. centrifugation or filtration) to separate the solid modified zeolite from the aqueous mixture.

[0042] Once isolated, the modified zeolite may be washed one or more times with distilled water.

[0043] Once isolated (and optionally washed with distilled water), the modified zeolite is then dried. Drying suitably takes place at 40 – 90°C.

[0044] When the zeolite provided in step a) has a FAU framework type, the inventors have demonstrated that the microwave radiation selectively targets the double 6-ring (D6R) of the framework to produce extra-framework aluminium. Without wishing to be bound by theory, the inventors have determined that the mechanism involves the spontaneous interaction of water, Brønsted acid sites in the zeolite and microwaves, which is fundamentally different from that observed in respect of the conventional chemical treatment under hydrothermal conditions. As a consequence of this mechanism, FAU zeolites (e.g. zeolite Y) modified according to the first aspect exhibit a diminished signal at 580 cm⁻¹ (when compared with the same FAU zeolite that has been subjected to hydrothermal treatment) when analysed by FTIR spectroscopy.

Modified zeolites

[0045] As described hereinbefore, the second aspect of the invention provides a modified zeolite obtained, directly obtained or obtainable by the process of the first aspect.

[0046] The microwave-assisted chelation (also termed herein MWAC) process of the first aspect allows for the preparation of modified zeolites having notably increased mesoporosity when compared with the unmodified (e.g. parent) zeolite.

[0047] In an embodiment, the modified zeolite has a framework type selected from the group consisting of FAU, BEA and MFI. Suitably, the modified zeolite has a FAU framework type.

[0048] In an embodiment, the modified zeolite has a Si/Al ratio of 1:1 to 18:1. Suitably the modified zeolite has a Si/Al ratio of 1:1 to 8:1. More suitably, the modified zeolite has a Si/Al ratio of 2:1 to 7:1.

[0049] The modified zeolites having FAU framework type (e.g. zeolite Y) obtainable by the process of the first aspect have a fundamentally different structure to the same zeolite modified by a hydrothermal technique. Due to the fact that the microwave radiation selectively targets the double 6-ring (D6R) of the framework, the MWAC process gives rise to FAU modified zeolites (e.g. zeolite Y) having a diminished signal at 580 cm⁻¹ when analysed by FTIR spectroscopy. This reduction in signal at 580 cm⁻¹ is not apparent when the same FAU zeolite is modified by a conventional hydrothermal technique.

[0050] As described hereinbefore, the third aspect of the invention provides a zeolite Y having a specific mesopore volume of at least $0.470 \text{ cm}^3 \text{ g}^{-1}$.

[0051] The modified zeolite Y materials of the invention exhibit notably high mesoporosity, thus rendering them particularly well-suited to a number of applications, including catalysis.

[0052] As used herein, the term “specific mesopore volume” will be understood to be represent the “total pore volume” of the zeolite minus the “micropore volume” of the zeolite. As used herein, the term micropore volume will be understood to be represent the total porosity of those pores within the zeolite material having a pore diameter in the range of 0-2 nm. Micropore volumes were measured by N_2 physisorption analysis (t -plot method). Total pore volumes were measured by N_2 physisorption analysis (the single point adsorption total pore volume at $p/p^0 = 0.99$).

[0053] The following embodiments will be understood to be applicable to both the second and third aspects of the invention.

[0054] In an embodiment, the zeolite has a specific mesopore volume of at least $0.470 \text{ cm}^3 \text{ g}^{-1}$. Suitably, the zeolite has a specific mesopore volume of $\geq 0.480 \text{ cm}^3 \text{ g}^{-1}$. More suitably, the zeolite has a specific mesopore volume of $\geq 0.490 \text{ cm}^3 \text{ g}^{-1}$. Even more suitably, the zeolite has a specific mesopore volume of $\geq 0.50 \text{ cm}^3 \text{ g}^{-1}$. Yet more suitably, the zeolite has a specific mesopore volume of $\geq 0.520 \text{ cm}^3 \text{ g}^{-1}$. Yet even more suitably, the zeolite has a specific mesopore volume of $\geq 0.540 \text{ cm}^3 \text{ g}^{-1}$.

[0055] In an embodiment, the zeolite has a total pore volume of $\geq 0.40 \text{ cm}^3 \text{ g}^{-1}$. Suitably, the total pore volume of the zeolite is $\geq 0.50 \text{ cm}^3 \text{ g}^{-1}$. More suitably, the total pore volume of the zeolite is $\geq 0.60 \text{ cm}^3 \text{ g}^{-1}$. Even more suitably, the total pore volume of the zeolite is $\geq 0.650 \text{ cm}^3 \text{ g}^{-1}$. Yet more suitably, the total pore volume of the zeolite is $\geq 0.680 \text{ cm}^3 \text{ g}^{-1}$. Yet even more suitably, the total pore volume of the zeolite is $\geq 0.70 \text{ cm}^3 \text{ g}^{-1}$.

[0056] In an embodiment, the zeolite has a specific external surface area of at least $220 \text{ m}^2 \text{ g}^{-1}$. Specific surface areas were measured by N_2 physisorption analysis (t -plot method). Suitably, the zeolite has a specific external surface area of at least $240 \text{ m}^2 \text{ g}^{-1}$. More suitably, the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$. Even more suitably, the zeolite has a specific external surface area of at least $325 \text{ m}^2 \text{ g}^{-1}$. Yet more suitably, the zeolite has a specific external surface area of at least $350 \text{ m}^2 \text{ g}^{-1}$. Yet even more suitably, the zeolite has a specific external surface area of at least $400 \text{ m}^2 \text{ g}^{-1}$. Most suitably, the zeolite has a specific external surface area of at least $450 \text{ m}^2 \text{ g}^{-1}$.

[0057] In an embodiment, the zeolite has a Brunauer-Emmett-Teller (BET) surface area of at least $220 \text{ m}^2 \text{ g}^{-1}$. BET surface areas were measured by N_2 physisorption analysis (Brunauer-Emmett-Teller method). Suitably, the zeolite has a BET surface area of at least $240 \text{ m}^2 \text{ g}^{-1}$. More

suitably, the zeolite has a BET surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$. Yet more suitably, the zeolite has a BET surface area of at least $450 \text{ m}^2 \text{ g}^{-1}$. Yet even more suitably, the zeolite has a BET surface area of at least $650 \text{ m}^2 \text{ g}^{-1}$. Yet even more suitably still, the zeolite has a BET surface area of at least $750 \text{ m}^2 \text{ g}^{-1}$. More suitably, et even more suitably, the zeolite has a BET surface area of at least $850 \text{ m}^2 \text{ g}^{-1}$.

[0058] It will be understood that any of the pore volume values recited above may be taken in combination with any of the surface area values, as will be clear from numbered statements 1-86 outlined below. As a non-limiting example, the zeolite has a specific mesopore volume of $\geq 0.490 \text{ cm}^3 \text{ g}^{-1}$ and a specific external surface area of at least $350 \text{ m}^2 \text{ g}^{-1}$.

Applications of the modified zeolites

[0059] As described hereinbefore, the fourth aspect of the invention provides a use of a zeolite according to the second or third aspect in one or more applications selected from catalysis, sorption, ion exchange, molecular sieving, water purification, odour control and desiccation.

[0060] As a result of their favourable porosity characteristics, in particular their increased mesoporosity, the modified zeolites of the invention are particularly well suited to a variety of applications wherein mesoporosity plays a key role. Furthermore, the modified zeolites of the invention exhibit excellent hydrothermal stability, being able to withstand steaming at 600°C for 4 hours, thus rendering them suitable for use in a wide variety of applications.

[0061] In an embodiment, the zeolite is used in catalysis. Suitably, the zeolite is used as a catalyst in the catalytic cracking of hydrocarbons. More suitably, the zeolite is used as a catalyst in a fluid catalytic cracking (FCC) process.

[0062] As described hereinbefore, the fifth aspect of the invention provides a catalytic cracking process comprising the step of:

- a) cracking a hydrocarbon feed stream in the presence of a zeolite according to the second or third aspect.

[0063] The modified zeolites of the invention have properties that render them particularly well-suited to be used as catalysts in the catalytic cracking of hydrocarbons (e.g. FCC). In particular, when compared with parent zeolites and zeolites that have been modified according to conventional hydrothermal techniques, the modified zeolites of the invention (i.e. those obtainable via the MWAC process) demonstrate increased selectivity towards those cracking products that are favoured by industry (such a benzene, toluene and xylenes) as well as reduced selectivity towards undesirable pre-cracking products (such as cumene).

[0064] The skilled person familiar with catalytic cracking processes will be readily able to select appropriate conditions (e.g. temperatures, pressures, durations, additives, etc) for carrying out the fifth aspect of the invention.

[0065] The following numbered statements 1-86 are not claims, but instead describe particular aspects and embodiments of the invention:

1. A process for the modification of a zeolite, the process comprising the steps of:
 - a) providing a zeolite;
 - b) modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent, and subjecting the resulting mixture to microwave radiation; and
 - c) isolating the modified zeolite.
2. The process of statement 1, wherein the zeolite provided in step a) has a framework type selected from the group consisting of FAU, BEA and MFI.
3. The process of statement 1 or 2, wherein the zeolite provided in step a) has a FAU framework type.
4. The process of any one of statements 1, 2 and 3, wherein the zeolite provided in step a) is selected from the group consisting of Zeolite Y and Zeolite X.
5. The process of any preceding statement, wherein the zeolite provided in step a) is Zeolite Y.
6. The process of any preceding statement, wherein the at least one chelating agent is capable of sequestering aluminium ions.
7. The process of any preceding statement, wherein the at least one chelating agent is an organic acid.
8. The process of any preceding statement, wherein the at least one chelating agent has 2 – 8 donor groups.

9. The process of statement 8, wherein at least one of the donor groups is carboxyl or carboxylate.
10. The process of any preceding statement, wherein the at least one chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid (EDTA), citric acid, tartaric acid, pentetic acid and oxalic acid.
11. The process of any preceding statement, wherein the at least one chelating agent is ethylenediaminetetraacetic acid (EDTA).
12. The process of any preceding statement, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.02 M to 0.25 M.
13. The process of any preceding statement, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.03 M to 0.24 M.
14. The process of any preceding statement, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.04 M to 0.23 M.
15. The process of any preceding statement, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.05 M to 0.22 M.
16. The process of any preceding statement, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.075 M to 0.22 M.
17. The process of any preceding statement, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.09 M to 0.21 M.
18. The process of any preceding statement, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.08 – 0.12 M or 0.18 – 0.3 M.
19. The process of any preceding statement, wherein step b) is performed at a temperature of 25 – 125°C.
20. The process of any preceding statement, wherein step b) is performed at a temperature of 40 – 110°C.

21. The process of any preceding statement, wherein step b) is performed at a temperature of 75 – 110°C.
22. The process of any preceding statement, wherein step b) is performed at a temperature of 90 – 110°C.
23. The process of any preceding statement, wherein step b) is performed with agitation (e.g. stirring).
24. The process of any preceding statement, wherein step c) comprises isolating the modified zeolite from:
 - i) the aqueous mixture of at least one chelating agent, and/or
 - ii) one or more reaction by-products formed during step b).
25. The process of statement 24, wherein the modified zeolite is isolated by centrifugation.
26. The process of statement 24 or 25, wherein the modified zeolite is isolated by washing the modified zeolite with a basic solution (e.g. having a pH of 11 – 14).
27. The process of statement 24, 25 or 26, wherein the modified zeolite is isolated by subjecting the modified zeolite to ultrasonic treatment.
28. The process of any preceding statement, wherein the isolated zeolite is dried at a temperature of 40 – 90°C.
29. The process of any one of statements 1 to 28, wherein
 - step a) comprises providing a zeolite having a FAU framework type;
 - step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one organic acid chelating agent, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.03 M to 0.24 M.
30. The process of any one of statements 1 to 28, wherein
 - step a) comprises providing a zeolite having a FAU framework type;
 - step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent having at least two carboxyl or carboxylate donor groups, and subjecting the resulting mixture to microwave radiation, wherein the

concentration of the at least one chelating agent in the aqueous mixture is 0.075 M to 0.22 M.

31. The process of any one of statements 1 to 28, wherein
step a) comprises providing a zeolite having a FAU framework type; and
step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent selected from EDTA, citric acid, oxalic acid, tartaric acid and pentetic acid, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.03 M to 0.24 M.
32. The process of any one of statements 1 to 28, wherein
step a) comprises providing a zeolite having a FAU framework type;
step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent selected from EDTA, citric acid, oxalic acid, tartaric acid and pentetic acid, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.03 M to 0.24 M; and
step c) comprises isolating the modified zeolite resulting from step b) by centrifugation or filtration and then washing the modified zeolite with a basic solution.
33. The process of any one of statements 1 to 28, wherein
step a) comprises providing a zeolite, wherein the zeolite is Zeolite Y;
step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent selected from EDTA, citric acid, oxalic acid, tartaric acid and pentetic acid, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.03 M to 0.24 M; and
step c) comprises isolating the modified zeolite resulting from step b) by centrifugation or filtration and then washing the modified zeolite with a basic solution, wherein the basic solution has a pH of 11 – 14.
34. The process of any one of statements 1 to 28, wherein
step a) comprises providing a zeolite having a FAU framework type; and
step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent selected from EDTA and pentetic acid, and

subjecting the resulting mixture to microwave radiation, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.075 M to 0.22 M.

35. The process of any one of statements 1 to 28, wherein
step a) comprises providing a zeolite having a FAU framework type;
step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising EDTA, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the EDTA in the aqueous mixture is 0.075 M to 0.22 M; and
step c) comprises isolating the modified zeolite resulting from step by centrifugation or filtration and then washing the modified zeolite with a basic solution.
36. The process of any one of statements 1 to 28, wherein
step a) comprises providing a zeolite, wherein the zeolite is Zeolite X or Zeolite Y;
step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising EDTA, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the EDTA in the aqueous mixture is 0.02 M to 0.25 M; and
step c) comprises isolating the modified zeolite resulting from step by centrifugation or filtration and then washing the modified zeolite with a basic solution, wherein the basic solution has a pH of 11 – 14.
37. A modified zeolite obtainable by the process of any preceding statement.
38. A zeolite Y having a specific mesopore volume of at least $0.470 \text{ cm}^3 \text{ g}^{-1}$.
39. The zeolite of statements 37 or 38, wherein the specific mesopore volume of the zeolite is $\geq 0.480 \text{ cm}^3 \text{ g}^{-1}$.
40. The zeolite of statements 37, 38 or 39, wherein the specific mesopore volume of the zeolite is $\geq 0.490 \text{ cm}^3 \text{ g}^{-1}$.
41. The zeolite of any one of statements 37 to 40, wherein the specific mesopore volume of the zeolite is $\geq 0.50 \text{ cm}^3 \text{ g}^{-1}$.
42. The zeolite of any one of statements 37 to 41, wherein the specific mesopore volume of the zeolite is $\geq 0.520 \text{ cm}^3 \text{ g}^{-1}$.

43. The zeolite of any one of statements 37 to 42, wherein the specific mesopore volume of the zeolite is $\geq 0.540 \text{ cm}^3\text{g}^{-1}$.
44. The zeolite of any one of statements 37 to 43, wherein the total pore volume of the zeolite is $\geq 0.40 \text{ cm}^3\text{g}^{-1}$.
45. The zeolite of any one of statements 37 to 44, wherein the total pore volume of the zeolite is $\geq 0.50 \text{ cm}^3\text{g}^{-1}$.
46. The zeolite of any one of statements 37 to 45, wherein the total pore volume of the zeolite is $\geq 0.60 \text{ cm}^3\text{g}^{-1}$.
47. The zeolite of any one of statements 37 to 46, wherein the total pore volume of the zeolite is $\geq 0.650 \text{ cm}^3\text{g}^{-1}$.
48. The zeolite of any one of statements 37 to 47, wherein the total pore volume of the zeolite is $\geq 0.680 \text{ cm}^3\text{g}^{-1}$.
49. The zeolite of any one of statements 37 to 48, wherein the total pore volume of the zeolite is $\geq 0.70 \text{ cm}^3\text{g}^{-1}$.
50. The zeolite of any one of statements 37 to 49, wherein the zeolite has a specific external surface area of at least $240 \text{ m}^2 \text{ g}^{-1}$.
51. The zeolite of any one of statements 37 to 50, wherein the zeolite has a specific external surface area of at least $280 \text{ m}^2 \text{ g}^{-1}$.
52. The zeolite of any one of statements 37 to 51, wherein the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
53. The zeolite of any one of statements 37 to 52, wherein the zeolite has a specific external surface area of at least $325 \text{ m}^2 \text{ g}^{-1}$.
54. The zeolite of any one of statements 37 to 53, wherein the zeolite has a specific external surface area of at least $350 \text{ m}^2 \text{ g}^{-1}$.

55. The zeolite of any one of statements 37 to 54, wherein the zeolite has a specific external surface area of at least $375 \text{ m}^2 \text{ g}^{-1}$.
56. The zeolite of any one of statements 37 to 55, wherein the zeolite has a specific external surface area of at least $400 \text{ m}^2 \text{ g}^{-1}$.
57. The zeolite of any one of statements 37 to 56, wherein the zeolite has a specific external surface area of at least $450 \text{ m}^2 \text{ g}^{-1}$.
58. The zeolite of any one of statements 37 to 57, wherein the zeolite has a BET surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
59. The zeolite of any one of statements 37 to 58, wherein the zeolite has a BET surface area of at least $450 \text{ m}^2 \text{ g}^{-1}$.
60. The zeolite of any one of statements 37 to 59, wherein the zeolite has a BET surface area of at least $650 \text{ m}^2 \text{ g}^{-1}$.
61. The zeolite of any one of statements 37 to 60, wherein the zeolite has a BET surface area of at least $750 \text{ m}^2 \text{ g}^{-1}$.
62. The zeolite of any one of statements 37 to 61, wherein the zeolite has a BET surface area of at least $800 \text{ m}^2 \text{ g}^{-1}$.
63. The zeolite of any one of statements 37 to 62, wherein the zeolite has a Si/Al ratio of 1:1 to 18:1.
64. The zeolite of any one of statements 37 to 63, wherein the zeolite has a Si/Al ratio of 1:1 to 8:1.
65. The zeolite of any one of statements 37 to 64, wherein the zeolite has a Si/Al ratio of 2:1 to 7:1.
66. The zeolite of any one of statements 37 to 65, wherein
the specific mesopore volume of the zeolite is at least $0.470 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $240 \text{ m}^2 \text{ g}^{-1}$.

67. The zeolite of any one of statements 37 to 66, wherein
the specific mesopore volume of the zeolite is at least $0.470 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $280 \text{ m}^2 \text{ g}^{-1}$.
68. The zeolite of any one of statements 37 to 67, wherein
the specific mesopore volume of the zeolite is at least $0.470 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
69. The zeolite of any one of statements 37 to 68, wherein
the specific mesopore volume of the zeolite is at least $0.470 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $350 \text{ m}^2 \text{ g}^{-1}$.
70. The zeolite of any one of statements 37 to 69, wherein
the specific mesopore volume of the zeolite is at least $0.470 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $375 \text{ m}^2 \text{ g}^{-1}$.
71. The zeolite of any one of statements 37 to 70, wherein
the specific mesopore volume of the zeolite is at least $0.470 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $400 \text{ m}^2 \text{ g}^{-1}$.
72. The zeolite of any one of statements 37 to 71, wherein
the specific mesopore volume of the zeolite is at least $0.480 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $240 \text{ m}^2 \text{ g}^{-1}$.
73. The zeolite of any one of statements 37 to 72, wherein
the specific mesopore volume of the zeolite is at least $0.480 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $280 \text{ m}^2 \text{ g}^{-1}$.
74. The zeolite of any one of statements 37 to 73, wherein
the specific mesopore volume of the zeolite is at least $0.480 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
75. The zeolite of any one of statements 37 to 74, wherein
the specific mesopore volume of the zeolite is at least $0.480 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $350 \text{ m}^2 \text{ g}^{-1}$.
76. The zeolite of any one of statements 37 to 75, wherein

the specific mesopore volume of the zeolite is at least $0.480 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $375 \text{ m}^2 \text{ g}^{-1}$.

77. The zeolite of any one of statements 37 to 76, wherein
the specific mesopore volume of the zeolite is at least $0.480 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $400 \text{ m}^2 \text{ g}^{-1}$.
78. The zeolite of any one of statements 37 to 77, wherein
the specific mesopore volume of the zeolite is at least $0.50 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
79. The zeolite of any one of statements 37 to 78, wherein
the specific mesopore volume of the zeolite is at least $0.50 \text{ cm}^3 \text{ g}^{-1}$,
the total pore volume of the zeolite is $\geq 0.50 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
80. The zeolite of any one of statements 37 to 79, wherein
the specific mesopore volume of the zeolite is at least $0.52 \text{ cm}^3 \text{ g}^{-1}$,
the total pore volume of the zeolite is $\geq 0.50 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
81. The zeolite of any one of statements 37 to 80, wherein
the specific mesopore volume of the zeolite is at least $0.52 \text{ cm}^3 \text{ g}^{-1}$,
the total pore volume of the zeolite is $\geq 0.60 \text{ cm}^3 \text{ g}^{-1}$, and
the zeolite has a specific external surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
82. Use of a zeolite as claimed in any one of statements 37 to 81 in one or more
applications selected from catalysis, sorption, ion exchange, molecular sieving, water
purification, odour control and desiccation.
83. The use of statement 82, wherein the zeolite is used as a catalyst.
84. The use of statement 83, wherein the zeolite is used as a catalyst in the catalytic
cracking of hydrocarbons.
85. A catalytic cracking process comprising the step of:

- a) cracking a hydrocarbon feed stream in the presence of a zeolite as claimed in any one of statements 37 to 81.

86. The catalytic cracking process of statement 85, wherein the catalytic cracking process is a fluid catalytic cracking (FCC) process.

EXAMPLES

[0066] One or more examples of the invention will now be described, for the purpose of illustration only, with reference to the accompanying figures:

Fig. 1: Textural properties of MWAC-treated (using EDTA as chelating agent) Y zeolites and parent zeolite Y. **a.** N₂ sorption isotherms; **b.** H-K pore size distribution for micropores; **c.** BJH adsorption pore size distribution for mesopores. Conditions of the post-synthetic MW treatment: $T = 100\text{ }^{\circ}\text{C}$, $t = 90\text{ min}$.

Fig. 2: Tuning properties of FAU zeolite Y using the MWAC method, and the effect of EDTA concentration. **a.** N₂ sorption isotherms; **b.** BJH adsorption pore size distribution; **c.** Specific surface areas (the t -plot method for micropore surface areas; external surface areas are obtained by subtracting the micropore surface area from the according BET surface area); **d and e.** Relative crystallinity and yield as the function of EDTA concentration. Conditions of the MWAC treatment: $T = 100\text{ }^{\circ}\text{C}$, $t = 90\text{ min}$; Conditions of the base washing: $T = 65\text{ }^{\circ}\text{C}$, $t = 30\text{ min}$; $C_{\text{NaOH}} = 0.2\text{ M}$.

Fig. 3: IR spectra in the FAU framework vibration region. **a.** parent Y and samples after the MWAC and HT treatments (using EDTA as chelating agent); **b.** parent Y and samples from Figure 3a after the base washing. **c.** empirical fraction of the framework Al ratio in materials Conditions of the base washing: $T = 65\text{ }^{\circ}\text{C}$, $t = 30\text{ min}$; $C_{\text{NaOH}} = 0.2\text{ M}$.

Fig. 4: Superior mesoporosity of the MWAC treated (using EDTA as chelating agent) FAU zeolites compared to a sample treated by the conventional hydrothermal method (YHT-0.1-360-100). Comparisons of **a.** specific pore volumes (micropore volumes are based on the t -plot method; mesopores volumes are based on the BJH adsorption cumulative pore volume); **b.** specific surface areas (micropore surface areas are based on the t -plot method; external surface areas are obtained by subtracting the micropore surface area from the according BET surface area); **c.** cumulative pore volume; **d.** pore size distributions (H-K method for the micropore PSDs; BJH method on the adsorption branches for the mesopores PSDs). Conditions of the post-synthetic MW treatment: $T = 100\text{ }^{\circ}\text{C}$; $C_{\text{EDTA}} = 0.10\text{ M}$. Conditions of the post-synthetic HT

treatment: $T = 100\text{ }^{\circ}\text{C}$; $C_{\text{EDTA}} = 0.10\text{ M}$; $t = 360\text{ min}$. Conditions of the alkaline treatment: $T = 65\text{ }^{\circ}\text{C}$, $t = 30\text{ min}$; $C_{\text{NaOH}} = 0.2\text{ M}$.

Fig. 5: TEM micrographs of **a and b**. parent zeolite Y; **c and d**. YMW-0.1-1-100-B; **e and f**. YMW-0.2-1-100-B. All MWAC treated samples used EDTA as chelating agent.

Fig. 6: Superior catalytic performance of the MWAC treated (using EDTA as chelating agent) FAU zeolites in aldol condensation. Comparisons of **a**. heptane conversion and **b**. jasminaldehyde production.

Fig. 7: Superior catalytic performance of the MWAC treated (using EDTA as chelating agent) FAU zeolites in cracking 1,3,5-triisopropylbenzene. **a**. Comparisons of 1,3,5-triisopropylbenzene conversion; Selectivity to cumene and BTX achieved by **b**. YMW-0.1-30-100-B; **c**. YHT-0.1-360-100-B; **d**. parent Y.

Fig. 8: XRD diffractogram of FAU zeolite Y samples. **a**. Zeolite Y after the MW treatment at $100\text{ }^{\circ}\text{C}$ with DI water and EDTA with different concentrations ($t = 90\text{ min}$); **b**. MW treated zeolite Y after base washing, conditions of the base washing: $T = 65\text{ }^{\circ}\text{C}$, $t = 30\text{ min}$; $C_{\text{NaOH}} = 0.2\text{ M}$.

Fig. 9: N_2 adsorption–desorption isotherms of MW-EDTA treated and HT-EDTA treated zeolite Y samples. **a**. YHT-0.1 and YMW-0.1 samples (vertical offset = $600\text{ cm}^3\text{ g}^{-1}\text{ STP}$); **b**. YHT-0.2 and YMW-0.2 samples (vertical offset = $500\text{ cm}^3\text{ g}^{-1}\text{ STP}$).

Fig. 10: IR spectra in the FAU framework vibration region. **a**. parent Y and samples after the MWAC treatments (0.2 M EDTA) with different treatment time; **b**. Fraction of framework Al in MWAC treated samples as a function of time. Conditions of the base washing: $T = 65\text{ }^{\circ}\text{C}$, $t = 30\text{ min}$; $C_{\text{NaOH}} = 0.2\text{ M}$.

Fig. 11: Silicon-to-aluminium (Si/Al) ratios of materials by ICP-OES and EDX. All samples used EDTA as chelating agent.

Fig. 12: Weight loss by thermogravimetric analysis of the spent catalysts from the cracking reactions (Example 4).

Fig. 13: IR spectra, in the region characteristic of adsorbed pyridine vibrations, of the catalysts after pyridine sorption and evacuation at $150\text{ }^{\circ}\text{C}$ and $350\text{ }^{\circ}\text{C}$.

Materials, instrumentation and standard techniques

[0067] Nitrogen (N_2) sorption analysis of materials at $-196.15\text{ }^{\circ}\text{C}$ was obtained using a Micromeritics 3Flex Surface Characterization Analyzer. Prior to the N_2 sorption measurements, samples (70–200 mg) were degassed at $90\text{ }^{\circ}\text{C}$ for 1 h then heated to $350\text{ }^{\circ}\text{C}$ (heating rate = $10\text{ }^{\circ}\text{C min}^{-1}$) and held at for 6 h under vacuum. Specific surface area of materials was determined

based on Brunauer-Emmett-Teller (BET) method. Pore size distribution analysis was performed using Barrett-Joyner-Halenda (BJH, the adsorption branch of isotherms) and Horvath-Kawazoe (H-K, with Saito-Foley modification) method.

[0068] Mercury (Hg) intrusion porosimetry on Micromeritics' AutoPore IV 9510 (pressure range: 0.10 to 60000 psia).

[0069] X-ray diffraction (XRD) characterisation was performed on Philips X'pert Pro PW3719 where Cu K α_1 and Cu K α_2 were used as radiation sources (40 kV, 30 mA) and $\lambda = 1.540598 \text{ \AA}$ and $1.544426 \text{ \AA}$, respectively. The scan range is from 3° to 50° with a step size of 0.0167° at a scanning speed of 2° min^{-1} is used to determine the topology structure and the material crystallinity degree for the modified zeolites²⁷. The relative crystallinity (or percent crystallinity) of FAU Y zeolites was determined by using a standard Integrated Peak Area Method (ASTM D3906-03²⁸), which involves a comparison of the integrated peak areas of the eight peaks at 2θ values of 15.7° (331), 18.7° (511), 20.4° (440), 23.7° (533), 27.1° (642), 30.8° (822), 31.5° (555) and 34.2° (664) from the diffraction pattern. This XRD method provides the best determination of relative crystallinity when the sample zeolites have a similar history of preparation. The calculation the relative crystallinity was performed using the Eq. (1) and the reference used in this work was the parent Y.

$$\text{Relative crystallinity}\% = \frac{\sum \text{Total area of the eight peaks of the sample}}{\sum \text{Total area of the eight peaks of the reference}} \quad (1)$$

[0070] The infrared (IR) absorption spectroscopy was performed on VERTEX 70 spectrometer equipped with the HeNe laser, KBr beamsplitter, and DLaTGS detector. The spectra in the zeolite framework vibration region ($400\text{--}4000 \text{ cm}^{-1}$) were obtained at ambient temperature by averaging 200 scans per sample at 1 cm^{-1} resolution.

[0071] Ammonia temperature-programmed desorption (NH₃-TPD) measurements were performed using a Micromeritics AutoChem II 2920 chemisorption analyzer (Micromeritics, USA) to determine the acidity and the amount of the acidic sites of the structured zeolite catalysts. The catalyst ($\sim 100 \text{ mg}$) was pre-treated at 550°C for 1 h and then cooled down 50°C under Helium (He). A gas mixture of NH₃ in He (10%:90%, $30 \text{ cm}^3 \text{ min}^{-1}$) was then introduced to saturate the catalyst followed by the purge of pure He ($60 \text{ cm}^3 \text{ min}^{-1}$) at 100°C K for 2 h to remove the physically adsorbed NH₃. Finally, NH₃-TPD was performed by heating the catalyst from 100 K to 600°C with a heating rate of $10^\circ \text{C min}^{-1}$ under He flow ($30 \text{ cm}^3 \text{ STP min}^{-1}$) and the desorbed NH₃ was monitored by a gas chromatography (GC) equipped with a thermal conductivity detector (TCD).

[0072] Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a TG analyser (Q600 TGA-DSC, TA Instruments, Germany) for evaluating the thermal stability of materials under air (flow rate = 100 ml min⁻¹). The temperature ramp was from room temperature to 800 °C with the heating rate of 10 °C min⁻¹.

[0073] Si and Al fractions in materials are detected using the inductively coupled plasma optical emission spectrometry (ICP-OES, PlasmaQuant PQ9000Elite-analytik jena). Zeolites (100 mg) were digested in an acid solution (1 ml HNO₃ 65%, 30 HCl 32%, 1 ml HF 40%) with the CEM microwave digestion system. The digestion was performed with a 10 ml reactor vessel and a temperature programme of 170 °C for 5 min, 190 for 5 min and 240 for 10 min (ramp = 2 min for all stages).

[0074] Scanning electron microscopy (SEM) characterisation was performed on FEI Quanta 200 in high voltage mode of 20 kV and high vacuum of 10⁻⁶ to 10⁻⁷ torr. Samples were coated with platinum particles prior to scanning using Emitech K550X sputter coater under vacuum conditions of 1×10⁻⁴ mbar, with the aim of creating a conductive layer on the surface of the zeolites and preventing image distortion caused by the charging effect. The surface elemental analyses (100 µm diameter) were conducted by Energy dispersive X-ray (EDX) on TM3030 Plus (15 kV) to determine the bulk surface Si and Al fractions of samples. The EDX analyses were carried out three times for each sample on different locations to obtain average values.

[0075] Transmission electron microscopy (TEM) bright field imaging was completed using an FEI Tecnai G2 20 operating at 200 kV. Samples were dispersed in ethanol and pipetted onto 200 Mesh Cu Holey Carbon Grids and dried prior to the examination.

[0076] Zeolite hydrothermal stability test: The hydrothermal treatment of zeolite Y was carried out in a tube furnace (Carbolite Gero Ltd., UK) at 600 °C. A HPLC pump (KNAUER P.4.1S) was used to deliver DI water at 10 ml min⁻¹ to be evaporated for steam generation. All samples were treated by steaming for 4 h prior to XRD analysis.

[0077] Catalytic tests: Catalytic aldol condensation of benzaldehyde was carried out using Schlaker reaction tubes (25 ml, Aldrich®) under N₂. Prior to the catalytic tests, all catalysts were dried in an oven at 150 °C overnight to remove the moisture. Typically the catalyst (200 mg) was loaded into the tube followed by the addition of benzaldehyde (5 ml, 48.7 mmol), heptanal (1.2 ml, 8.7 mmol) and dodecane (0.2 ml, 0.87 mmol). The resulting suspension was then heated at 130 °C (in an oil bath) under stirring (300 rpm) and inert atmosphere. The reaction mixture was sampled periodically for the gas chromatography (GC) analysis (Agilent 7820A GC System with a Agilent J&W HP-5 capillary column, stationary phase = (5%-Phenyl)-methylpolysiloxane, dimension = 30 m×0.32×0.25 µm). Products identification was performed in an Agilent 6890N GC with 5973N Inert MSD (mass selective detectors) system using the same capillary column.

Example 1 – Preparation of modified zeolites

MWAC technique

[0078] All the zeolite Y modification experiments were carried out using a commercial zeolite Y (NH₃Y, CBV 300 from Zeolyst, Si/Al = 2.6). MWAC treatment of zeolite Y was performed in a monomode microwave reactor (CEM Discover SP-D MW reactor) at 100 °C with the variable MW power input of maximum 150 W. To prepare the mixture, 1.667 g zeolite Y was first charged into the aqueous solution of chelating agent (25 ml, chelating agent concentration varying from 0.05 to 0.2 M) in a 35 mL Pyrex pressure vessel. The vessel containing the mixture was then inserted into the MW reactor and treated at 50-100 °C under stirring for various retention times. After the MWAC treatment, the mixture was quenched using an ice water bath for 15 min, followed by the centrifugation at 4400 rpm to separate the solid from the solution. The resulting solid samples were washed using deionized water four times and dried at 70 °C in an oven overnight. A base washing protocol was used to remove any detrital material remaining in the zeolite pores. In the base washing, the treated zeolite Y was added into the alkaline solution of 0.2 M NaOH (in a plastic beaker, 3.3 g of the zeolite per 100 cm³ of alkaline solution) and vigorously stirred for 1-30 min at 65-100 °C. After the base washing, the mixture was quenched using an ice water bath then washed thoroughly to obtain the final products, which were dried at 70 °C overnight prior to the characterisation. The resulting modified zeolites were labelled YMW-a-b-c-B (a: chelating agent concentration in M; b: MW treatment time in min, c: MW treatment temperature in °C and B: base washed samples).

[0079] An analogous procedure was used to prepare those zeolites appearing in Table 3.

Conventional hydrothermal (HT) technique

[0080] Conventional hydrothermal treatment of zeolite using EDTA as a chelating agent was carried out in a round-bottom flask (250 ml) under reflux. In a typical experiment, the zeolite sample of 6.67 g zeolite Y was added to 100 cm³ EDTA aqueous solution and the mixture was vigorously stirred at 100°C under reflux for 1.5-6 h. After the reaction, the same work-up and base washing procedures as those described in respect of the MWAC technique were applied. The resulting modified zeolites were labelled YHT-a-b-c-B (a: EDTA concentration in M; b: HT treatment time in min, c: HT treatment temperature in °C and B: base washed samples).

Example 2 – Characterisation

Textural properties

[0081] The results of N₂ sorption analysis on MWAC treated samples (using EDTA as chelating agent) in comparison to parent zeolite Y are shown in Figure 1. N₂ adsorption-desorption isotherms (Figure 1a) shows that the MWAC treatment can effectively destruct microporous crystalline phase in zeolite Y, as evidenced by the decreased uptake of gas at low relative pressures ($P/P^0 < 0.03$) in relation to the increased quantity of chelator used. Even with DI water (YMW-0-90-100), micropore gas uptake decreased by *ca.* 27% after the MW treatment, which was associated with the development of mesoporosity in the resulting material (e.g. specific mesopore volumes: 0.151 cm³ g⁻¹ and external surface areas 260 cm² g⁻¹, as shown in Table 1). Conversely, in zeolite Y, the two parameters are insignificant (Table 1). Conversely, in zeolite Y, the two parameters are insignificant (Table 1). EDTA concentration has a noteworthy effect on the pore size distributions (PSDs) of MWAC treated samples (Figures 1b and 1c) showing the shrinking micropores PSD at around 0.74 nm and the growing mesopores PSDs at around 3 nm by increasing the EDTA concentration from 0.05 M to 0.20 M (with 0.05 M incremental interval) in the MWAC system.

Table 1. Comprehensive analysis of pore structures of Y zeolite and materials developed by MWAC treating (chelating agent = EDTA) Y zeolite.

Sample	Specific surface areas [$\text{m}^2 \text{g}^{-1}$]			Specific pore volumes [$\text{cm}^3 \text{g}^{-1}$]		
	$S_{\text{micro}}^{\text{a}}$	$S_{\text{external}}^{\text{a}}$	BET	$V_{\text{micro}}^{\text{a}}$	$V_{\text{meso}}^{\text{b}}$	$V_{\text{total}}^{\text{c}}$
Parent Y	858	9	867	0.35	0.01	0.36
YHT-0.1-360-100-B	626	137	762	0.28	0.20	0.48
YHT-0.2-360-100-B	0	275	275	0	0.40	0.40
YMW-0-90-100	279	260	540	0.12	0.25	0.37
YMW-0-90-100-B	547	142	689	0.23	0.14	0.37
YMW-0.05-90-100	441	289	730	0.18	0.20	0.38
YMW-0.1-90-100	60	395	454	0.03	0.36	0.39
YMW-0.15-90-100	0	251	251	0	0.23	0.23
YMW-0.2-90-100	0	333	333	0	0.31	0.31
YMW-0.05-90-100-B	804	312	1117	0.33	0.40	0.73
YMW-0.1-90-100-B	523	407	930	0.22	0.57	0.79
YMW-0.1-30-100-B	415	571	986	0.24	0.58	0.82
YMW-0.1-10-100-B	495	340	835	0.21	0.48	0.69
YMW-0.1-1-100-B	491	331	822	0.21	0.48	0.69
YMW-0.1-1-50-B	502	306	811	0.22	0.46	0.68
YMW-0.15-90-100-B	67	439	506	0.03	0.60	0.63
YMW-0.2-90-100-B	0	397	397	0	0.57	0.57
YMW-0.2-30-100-B	18	218	236	0.01	0.34	0.35
YMW-0.2-1-100-B	20	260	280	0.01	0.37	0.38
YMW-0.2-1-50-B	31	179	210	0.01	0.34	0.35
YMW-0.1-1-100-B ^d	-	272	931	0.27	0.25	0.52
YMW-0.15-90-100-B ^e	-	310	933	0.26	0.31	0.57

Unless otherwise stated, base washing was carried out using 0.2 M NaOH at 65°C for 0.5h. ^a t -plot method; ^b $V_{\text{total}} - V_{\text{micro}}$; ^c single point adsorption total pore volume at $p/p^0 = 0.99$. ^d Base washing carried out under application of MW using 0.2 M NaOH at 100°C for 1 min. ^e Base washing carried out under sonication using 0.2 M NaOH at 65°C for 1 min.

[0082] Figure 2 and Table 1 show the comprehensive analysis of the resulting samples by the MWAC method (using EDTA as chelating agent) after the base washing. The significant evaluation of mesoporosity in the resulting aluminosilicates is obvious, as depicted in Figures 2a–2d, by increasing the quantity of chelator in the MWAC technique. Figure 2a shows the clear development of hysteresis loops of MWAC treated samples as a function of EDTA quantity used, corresponding to evolution of mesopore PSDs (Figure 2b) and specific surface areas (Figure 2c).

For example, the increase of EDTA quantity from 0.05 M to 0.20 M resulted in the enlargement of specific mesopore volume by 76% and specific external surface area by 48%.

[0083] The developed MWAC protocol represents a top-down approach of modifying FAU zeolites, affecting the crystallinity (Figure 2d and 8), as well as causing the mass loss (Figure 2e), due to the post-synthetic dealumination/desilication. In the MWAC method, an inverse linear correlation between the relative crystallinity of the resulting materials and the chelator quantity was observed. A mesoporous aluminosilicate (YMW-0.2-90-100 with the typical type IV isotherm) having notably reduced crystallinity was produced when 0.2 M EDTA was used. The mass loss is inevitable for this top-down method to create mesoporosity from zeolite Y. Figure 2e shows the linear decrease of the solid yield as a function of chelator quantity, *i.e.* down to 70% after the MWAC treatment and to 34% after the base washing.

[0084] Control experiments using conventional HT methods^{4,5} were performed and the summary of porous properties are presented in Table 1. By comparing the relevant porous features of zeolites, the MWAC treated sample, *i.e.* YMW-0.1-90-100, shows the overall superiority over its counterparts of YHT-0.1-90-100 and YHT-0.1-360-100 obtained by conventional HT treatment with 0.1 M EDTA.

[0085] The developed MWAC protocol is generic and applicable to the systems of treating FAU Y using other chelating agents such as oxalic and citric acids (Table 2), as well as the systems of treating other types of zeolites, such as MFI (ZEM-5) and BEA (zeolite beta), with EDTA (Table 3).

Table 2. Analysis of pore structures (in terms of specific surface areas and pore volumes) of MWAC treated Y zeolites using different chelating agents (at 100°C for 1 min).

Sample	Specific surface areas [$\text{m}^2 \text{g}^{-1}$]			Specific pore volumes [$\text{cm}^3 \text{g}^{-1}$]		
	$S_{\text{micro}}^{\text{a}}$	$S_{\text{external}}^{\text{a}}$	BET	$V_{\text{micro}}^{\text{a}}$	$V_{\text{meso}}^{\text{b}}$	$V_{\text{total}}^{\text{c}}$
Parent Y	858	9	867	0.36	0.01	0.36
Citric acid (0.1 M) treated Y	665	108	773	0.27	0.12	0.39
Citric acid (0.14 M) treated Y	573	154	727	0.24	0.20	0.44
Oxalic acid (0.1 M) treated Y	640	172	812	0.27	0.16	0.43
Oxalic acid (0.3 M) treated Y	549	206	755	0.23	0.22	0.45
Tartaric acid (0.16 M) treated Y	602	140	742	0.25	0.15	0.40
Pentetic acid (0.14 M) treated Y	549	206	755	0.23	0.22	0.45

^a *t*-plot method; ^b $V_{\text{total}} - V_{\text{micro}}$; ^c single point adsorption total pore volume at $p/p^0 = 0.99$.

Table 3. Comprehensive analysis of pore structures of MFI (ZSM-5) and BEA (zeolite Beta) type zeolites and the according materials developed by the developed MWAC method (chelating agent = EDTA).

Sample	Si/ Al	Specific surface areas [m ² g ⁻¹]			Specific pore volumes [cm ³ g ⁻¹]		
		<i>S</i> _{micro} ^a	<i>S</i> _{external} ^a	BET	<i>V</i> _{micro} ^a	<i>V</i> _{meso} ^b	<i>V</i> _{total} ^c
MFI (ZSM-5)	20	323	33	356	0.16	0.02	0.18
MFIMW-0.08-5-75-B	23	313	267	580	0.15	0.3	0.49
MFIMW-0.10-5-75-B	25	286	312	598	0.14	0.45	0.62
BEA (Zeolite Beta)	12	632	18	650	0.48	0.01	0.50
BEAMW-0.10-3-90-B	15	480	340	860	0.45	0.48	1.02
BEAMW-0.15-3-90-B	18	380	450	830	0.38	0.65	1.12

^a *t*-plot method; ^b *V*_{total} – *V*_{micro}; ^c single point adsorption total pore volume at *p/p*⁰ = 0.99.

Infra-red spectroscopy

[0086] The infrared (IR) absorption spectroscopic analysis of materials is presented in Figure 3, revealing the fundamental difference in the structure change caused by the MWAC and HT treatments (using EDTA as chelating agent), respectively. The spectral feature at 580 cm⁻¹ belongs to the the signature double 6 rings (D6R) of FAU Y zeolites. Therefore, the absence of D6R bands in MWAC treated samples (Figure 3a) suggest the unique interaction between the MW and Brønsted acid sites siting on D6R of Y zeolite in the presence of chemical water (presumably at low pH values, e.g. pH ≈ 2.3 for 0.1 M EDTA in water). Conversely, D6R absorption bands of HT treated samples are clearly present, even after 6 h.

[0087] Figure 3a also shows that all stretching bands shift towards higher frequencies upon dealumination, regardless of the post-synthetic treatment conditions. However, the samples prepared by MWAC technique show a more significant shift in the main asymmetric vibration (at ca. 1000–1100 cm⁻¹) than the HT treated samples, confirming the effectiveness of the MWAC method for the isomorphous substitution of Al for Si. After the base washing (Figure 3b), the main asymmetric frequencies of most samples are comparable, apart from the heavily dealuminated sample YMW-0.2-90-100. From the position of the main asymmetric vibration, it is possible to predict empirically the fraction of the framework Al ratio, according to the correlation developed by Klinowski²⁵, as summarized in Figure 3c. The quantitative analysis of the framework Al shows that after the 90 min treatment at 100 °C, the developed MWAC method was 171% more efficient than the HT method to produce EFAL.

[0088] Based on IR measurements, it can be confirmed that the MWAC treatment attack D6R selectively and effectively (*i.e.* diminished band at 580 cm^{-1}) relative to the conventional HT treatments, resulting in the improved mesoporosity in the materials (Table 1).

Mesoporosity

[0089] Considering the nature of the interaction between water molecules and the electric component of MW via dipolar polarization, the MWAC process should be activated instantly upon the MW irradiation. Therefore, the MW treatment should be able to create mesoporosity in zeolite with a significantly reduced treatment time. It was determined that the MW treatment time indeed does not play a significant role in creating mesoporosity in zeolite Y, confirmed by various characterisation (Figure 4, 9 and 10). Comparable porous characteristics were obtained over the MWAC treatment time ranging from 90 min to 1 min at $100\text{ }^{\circ}\text{C}$, as shown in Figure 4a, with 30 min being the optimum time. YMW-0.1-30-100 possesses surprisingly high values of external surface area = $571\text{ m}^2\text{ g}^{-1}$, total pore volume = $0.80\text{ cm}^3\text{ g}^{-1}$ and mesopore volume = $0.58\text{ cm}^3\text{ g}^{-1}$. Nevertheless, 1 min MWAC treatment was sufficient to produce Y zeolite with mesoporosity far more superior than the conventional HT treatment, as evidenced by the comparison of cumulative pore volumes in Figure 4b, *i.e.* by 134% for the mesopore volume and by 142% for the external surface area. This is indeed a technical leap which can be further exploited to enable the superefficient creation of intracrystalline mesopores within zeolite crystals. When compared to the parent zeolite Y used in this work, the substantial enhancement in the total pore volume ($0.823\text{ vs. }0.357\text{ cm}^3\text{ g}^{-1}$), mesopore volume ($0.58\text{ vs. }0.01\text{ cm}^3\text{ g}^{-1}$) and external surface area ($571\text{ vs. }9\text{ m}^2\text{ g}^{-1}$) promoted by MWAC treatment only compromises about 34% of the native micropore volume in the parent Y.

[0090] Interestingly, with the EDTA concentration of 0.20 M, a mesoporous aluminosilicate (YMW-0.2-90-100) having notably reduced crystallinity was produced (due to severe dealumination, *i.e.* framework Al dropped by 77%) with the characteristic BET specific surface area of $300\text{ m}^2\text{ g}^{-1}$, mesopore volume of $0.57\text{ cm}^3\text{ g}^{-1}$ and uniform mesopore sizes of *ca.* 5 nm (Figure 2b), wider than that of mesopores MCM-41 (*ca.* 2–3 nm)²⁶.

[0091] The data illustrate that 1 min of MWAC treatment was sufficient to produce materials with comparable porous features to those obtained with extended MWAC treatment time. Figure 4b shows the cumulative pore volume of the mesoporous aluminosilicates from different conditions under MW, showing that about $0.30\pm0.03\text{ cm}^3/\text{g}$ pore volume was present for all materials, comparable to the pore volume of about $0.35\text{ cm}^3/\text{g}$ for parent zeolite Y. At the same temperature and with the same EDTA quantity, the HT treatment (6 h^5 or 18 h^8) was not able to produce such mesoporous aluminosilicates, which confirms that the MWAC process is indeed

highly effective to accelerate the dealumination of FAU zeolite. Differential pore size distribution of the materials is shown in Figure 4c, in which unimodal pore size distribution is clear for all samples from the MWAC treatment. Figure 5 shows the TEM micrographs of exemplar materials confirming the intracrystalline mesoporosity created by the MWAC method. Interestingly, under mild conditions at 50 °C, the same results can also be achieved after 1 min MWAC treatment, confirming the importance of the water-MW interaction.

Example 3 – Comparative studies

[0092] To highlight the significance of the inventor's contribution, the properties of the zeolites obtained via the MWAC technique were compared with those of modified zeolites described in the literature.

[0093] Table 4 summarises the state-of-the art work in the post synthesis treatment of FAU zeolite (zeolite Y as the example), including mainly two technologies of (i) sequential treatments combining chelation (using chelating agents such as EDTA and citric acid), base washing (mainly using sodium hydroxide, NaOH) and steaming and (ii) sequential treatments combining citric acid washing and surfactant-templated method (using cetyltrimethylammonium bromide, CTAB).

[0094] Technology (i) was developed by a research group at ETH Zurich led by Prof Javier Pérez-Ramírez. The method was based on the conventional hydrothermal system involving several hours of treatment, as show in Table 1. This conventional method was reproduced in the present work, showing comparable results in terms of porous properties of the resulting materials (see Samples no.1 and no.3).

[0095] Technology (ii) was developed by Prof. Javier Garcia-Martinez at University of Alicante. This method uses citric acid treatment as the pre-step to treat zeolite Y then uses CTAB (as surfactant) in base solution (commonly NH₄OH solution) to construct the mesoporosity. The resulting treated Y zeolites (see Samples no.9 and no.10) shows the typical porous structures.

7	Steamed (5 h, 600°C) then Na ₂ H ₂ -EDTA·2H ₂ O (0.11 M, 2 h, 85°C) treated Y ^f	³²	798	81	0.52	0.30	0.22
8	Steamed (5 h, 600°C) then NH ₄ NO ₃ (6 N, 6 h, 180°C) treated then Na ₂ H ₂ -EDTA·2H ₂ O (0.09 M, 2 h, 85°C) treated Y ^f	³³	790	165	0.57	0.26	0.31
Sequential citric acid treatment-surfactant-templated method							
9	Citric acid (1 h, 0.01 M, 20°C) treated then CTAB in NH ₄ OH (6 h, 150°C) treated Y ^a	³¹	916	243	0.53	0.37	0.16
10	Citric acid (1 h, 0.01 M, 20°C) treated then CTAB in NH ₄ OH (6 h, 150°C) treated Y ^g	³⁴	757	394	0.50	0.19	0.31
Sequential mineral acid washing-base washing method							
11	HCl (0.25 M, 6 h, 100°C) washed then NaOH (0.4 M, 0.5 h, 65°C) washed Y ^a	⁶	-	111	0.35	0.19	0.16

^a based on zeolite Y from Zeolyst, CBV 300, NH₄-form, nominal Si/Al = 2.6; ^b Brunauer-Emmett-Teller (BET) method; ^c *t*-plot method; ^d single point adsorption total pore volume at p/p⁰ = 0.99; ^e V_{pore} minus V_{micro} used as an approximation of V_{meso}; ^f based on zeolite Y from Zeolyst, CBV 400, H-form, nominal Si/Al = 2.6; ^g based on zeolite Y from Nankai catalyst company, nominal Si/Al = 3.07.

It is clear from the data presented in Tables 1 and 4 that the MWAC process of the invention is considerably shorter in duration than conventional hydrothermal treatment protocols.

It is also clear that a large number of the zeolites modified by the MWAC process have textural properties (e.g. specific pore volume (V_{pore}), mesopores volume (V_{meso}) and specific external surface area (S_{meso})) that are far superior to those materials produced by the state-of-the-art methods (even in spite of the significantly reduced treatment time).

Example 4 – Catalytic properties

Aldol condensation reaction

[0096] The intracrystalline mesoporosity in FAU zeolites is highly beneficial to their catalytic applications, especially in reactions involving bulky molecules. Parent microporous zeolites commonly experience diffusion limitations of reactant and product molecules, leading to low activity and potential deactivation. Selected materials from this work were tested using an aldol condensation reaction for producing a bulky fragrance chemical, *i.e.* jasminaldehyde, showing outstanding catalytic activity and selectivity of materials from the MWAC treatment relative to that of parent Y and HT treated Y. For example, YMW-0.1-30-100 exhibited the highest catalytic activity among the tested catalysts (*i.e.* 79% conversion with 40% selectivity to jasminaldehyde (Figure 6). Conversely, for the parent Y and HT treated Y, only <20% selectivities to jasminaldehyde were obtained.

Hydrocarbon cracking

[0097] Since Y zeolite is commonly used for fluid catalytic cracking (FCC), the ability of YMW-0.1-30-100-B to crack 1,3,5-triisopropylbenzene (TIPB) at 350 °C was tested, and compared with parent Y and HT treated Y. The cracking activity of catalysts was evaluated using the TIPB conversion and the selectivity for the deep cracking products, *i.e.* the mixture of benzene, toluene, and xylenes (BTX). Cumene, on the other hand, is considered as the undesirable pre-cracking product. Again, the catalyst prepared by the MWAC process shows the best catalytic performance with the highest selectivity to BTX but zero selectivity to cumene, whereas the parent Y and HT treated Y deactivate over the course of the cracking, as well as showing selectivity to cumene, indicating insufficient cracking of TIPB (Figure 7).

Acidity studies

[0098] Ammonia temperature-programmed desorption (NH₃-TPD) and pyridine Fourier transform infrared (Py-FTIR) analyses were used to understand the acidic properties of selected samples, showing that the MWAC method is able to preserve the total acidity, especially Brønsted acidity, during the treatment (Tables 5 and 6). Brønsted acidity of zeolites is particularly important for their application in cracking reactions²⁸. Py-FTIR results (Table 6 and Figure 12) show that MWAC Y zeolites possess higher concentrations of Brønsted acidity than the HT treated sample (YHT-0.1-360-100-B). Therefore, the excellent catalytic activity of the MWAC treated Y zeolites in cracking reactions compared with the parent FAU Y zeolite and the HT treated Y zeolites is likely due to the combination of highly developed mesoporosity and preserved acidity by the MWAC protocol, which leads to efficient diffusion and reaction within the porous network of the MWAC treated materials, as well as preventing the coke formation. In Figure 13, by characterizing the weight loss in the temperature range of >200 °C, only ca. 6 wt.% was measured for the MWAC treated materials, while about 7.5 wt.% for HY-2.6 and HT treated sample, representing about 25% increase in coke formation. In addition, the MWAC treated FAU Y also showed excellent hydrothermal stability (steaming at 600 °C for 4 h), having important technological implications for many other catalytic reactions.

Table 5. NH₃-TPD analysis of acidity property of parent Y zeolite and materials from the MWAC and HT treatment (chelating agent = EDTA) of Y zeolite.

Catalyst	Temperature at maximum [°C]		Weak acidity ^a	Strong acidity ^b	Total acidity
	First peak	Second peak	[mmol g ⁻¹]	[mmol g ⁻¹]	[mmol g ⁻¹]
HY-2.6	209.1	320.4	1.053	0.819	1.872
YHT-0.1-360-100-B	207.6	301.5	0.492	0.314	0.721
YMW-0.1-30-100-B	204.7	318.6	0.333	0.453	0.786
YMW-0.1-1-100-B	214.8	319.8	0.585	0.194	0.779

^aacidity of the first peak; ^bacidity of the second peak

Table 6. Py-FTIR analysis of acidity property of parent Y zeolite and materials from the MWAC and HT treatment of Y zeolite.

Sample	Weak acidity ^a		Strong acidity ^b		Total acidity	
	[mmol g ⁻¹]		[mmol g ⁻¹]		[mmol g ⁻¹]	
	Brønsted ^c	Lewis ^c	Brønsted ^c	Lewis ^c	Brønsted ^c	Lewis ^c
HY-2.6	0.018	1.035	0.704	0.115	0.721	1.151
YHT-0.1-360-100-B	0.121	0.320	0.251	0.029	0.372	0.349
YMW-0.1-30-100-B	0.003	0.330	0.390	0.063	0.393	0.393
YMW-0.1-1-100-B	0.454	0.050	0.156	0.038	0.610	0.169

^aacidity of the first peak in the NH₃-TPD spectra; ^b acidity of the second peak in the NH₃-TPD spectra; ^c determined by the Py-FTIR.

Example 5 – Comparison of the modified Y zeolites from different microwave-assisted treatments using inorganic acids and carboxylic acids

[0099] Table 7 shows the porous properties of the modified Y zeolites from the treatments using the mineral (or inorganic) acids (e.g. hydrochloric and nitric acids) facilitated by the microwave irradiation at 100 °C. Specifically, 0.1 M hydrochloric and nitric acids were used in the treatment which were performed for different variations (i.e. 1 or 30 min). The resulting modified zeolites only show insignificant mesopores volumes (i.e. $V_{\text{pore}} - V_{\text{micro}}$) at $<0.1 \text{ cm}^3 \text{ g}^{-1}$, which cannot be claimed as the mesoporous zeolites.

Table 7: Comparative analysis of the modified zeolites (by N₂ physisorption) using the microwave-assisted treatments with inorganic acids.

Catalyst	Surface area [m ² g ⁻¹]		Pore volume [cm ³ g ⁻¹]		Pore size [nm]
	BET	S_{meso}	V_{pore}	$V_{\text{pore}} - V_{\text{micro}}$	
HCl-30 (Hydrochloric acid, 0.1 M)	719	74	0.33	0.03	2.7
HNO ₃ -1 (Nitric acid, 0.1 M)	796	109	0.38	0.06	2.7
HNO ₃ -30 (Nitric acid, 0.1 M)	835	137	0.41	0.07	2.7

[00100] Table 8 shows the porous properties of the modified Y zeolites from the MWAC treatment using different carboxylic acids (including citric acid (CA), oxalic acid (OA), tartaric acid (TA) and pentetic acid (DA)) at 100 °C. Either the concentration or treatment time were varied

show the effectiveness of the MWAC method, employing different chelating agents, for producing the modified Y zeolites with mesoporosity. All the resulting modified zeolites show the development of mesopores volumes (i.e. $V_{\text{pore}} - V_{\text{micro}}$) at $>0.1 \text{ cm}^3 \text{ g}^{-1}$.

Table 8: Comparative analysis of the modified zeolites (by N₂ physisorption) using the MWAC method with different organic acids.

Catalyst		Surface area [$\text{m}^2 \text{ g}^{-1}$]		Pore volume [$\text{cm}^3 \text{ g}^{-1}$]			Pore size [nm]
		BET	S_{meso}	V_{pore}	V_{micro}	$V_{\text{pore}} - V_{\text{micro}}$	
CA-1min	(Citric acid, 0.1 M)	773	108	0.39	0.27	0.12	5.0
CA-5min	(Citric acid, 0.1 M)	792	126	0.41	0.28	0.13	2–11
CA-10min	(Citric acid, 0.1 M)	784	130	0.42	0.27	0.15	5–7.6
CA-30min	(Citric acid, 0.1 M)	785	157	0.44	0.26	0.18	5.0–9.5
CA-1min	(Citric acid, 0.14 M)	727	154	0.44	0.24	0.2	4.9–8.7
CA-1min	(Citric acid, 0.16 M)	606	176	0.40	0.20	0.2	4.5–8.6
CA-1min	(Citric acid, 0.20 M)	162	101	0.18	0.03	0.15	5.0–12.4
OA-1min	(Oxalic acid, 0.1 M)	812	172	0.43	0.27	0.16	3.1
OA-5min	(Oxalic acid, 0.1 M)	807	204	0.45	0.25	0.2	2.7
OA-10min	(Oxalic acid, 0.1 M)	862	195	0.47	0.28	0.19	2.7
OA-30min	(Oxalic acid, 0.1 M)	825	124	0.41	0.29	0.12	2.7
OA-1min	(Citric acid, 0.14 M)	786	132	0.40	0.27	0.13	2.7
OA-1min	(Oxalic acid, 0.16 M)	774	148	0.42	0.26	0.16	3.1
OA-1min	(Oxalic acid, 0.20 M)	795	142	0.42	0.27	0.15	2.7–8.7

OA-1min (Oxalic acid, 0.30 M)	650	163	0.39	0.20	0.19	6.8
DA-1min (Pentetic acid, 0.12 M)	755	206	0.45	0.23	0.22	3.5–7.1
DA-1min (Pentetic acid, 0.14 M)	545	220	0.35	0.14	0.21	2–3
DA-1min (Pentetic acid, 0.16 M)	414	214	0.30	0.08	0.22	3.9
TA-1min (Tartaric acid, 0.14 M)	804	138	0.42	0.28	0.14	2–10
TA-1min (Tartaric acid, 0.16 M)	742	140	0.40	0.25	0.15	2.7–7.1

[00101] The data in Tables 7 and 8 shows that inorganic acids are less effective in the MWAC method. The present invention deals with microwave-assisted chelation instead of interaction of zeolites under microwave with a source of hydrogen ions. Typical chelating agents such as mono carboxylic, dicarboxylic and polycarboxylic acids including saturated and unsaturated, substituted and unsubstituted acids (e.g. amino carboxylic acids) can find utility in the practice of the invention. In addition to EDTA, organic chelating agents such as citric acid (CA), oxalic acid (OA), tartaric acid (TA) and pentetic acid (DA) can be effective in producing mesopores using the MWAC method.

[00102] While specific embodiments of the invention have been described herein for the purpose of reference and illustration, various modifications will be apparent to a person skilled in the art without departing from the scope of the invention as defined by the appended claims.

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CLAIMS

1. A process for the modification of a zeolite, the process comprising the steps of:
 - a) providing a zeolite;
 - b) modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent, and subjecting the resulting mixture to microwave radiation; and
 - c) isolating the modified zeolite.
2. The process of claim 1, wherein the zeolite provided in step a) has a framework type selected from the group consisting of FAU, BEA and MFI, preferably FAU.
3. The process of claim 1 or 2, wherein the zeolite provided in step a) is Zeolite Y.
4. The process of claim 1, 2 or 3, wherein the at least one chelating agent is an organic acid.
5. The process of any preceding claim, wherein the at least one chelating agent has 2 – 8 donor groups.
6. The process of any preceding claim, wherein the at least one chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid (EDTA), citric acid, tartaric acid, pentetic acid and oxalic acid.
7. The process of any preceding claim, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.05 M to 0.22 M.
8. The process of any preceding claim, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.09 M to 0.21 M.
9. The process of any preceding claim, wherein step b) is performed at a temperature of 25 – 125°C.
10. The process of any preceding claim, wherein the aqueous mixture that is contacted with the zeolite in step b) is basic.

11. The process of any preceding claim, wherein step c) comprises isolating the modified zeolite from:
 - i) the aqueous mixture of at least one chelating agent, and/or
 - ii) one or more reaction by-products formed during step b).
12. The process of claim 11, wherein the modified zeolite is isolated by centrifugation.
13. The process of claim 11 or 12, wherein the modified zeolite is isolated by washing the modified zeolite with a basic solution.
14. The process of any one of claim 1 to 13, wherein
 - step a) comprises providing a zeolite having a FAU framework type;
 - step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent having at least two carboxyl or carboxylate donor groups, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.075 M to 0.22 M.
15. The process of any one of claim 1 to 13, wherein
 - step a) comprises providing a zeolite, wherein the zeolite is Zeolite Y;
 - step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising at least one chelating agent selected from EDTA, citric acid, oxalic acid, tartaric acid and pentetic acid, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the at least one chelating agent in the aqueous mixture is 0.03 M to 0.24 M; and
 - step c) comprises isolating the modified zeolite resulting from step b) by centrifugation or filtration and then washing the modified zeolite with a basic solution, wherein the basic solution has a pH of 11 – 14.
16. The process of any one of claim 1 to 13, wherein
 - step a) comprises providing a zeolite, wherein the zeolite is Zeolite X or Zeolite Y;
 - step b) comprises modifying the zeolite by contacting it with an aqueous mixture comprising EDTA, and subjecting the resulting mixture to microwave radiation, wherein the concentration of the EDTA in the aqueous mixture is 0.02 M to 0.25 M; and
 - step c) comprises isolating the modified zeolite resulting from step b) by centrifugation or filtration and then washing the modified zeolite with a basic solution, wherein the basic solution has a pH of 11 – 14.

17. A zeolite Y having a specific mesopore volume of at least $0.47 \text{ cm}^3 \text{ g}^{-1}$.
18. The zeolite Y of claim 17, wherein the zeolite has a specific mesopore volume of at least $0.470 \text{ cm}^3 \text{ g}^{-1}$.
19. The zeolite Y of claim 17 or 18, wherein the total pore volume of the zeolite is $\geq 0.40 \text{ cm}^3 \text{ g}^{-1}$.
20. The zeolite Y of claim 17, 18 or 19, wherein the zeolite has a specific external surface area of at least $240 \text{ m}^2 \text{ g}^{-1}$.
21. The zeolite Y of claim any one of claims 17 to 20, wherein the zeolite has a BET surface area of at least $300 \text{ m}^2 \text{ g}^{-1}$.
22. The zeolite Y of claim any one of claims 17 to 21, wherein the zeolite has a Si/Al ratio of 1:1 to 18:1.
23. Use of a zeolite as claimed in any one of claims 17 to 22 in one or more applications selected from catalysis, sorption, ion exchange, molecular sieving, water purification, odour control and desiccation.
24. The use of claim 23, wherein the zeolite is used as a catalyst, preferably in the catalytic cracking of hydrocarbons.
25. A catalytic cracking process comprising the step of:
 - a) cracking a hydrocarbon feed stream in the presence of a zeolite as claimed in any one of claims 17 to 22.

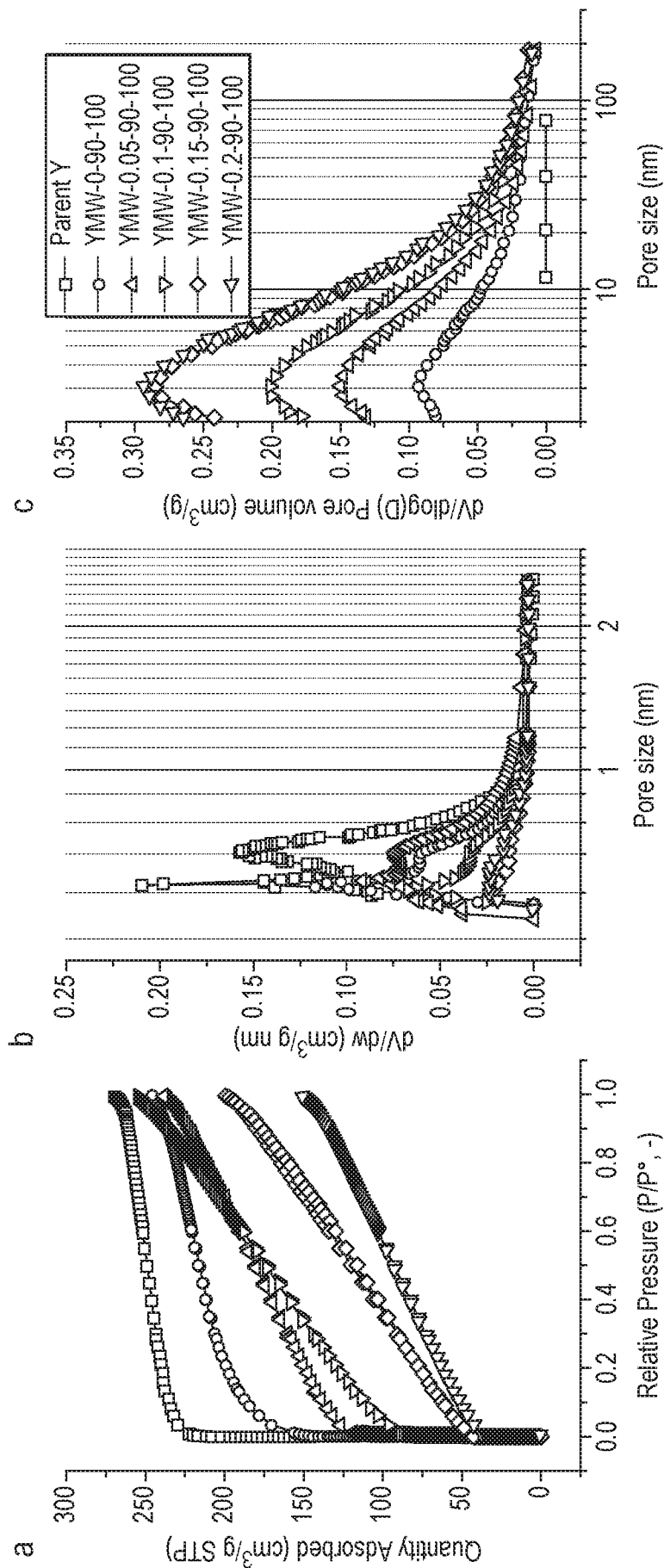


FIG. 1

2 / 14

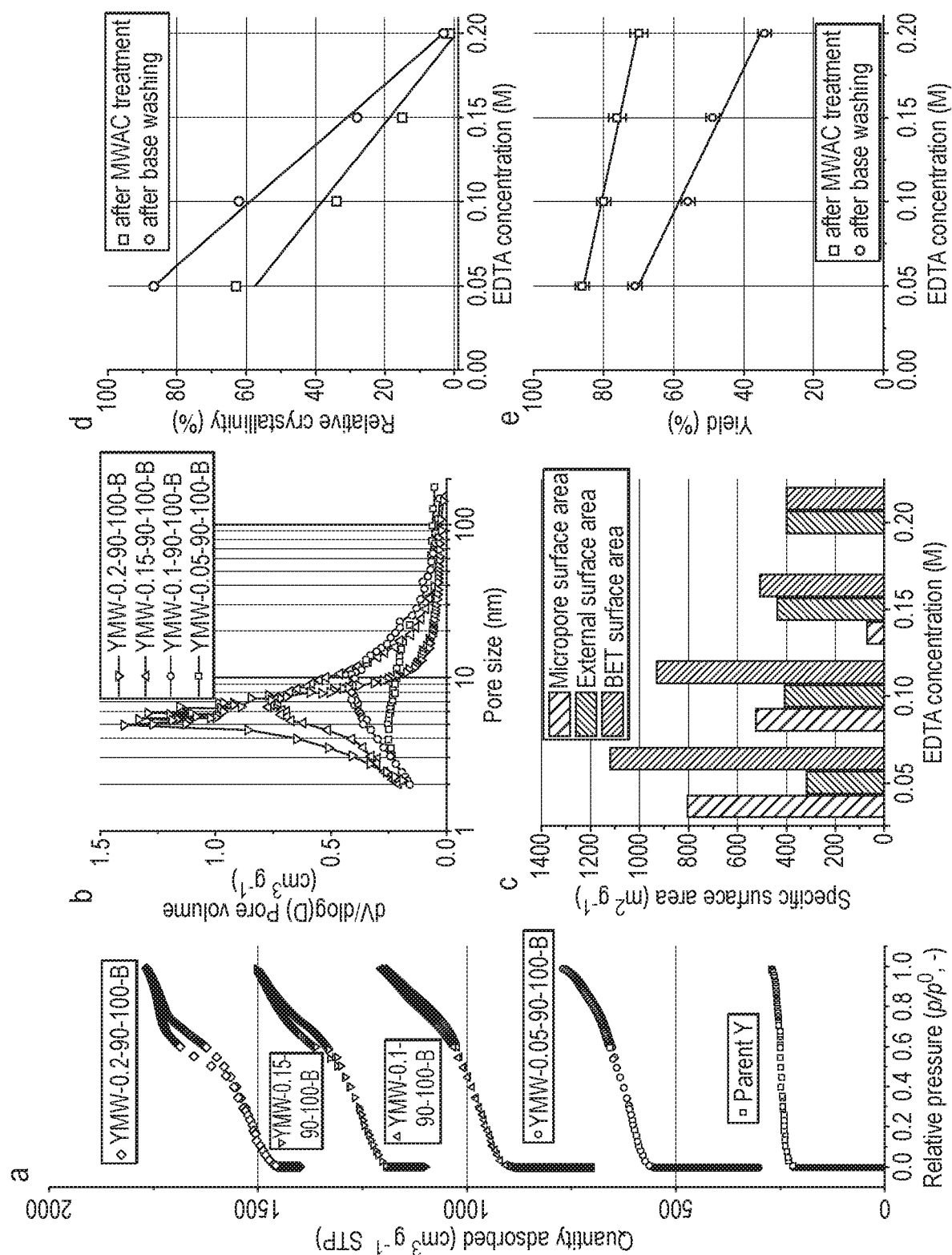


FIG. 2

3 / 14

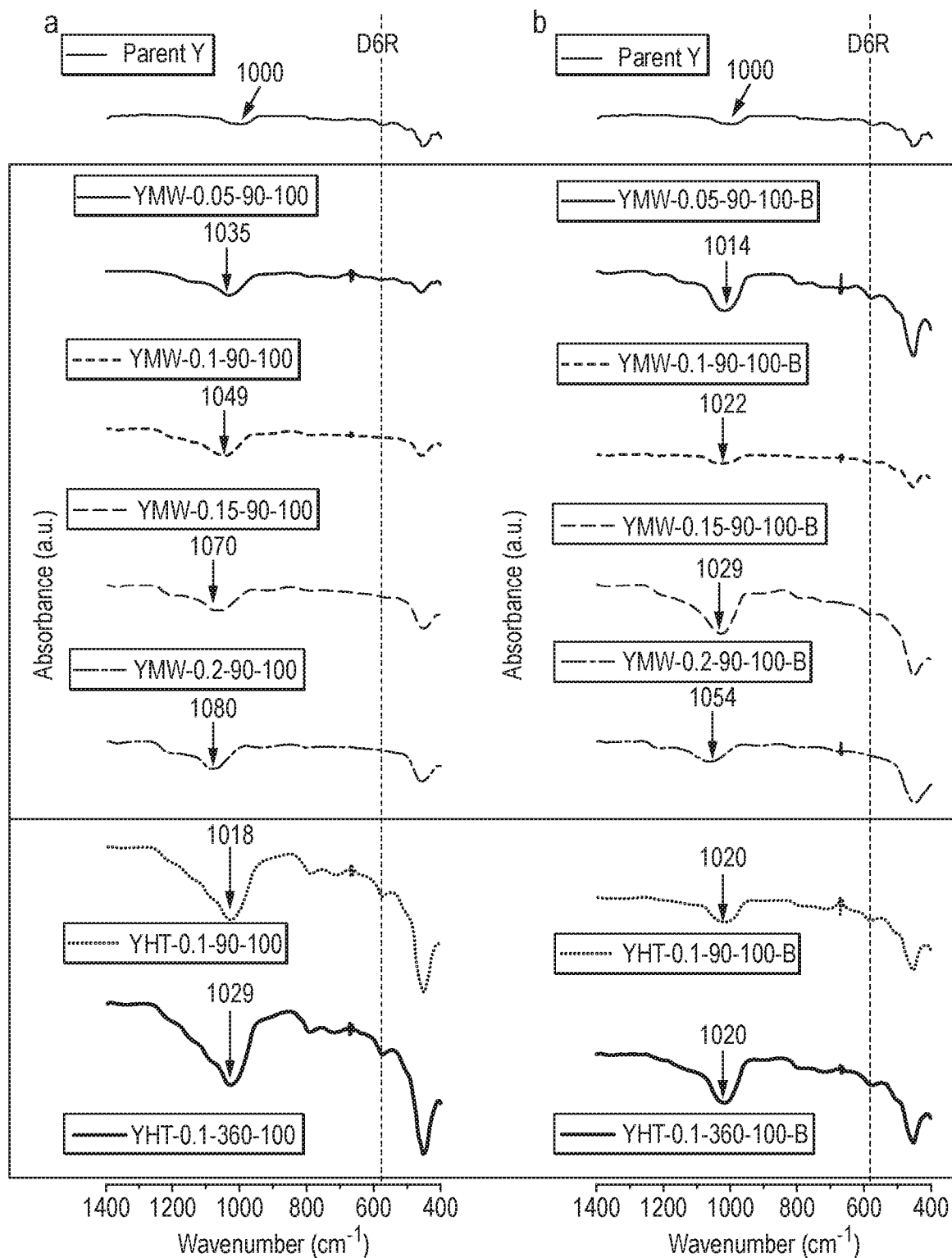


FIG. 3

4 / 14

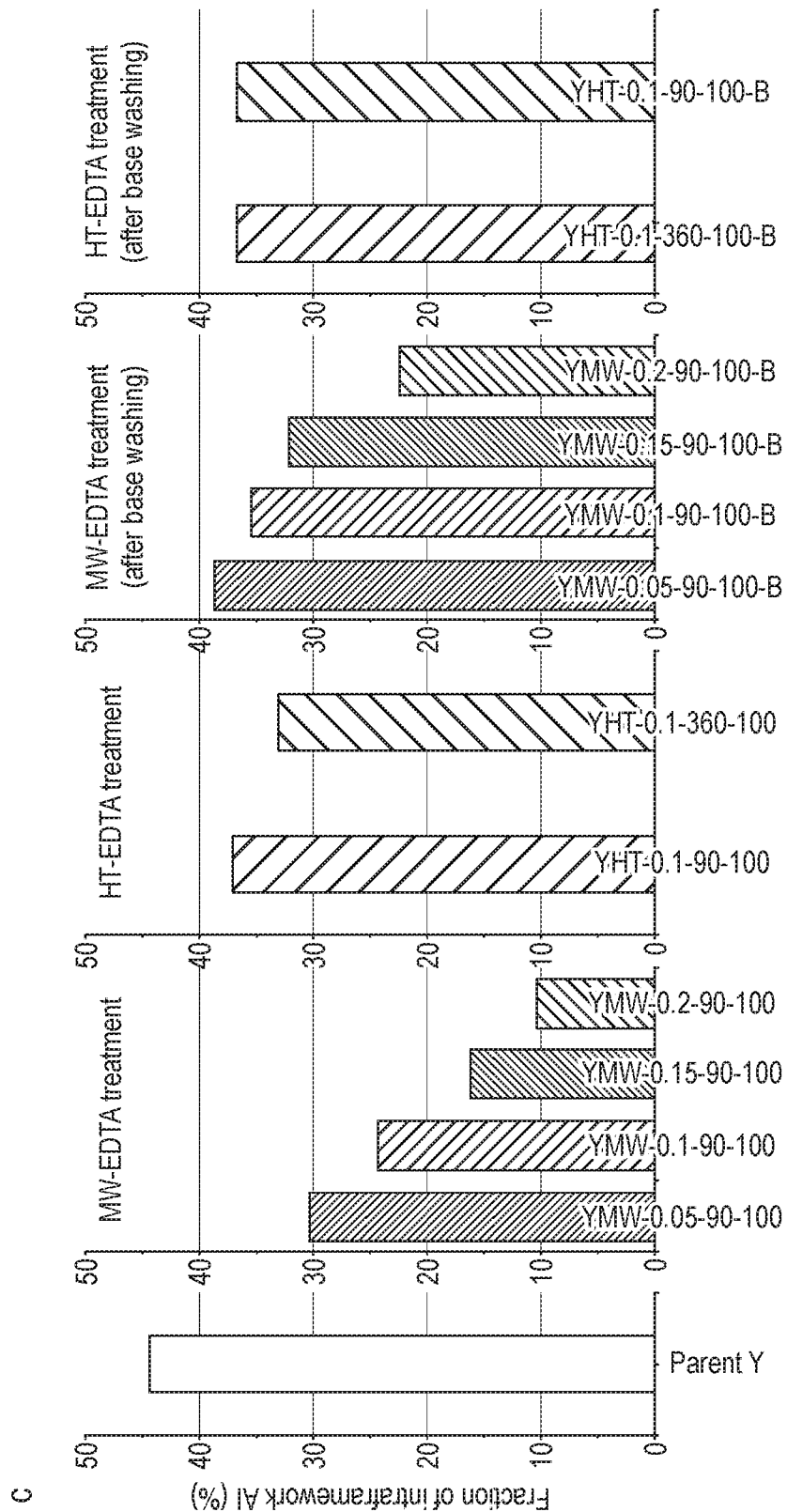
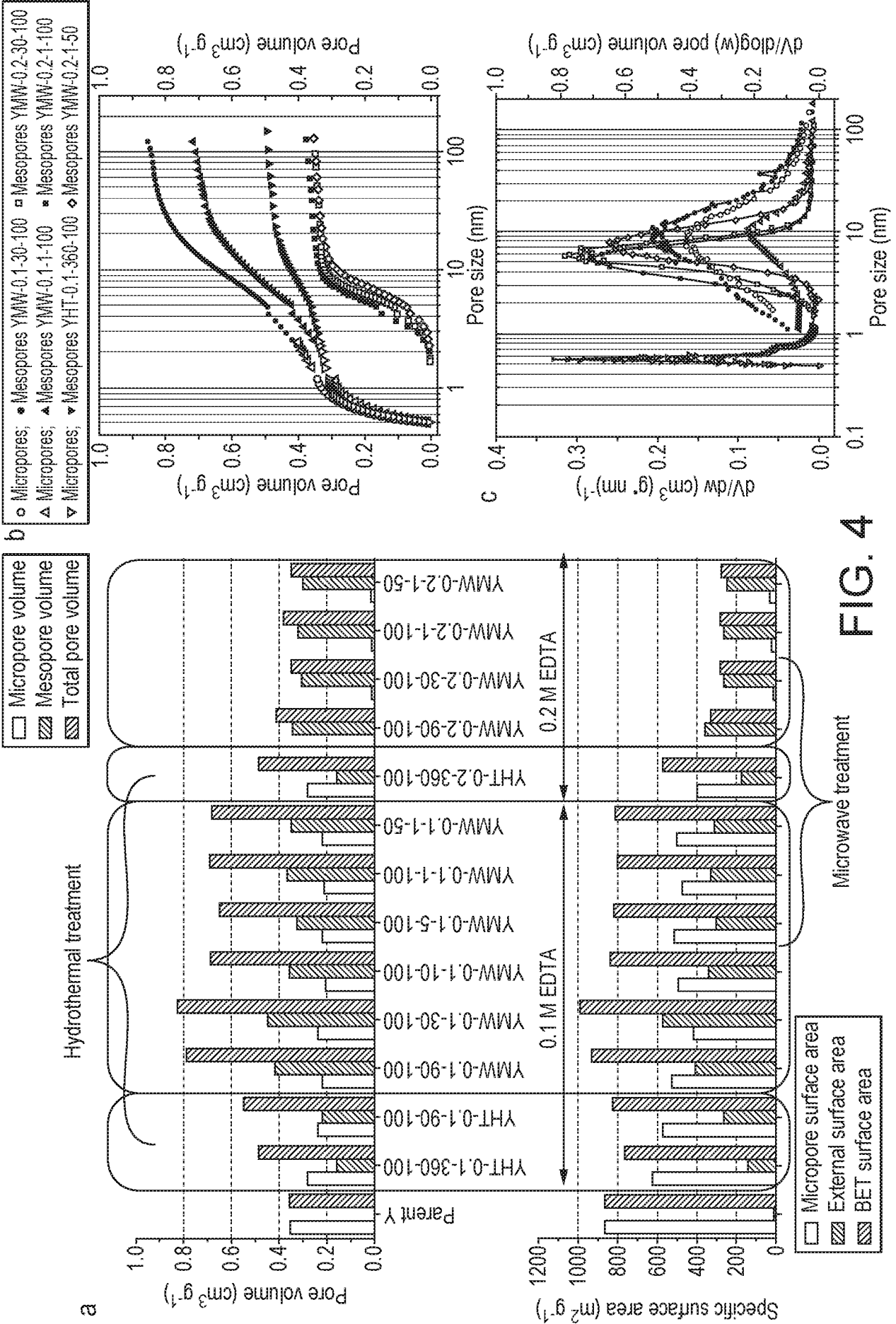


FIG. 3 (Cont.)



6 / 14

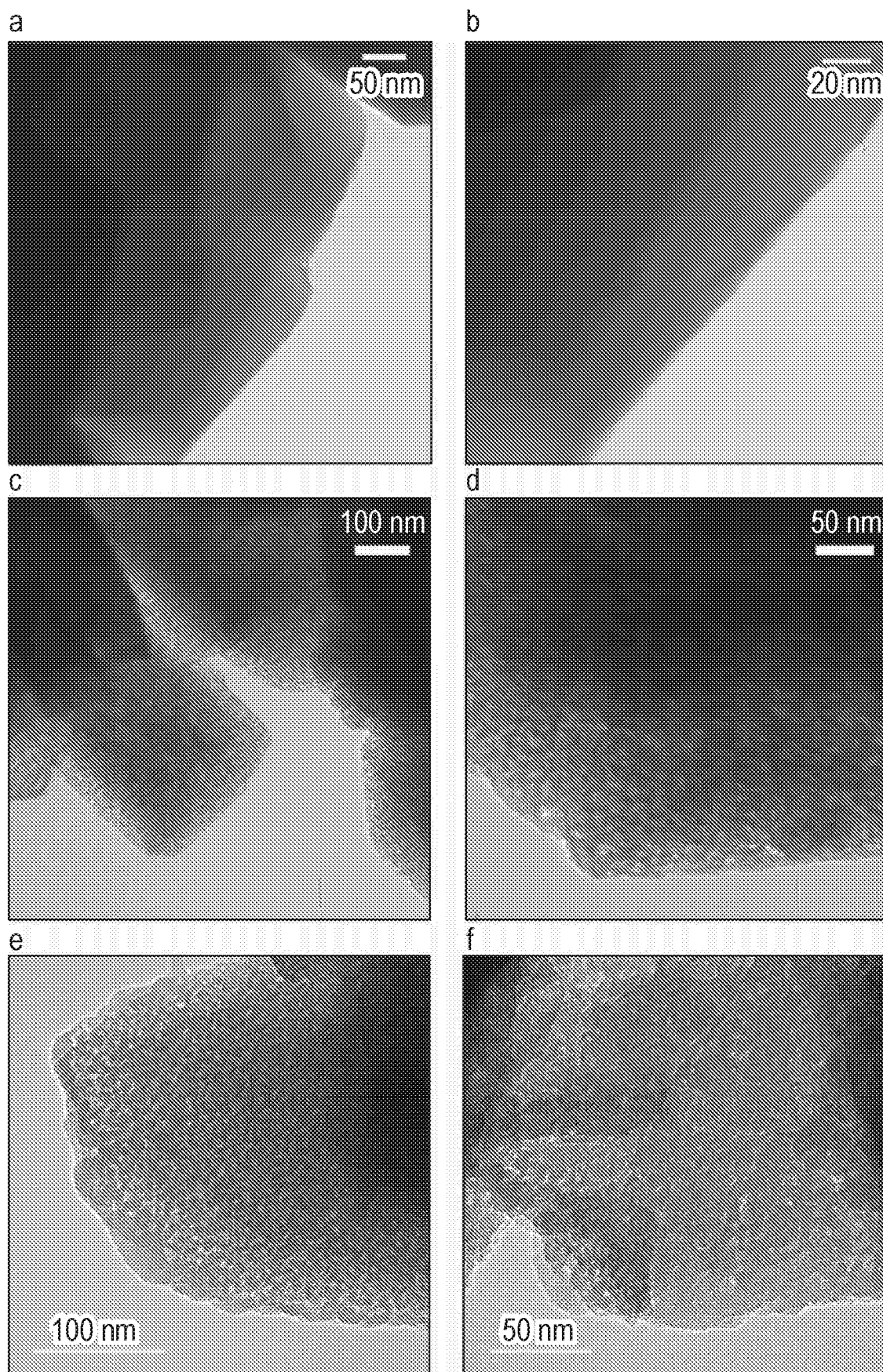


FIG. 5

7 / 14

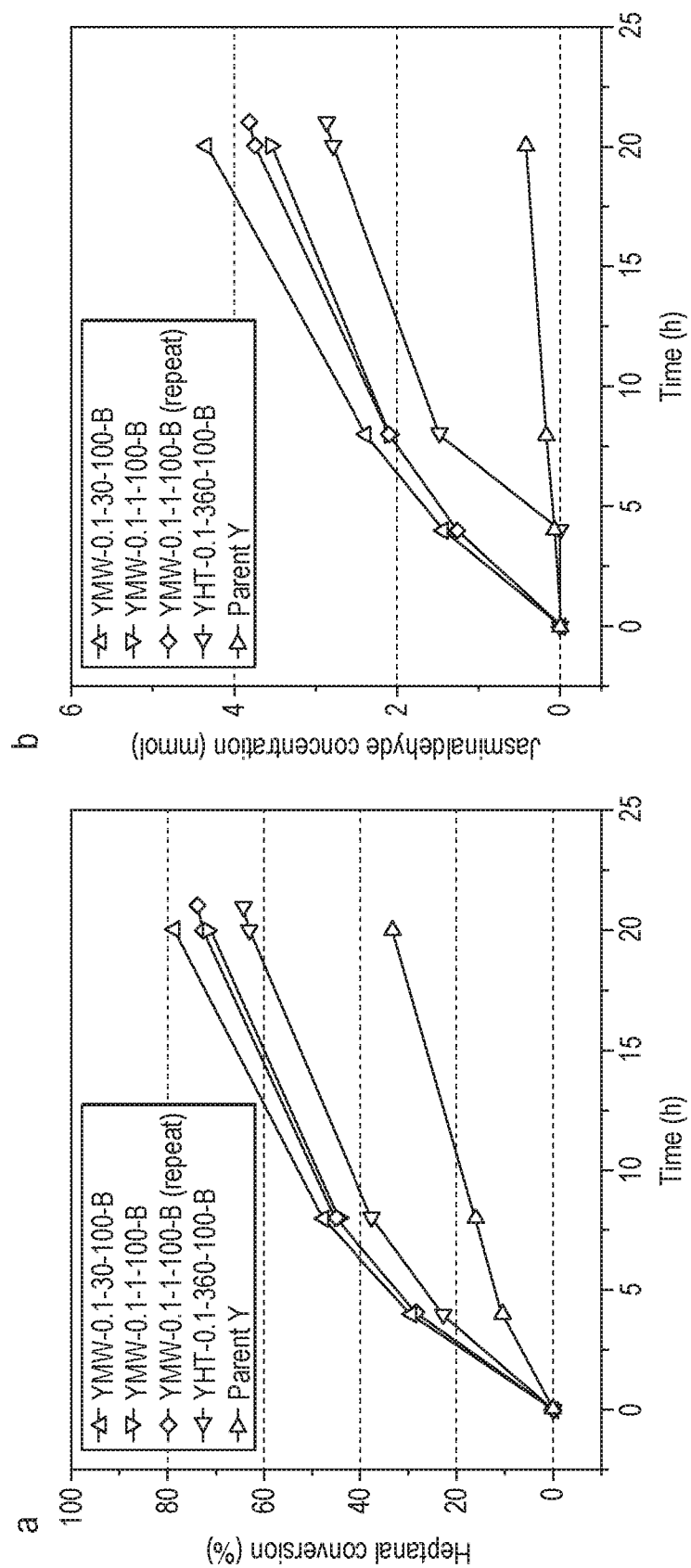


FIG. 6

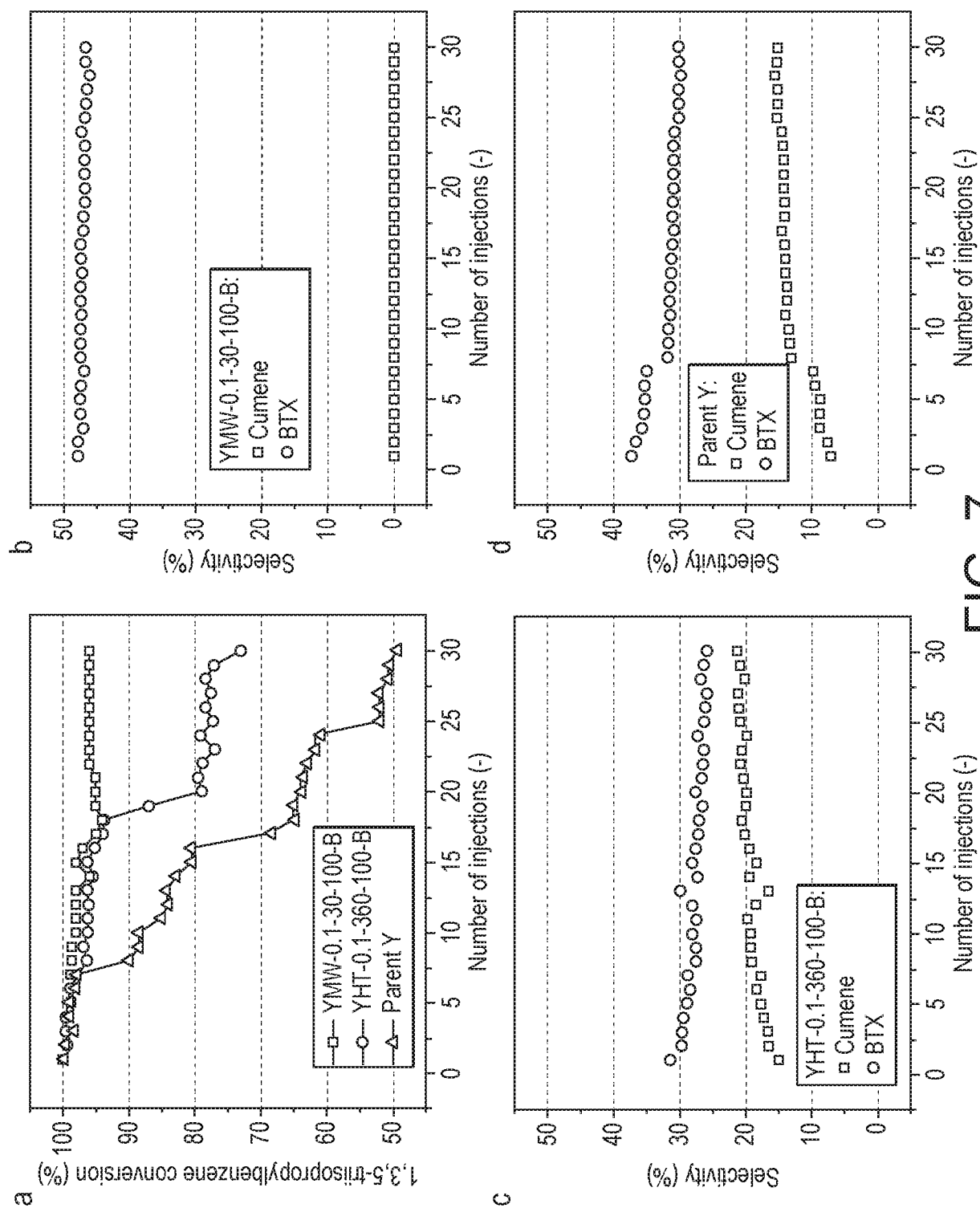


FIG. 7

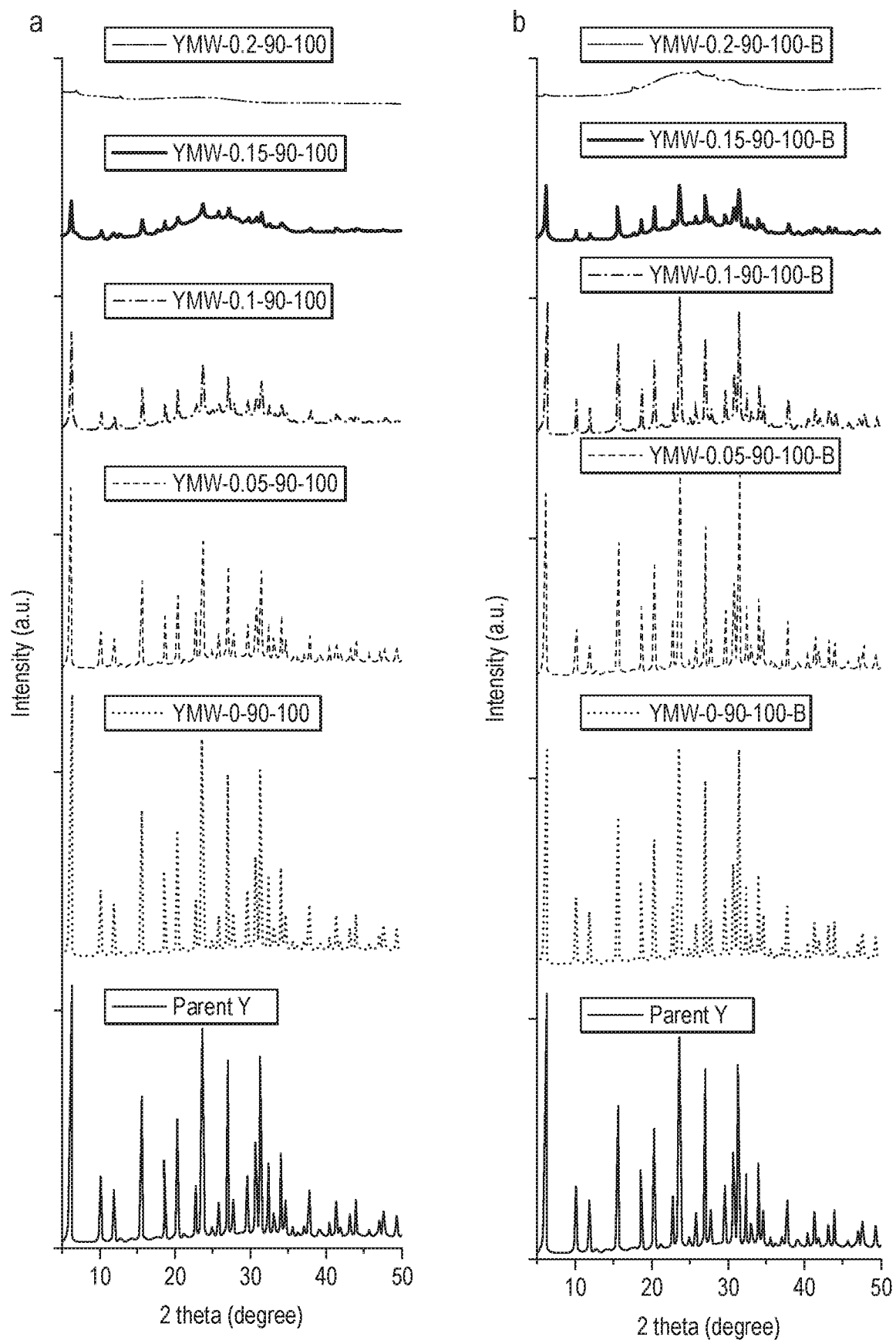


FIG. 8

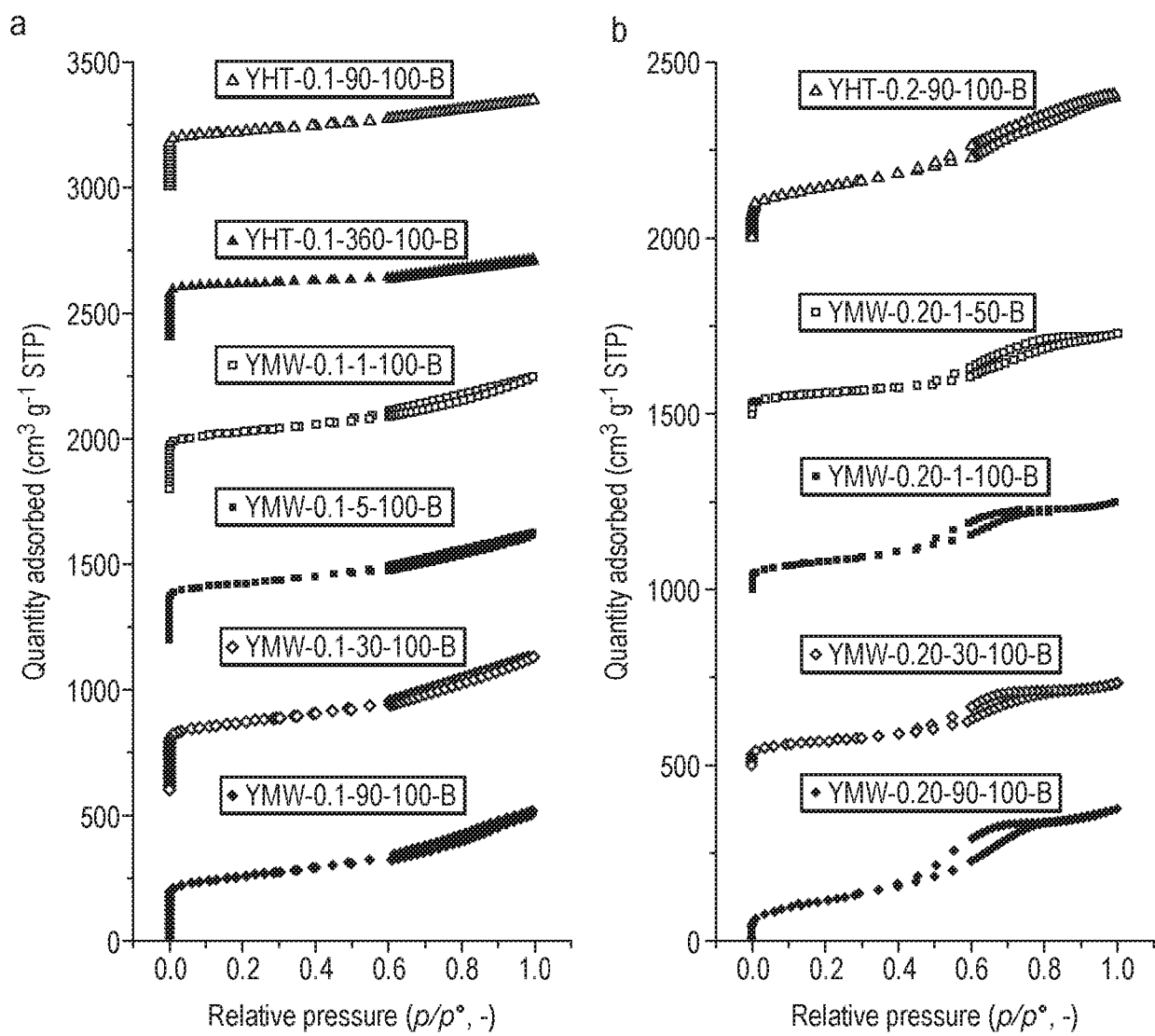


FIG. 9

11 / 14

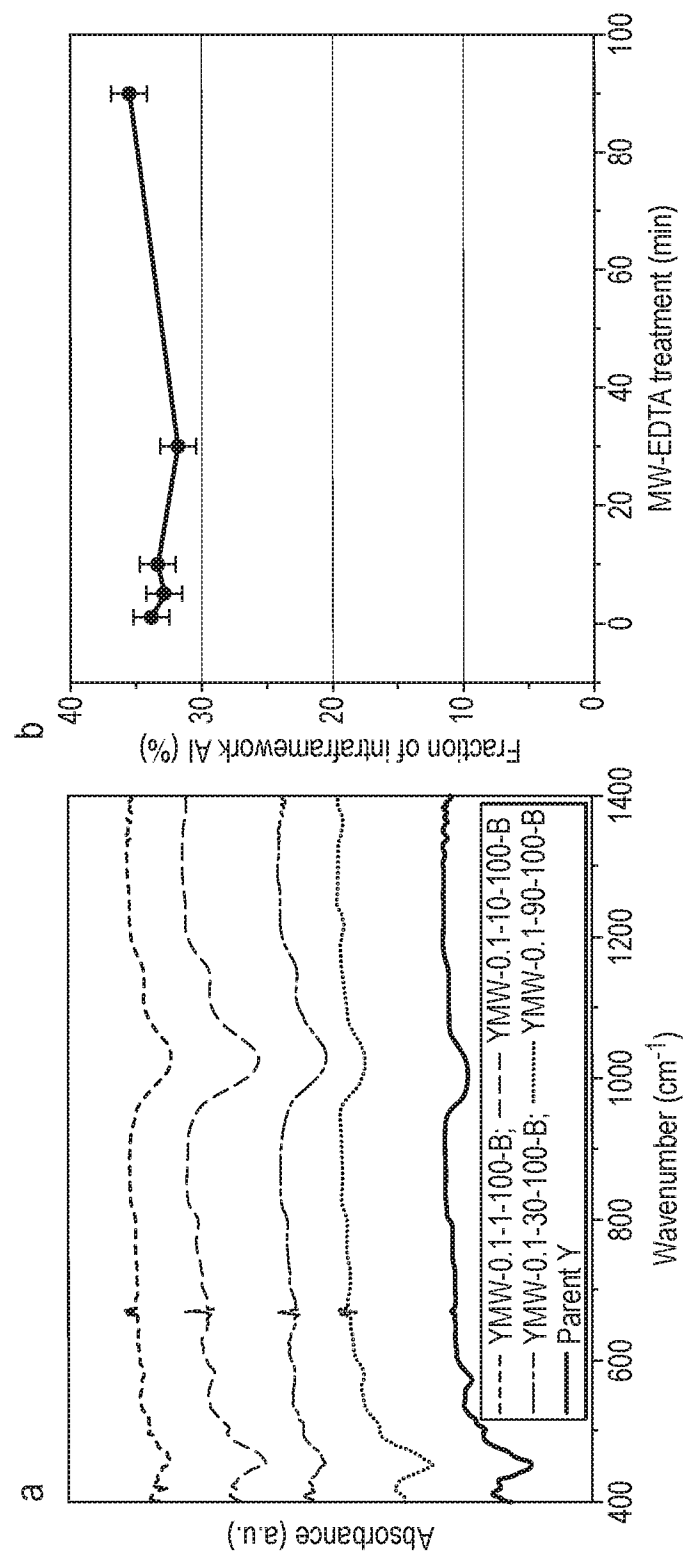


FIG. 10

12 / 14

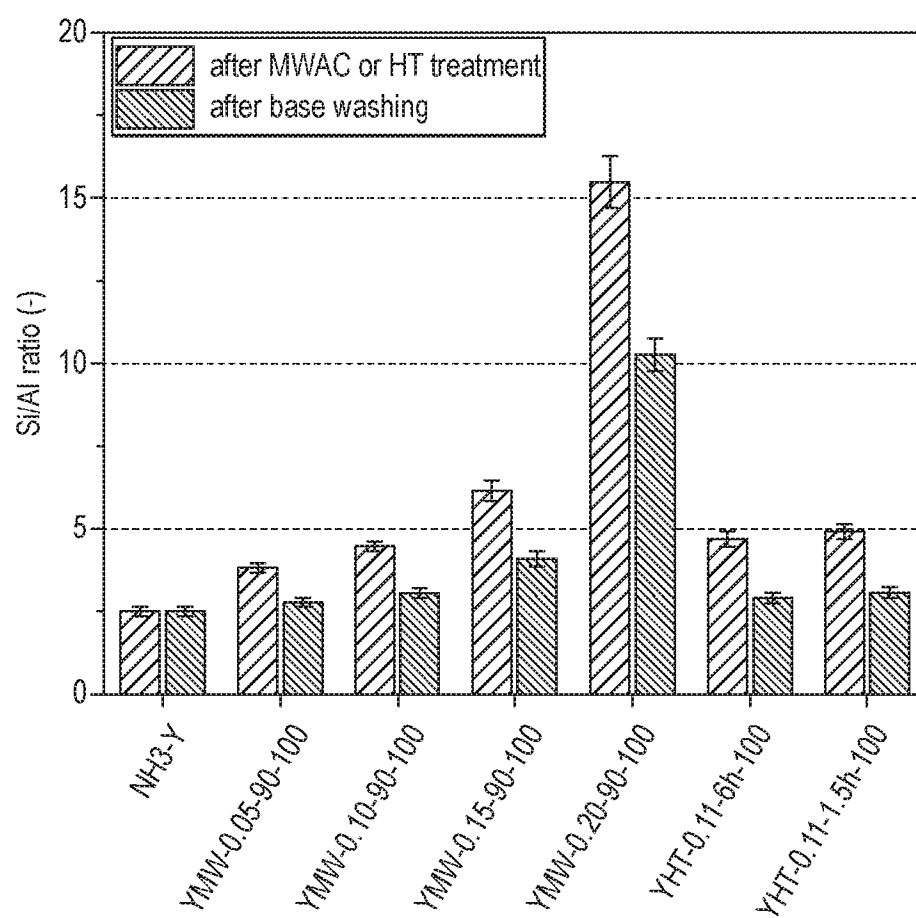


FIG. 11

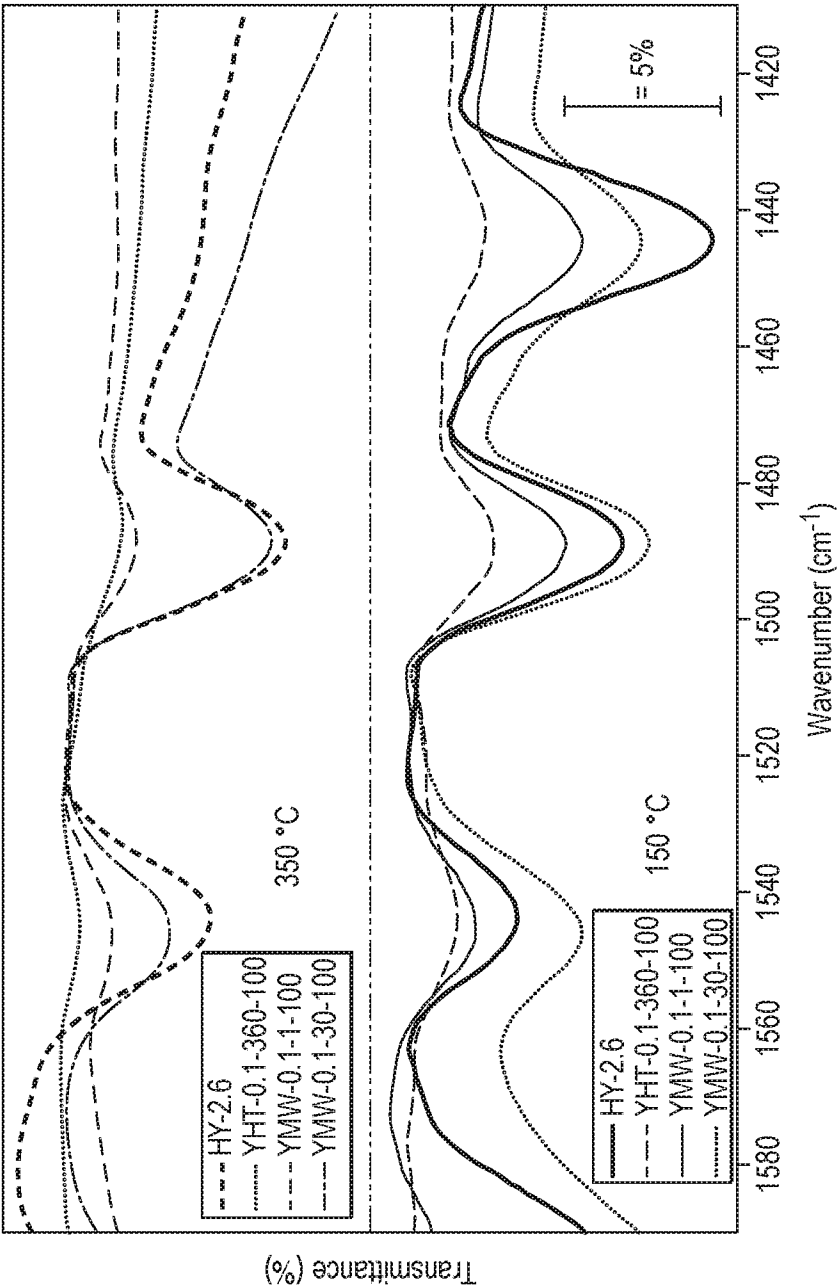


FIG. 12

14 / 14

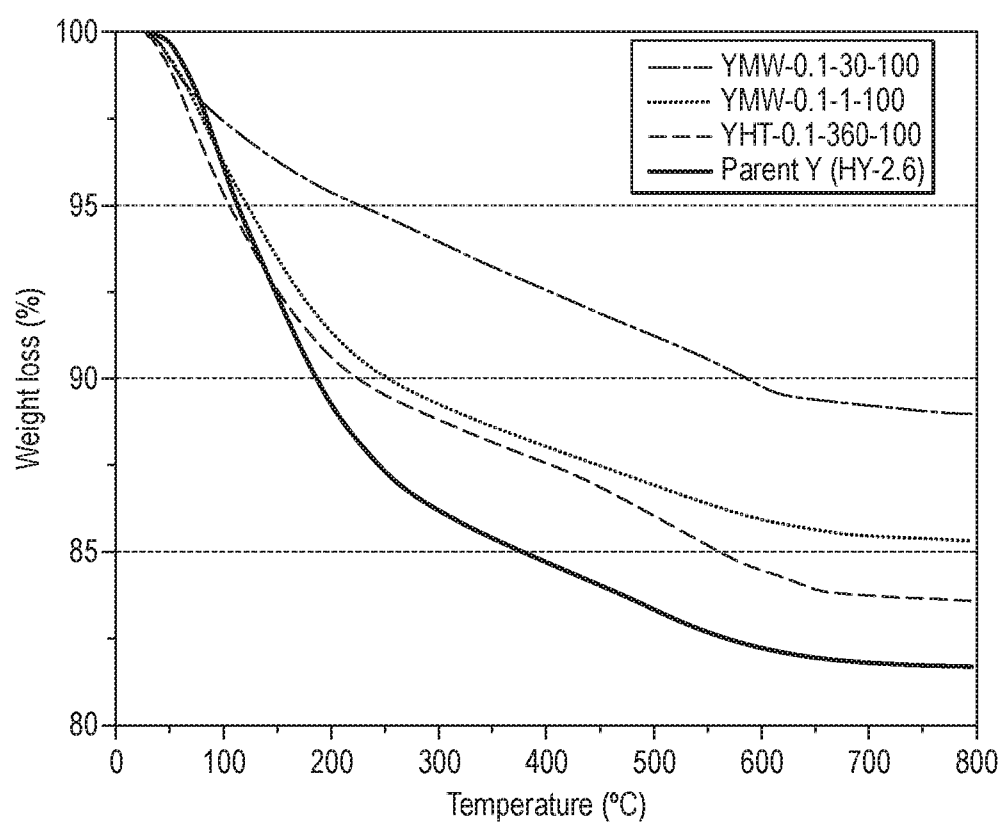


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/052566

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C01B39/02	B01J29/08	C01B39/24 C10G47/16 C10G49/08
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 C10G B01J		
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, COMPENDEX, INSPEC		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	B.M. CHANDRA SHEKARA ET AL: "Dealumination of Zeolite BEA under Microwave Irradiation", ACS CATALYSIS, vol. 1, no. 3, 4 March 2011 (2011-03-04), pages 193-199, XP055642688, US	1,2,4-13
A	ISSN: 2155-5435, DOI: 10.1021/cs1000448 page 194, left-hand column, lines 4-35; figures 1-4 the whole document ----- -/--	14-25
☒ 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 15 November 2019		Date of mailing of the international search report 22/11/2019
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 Follens, Lana

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/052566

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HASAN ZUBAIR ET AL: "Desilication of ZSM-5 zeolites for mesoporosity development using microwave irradiation", MATERIALS RESEARCH BULLETIN, ELSEVIER, KIDLINGTON, GB, vol. 61, 27 October 2014 (2014-10-27), pages 469-474, XP029112225, ISSN: 0025-5408, DOI: 10.1016/J.MATERRESBULL.2014.10.058	1-13
A	cited in the application page 470, left-hand column, line 2 - right-hand column, line 2; tables 1-2 the whole document	14-25
X	----- CN 106 315 609 A (UNIV LIAONING SHIHUA) 11 January 2017 (2017-01-11)	1-16
A	example 4 abstract the whole document	17-25
X	----- CN 104 923 286 B (ANHUI HAIDE PETROCHEMICAL CO LTD) 24 May 2017 (2017-05-24)	1,2,4-13
A	abstract examples 1-3 the whole document	14-25
X	----- AWALA H ET AL: "Template-free nanosized faujasite-type zeolites", NATURE MATERIALS,, vol. 14, no. 4, 5 January 2015 (2015-01-05), pages 447-451, XP002768408, DOI: 10.1038/NMAT4173	17-19, 21-25
A	cited in the application page 449, left-hand column, line 14 - page 450, right-hand column, line 44; figures 4,5 the whole document & Hussein Awala ET AL: "Supplementary information: template-free nanosized faujasite-type zeolites", Nature Materials, vol. 14, no. 4, 5 January 2015 (2015-01-05), pages 447-451, XP055642674, GB ISSN: 1476-1122, DOI: 10.1038/nmat4173 ----- -/--	1-16,20

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/052566

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DANNY VERBOEKEND ET AL: "Hierarchical FAU- and LTA-Type Zeolites by Post-Synthetic Design: A New Generation of Highly Efficient Base Catalysts", ADVANCED FUNCTIONAL MATERIALS, vol. 23, no. 15, 19 April 2013 (2013-04-19), pages 1923-1934, XP055117151, ISSN: 1616-301X, DOI: 10.1002/adfm.201202320 cited in the application	17-25
A	figures 11-12; table 3 2.1 Mesoporosity introduction; page 1924 the whole document	1-16
X	----- US 5 601 798 A (COOPER DAVID A [US] ET AL) 11 February 1997 (1997-02-11)	17-25
A	column 9, lines 18-22; example 44; table 14 column 1, lines 15-33 the whole document -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2019/052566

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 106315609	A	11-01-2017	NONE
CN 104923286	B	24-05-2017	NONE
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		WO 9507236 A1	16-03-1995