

Method of producing zeolite encapsulated nanoparticles.

Kegnæs, Søren; Abildstrøm, Jacob Oskar; Mielby, Jerrick Jørgen; Gallas-Hulin, Agata

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- (71) **Applicant:** DANMARKS TEKNISKE UNIVERSITET [DK/DK]; Anker Engelunds Vej 1, DK-2800 Kgs. Lyngby (DK).
- (72) **Inventors:** **KEGNÆS, Søren**; Hammars Parkvæg 7, S-216 30 Limhamn (SE). **ABILDSTRØM, Jacob, Oskar**; Store Kannikestræde 12, 2., 5., DK-1169 København K (DK). **MIELBY, Jerrick, Jørgen**; Kastanie Allé 13, 2. th., DK-2720 Vanløse (DK). **GALLAS-HULIN, Agata**; Søllerød Park 17, lejl. 21, DK-2840 Holte (DK).
- (74) **Agent:** ZACCO DENMARK A/S; Arne Jacobsens Allé 15, DK-2300 København S (DK).
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(54) **Title:** METHOD OF PRODUCING ZEOLITE ENCAPSULATED NANOPARTICLES

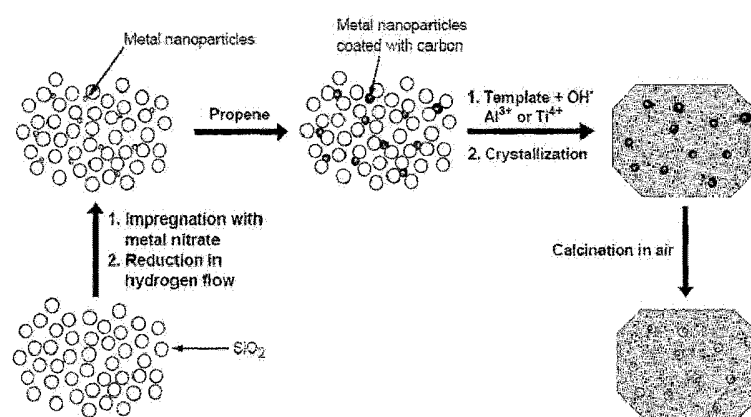


Fig. 2b

(57) **Abstract:** The invention therefore relates to a method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles, the method comprises the steps of: 1) Adding one or more metal precursors to a silica or alumina source; 2) Reducing the one or more metal precursors to form metal nanoparticles on the surface of the silica or alumina source; 3) Passing a gaseous hydrocarbon, alkyl alcohol or alkyl ether over the silica or alumina supported metal nanoparticles to form a carbon template coated zeolite, zeolite-like or zeotype precursor composition; 4a) Adding a structure directing agent to the carbon template coated zeolite, zeolite-like or zeotype precursor composition thereby creating a zeolite, zeolite-like or zeotype gel composition; 4b) Crystallising the zeolite, zeolite-like or zeotype gel composition by subjecting said composition to a hydrothermal treatment; 5) Removing the carbon template and structure directing agent and isolating the resulting zeolite, zeolite-like or zeotype encapsulated metal nanoparticles.

Method of producing zeolite encapsulated nanoparticles

Field of the invention

The invention concerns a method for making zeolite or zeotype encapsulated metal nanoparticles and zeolite or zeotype encapsulated metal nanoparticles produced by the method.

Background of the invention

In the view of the current environmental challenges there is an urgent need to develop a more sustainable chemical industry through more efficient chemical transformations and by developing new highly selective and cost-effective catalysts. One approach towards enhanced catalytic performance of supported metal catalysts is to increase the active metal surface by synthesizing small metal nanoparticles (often <10 nm in diameter). However, small nanoparticles are often prone to sintering which decreases the catalytic activity over time. The development of sinter-stable heterogeneous nanoparticle catalysts is therefore of great importance.

Zeolites are crystalline alumina silicate materials that exhibit a highly ordered porous structure with pores of molecular diameter. IUPAC identifies this type of porosity as microporous, as the size of the pores are not wider than 2 nm. The other groups of porosity are mesoporous (pore size between 2–50 nm) and macroporous (pore size larger than 50 nm). Zeolites consist of tetrahedral TO_4 units (T= Si or Al), which gives the framework an overall composition of TO_2 . These materials have a clear organized framework throughout the crystals, giving rise to highly ordered pores and a large internal surface area. By replacing a silicon atom with an aluminium atom, it is possible to generate a deficit of charge, which is compensated by a cation located nearby. The cation is usually an alkali metal (such as sodium), alkali earth metal, or possibly a H^+ ion. If the cation is a proton, the zeolite becomes a strong Brønsted acid. All these characteristics give rise to a lot of uses for zeolites.

Today, nearly 60 different natural occurring zeolites are known, while 201 can be prepared synthetically [1]. These zeolites have different structures, due to different Si-O-Al linkages, and a different number of Si or Al atoms linked in each “cage”. This also creates different pore system of one-, two-, or three-dimensions in the zeolite.

As the pores are very regular, and around the same size in diameter as molecules, it is possible for zeolites to function as molecular sieves. Due to their chemical structure and molecular sieve properties, zeolite catalysts exhibit high selectivity for a variety of chemical reactions. Since most of the surface area and the active sites are within the zeolite, the shape of the pores and channels give rise to shape selective catalysis. Commonly there is distinguished between three types of molecular sieving effects:

- 1) Reactant shape selectivity: Only molecules small enough can enter the zeolite pores and undergo chemical transformation or be adsorbed.
- 2) Product shape selectivity: The size of the pores is too small, that not all possible products can diffuse out of the zeolite after reaction. This leads to an increased selectivity towards smaller molecules or isomers.
- 3) Restricted transition-state shape selectivity: Here the formation of too large transition state intermediates are prevented due to zeolite pore size. Figure 1 illustrates the three different kinds of shape selectivity.

Zeolite Synthesis

In general, zeolite synthesis is a crystallization process, where silica and alumina species dissolve and react to give a less soluble crystalline alumina/silicate product. The crystallization process is typically performed in a hydrothermal process where the zeolite precursors is put in an autoclave and heated to relatively high temperatures and autogenous pressures. The high pressure is due to the evaporation of water inside the autoclave, and is very important for the synthesis. In a typical synthesis the zeolite precursors is dissolved or suspended in an aqueous solution of a structure directing agent (SDA) and an alkali hydroxide to catalyze the breaking and formation of chemical bonds [4].

The structure directing agents are almost always organic amine cations. Some of the most commonly used organic structure directing agents are tetramethylammonium (TMA), tetraethylammonium (TEA), and tetrapropylammonium (TPA), though compounds as diverse as Choline, 1,6-diaminohexane, and hexanediol have been used. During the zeolite crystallization process, the zeolites form around molecules of the structure directing agent. The shape and properties of the structure

directing agent causes the zeolites forming around it to take a certain shape.

Stoichiometric analysis of samples of ZSM-5 has indicated that one TPA⁺ molecule occupies each intersection between pores in the zeolite [2].

5 For sources of silicon, mostly sodium silicate, fumed silica or tetraethoxy ortho-
silicate is used, while sodium aluminate, aluminum nitrate or –chloride are typical
sources of aluminum [3]. The mixture of zeolite precursors or zeolite gel is then
transferred to an autoclave and heated to a predetermined temperature, often
between 120-200 °C. Within days, possible weeks, the precursors begin to
10 crystallize and form the zeolite. After the synthesis, the autoclave is cooled to room
temperature, and the zeolite material is washed with water and isolated by filtration
or centrifugation. The zeolite is then calcined at around 500-600 °C to remove
residual SDA and framework water. At last the zeolite can be ion exchanged. This
can either be done to introduce hydrons, alkali metal, alkali earth metal, lanthanoid
15 or transition metal cations.

One method to produce a porous system inside a zeolite is templating. Several
types of templates have been utilised for the introduction of pores in zeolites. One of
them; hard templating applies a solid material to generate a porous system in
20 addition to the inherent micropores. This method has proved to be very effective and
a highly versatile approach. Templates include organic aerogels, polymers, and
carbon in different forms. Here, only carbon will be discussed. One of the well-
known methods is the crystallization of zeolite gel in porous carbon particles. If the
amount of synthesis gel relative to the carbon template is sufficient, the zeolite
25 crystals continue to grow after nucleation in the cavities of the carbon. This will allow
the zeolite crystal to encapsulate the carbon. Combustion of the carbon particles
embedded in the zeolite crystal, will lead to the formation of mesopores [37]. Several
types of carbon nanoparticles have been used [38], including carbon nanotubes [39]
and nanofibers.

30

In 1983 Taramasso et al. incorporated titanium ions into silicalite-1 (denominated as
TS-1) [56]. The incorporation of titanium, is a isomorphous substitution in the MFI
lattice of the silicalite-1. The presence of a titanium atom gave rise to different
catalytic properties, than the selective acid catalytic properties displayed by

conventional alumina silicate zeolites. The TS-1 has been found useful in selective oxidation reactions, such as the hydroxylation of phenols, epoxidation of alkenes, and ammoxidation of ketones [57–61].

- 5 Encapsulation of metal nanoparticles in a zeolite structure can improve the physical properties of the zeolite, but in addition to that; the encapsulated metal nanoparticles can have catalytically properties themselves. As a further potential advantage, the encapsulation can protect the individual nanoparticles from contact with other nanoparticles, thereby preventing sintering of the nanoparticles when these are
10 subjected to elevated temperatures.

In spite of the great technological, environmental and economic interests, general methods for the stabilization of metal nanoparticles against sintering are far from being fully developed, although for some specific systems it has been achieved by
15 optimizing the interaction of nanoparticles with a support material or by encapsulation of the metal particles [52, 93, 94]. However, these known catalytic systems are in general very expensive and difficult to synthesize and they cannot be produced in industrial scale. Nanoparticles encapsulated in zeolite-like structure have only been reported in a handful of papers [46, 52, 95-99].

20 The encapsulation of nanoparticles is an area of increasing interest. This is a possible solution to the widely known problem of deactivation due to sintering. Several methods have been developed to produce sinter-stable nanoparticle catalyst, including encapsulating in mesoporous silica matrix or by using a protective
25 shell [45–48]. None of these materials are however shape-selective. By encapsulating metal nanoparticles in a zeolite matrix, on the other hand, shape selective catalysis is possible. In addition, the thermal stability of zeolites and high surface area, makes zeolites particularly useful for this application. Post treatment deposition of nanoparticles inside zeolites has been reported in literature [49–51]. A
30 limitation of these methods is however that they require zeolites containing cages.

By post-synthesis treatments the nanoparticles are in the cages and/or in the pores of the zeolite and it can be difficult to control the size and location of the nanoparticles. Both Laursen et al. and Tøjholt et al. have successfully synthesised a

MFI zeolite containing gold nanoparticles (size 1–3 nm), which showed to be highly stably versus sintering [52, 53]. In addition, the gold nanoparticles were only accessible through the micropores of the zeolite. The synthesis is however difficult, and requires a lot of exotic materials and time.

5

So, despite the growing demand, a fast, efficient and economically process for manufacturing zeolite or zeotype encapsulated metal nanoparticles which are sinter-resistant that can be scaled up for industrial application has not yet been reported.

10 **Summary of the invention**

The present invention relates to method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles, the method comprises the steps of:

- 1) Adding one or more metal precursors to a silica or alumina source;
- 2) Reducing the one or more metal precursors to form metal nanoparticles on
15 the surface of the silica or alumina source;
- 3) Passing a gaseous hydrocarbon, alkyl alcohol or alkyl ether over the silica or alumina supported metal nanoparticles to form a carbon template coated zeolite, zeolite-like or zeotype precursor composition;
- 4a) Adding a structure directing agent to the carbon template coated zeolite,
20 zeolite-like or zeotype precursor composition thereby creating a zeolite, zeolite-like or zeotype gel composition;
- 4b) Crystallising the zeolite, zeolite-like or zeotype gel composition by subjecting said composition to a hydrothermal treatment;
- 5) Removing the carbon template and structure directing agent and isolating the
25 resulting zeolite, zeolite-like or zeotype encapsulated metal nanoparticles.

The present invention also relates to a zeolite, zeolite-like or zeotype encapsulated metal nanoparticles manufactured by the method according to the present invention.

30 **Figures**

Figure 1: The three types of shape selectivity [3].

Figure 2a: Overview of principles of zeolite synthesis.

Figure 2b: Overview of developed procedure for the synthesis of carbon template mesoporous zeolites and sintering stable heterogeneous nanoparticle catalysts.

Figure 3: The six types of isotherms as classified by IUPAC [80].

5

Figure 4: XRPD patterns of conventional (TS-1), carbon-templated (cTS-1), desilicated (dTS-1), and TS-1 subjected to both carbon-templating and desilication (cdTS-1).

10 Figure 5: XRPD pattern of Ni-0.74-TS-1 synthesized using propene.

Figure 6: Scanning electron microscope images of conventional and mesoporous TS-1, plus their desilicated counterparts.

15 Figure 7: Scanning electron microscope images of silica samples prepared by coking of nickel and iron nanoparticles.

Figure 8: Scanning electron microscope images of TS-1 prepared with nickel nanoparticles.

20

Figure 9: Nitrogen adsorption/desorption isotherms of conventional and mesoporous **samples**. (□) TS-1, (○) dTS-1, (◇) cTS-1, (Δ) cdTS-1. **Blank symbols represent the adsorption isotherm, while filled represent the desorption.** (please note the offset).

25 **Figure 10: BJH pore size distribution based on the desorption isotherms.** (□) TS-1, (○) dTS-1, (◇) cTS-1, (Δ) cdTS-1.

Figure 11: Nitrogen adsorption/desorption isotherms of Ni-0.74-TS-1.

30 Figure 12: BJH pore size distribution of Ni-0.74-TS-1 based on the desorption isotherms.

Figure 13: UV-Vis spectra of TS-1 and its mesoporous derivates.

Figure 14: UV-Vis spectra of Ni-0.74-TS-1 and conventional TS-1.

Figures 15: Transmission electron microscopy of a mesoporous MFI zeolite synthesized using methane, where the material is heated to 550 °C under argon before methane gas is added.

Figure 16: Scanning electron microscope images of a MFI zeolite synthesized using methane, where the material is heated to 700 °C under argon before methane gas is added.

Figures 17a-b: XRPD pattern of MFI synthesized using methane, where Figure 17a represents a synthesis method, where the material is heated to 550 °C under argon before methane gas is added and Figure 17b represents a synthesis method, where the material is heated to 700 °C under argon before methane gas is added.

Detailed description of the invention

In the following detailed description of the invention, reference is made to the examples, including tables and figures.

In this application a method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles is presented. This is a new method to synthesize zeolite, zeolite-like or zeotype encapsulated metal nanoparticles where the carbon template is generated by a direct coking process facilitated by pre-formed metal nanoparticles on the silica/aluminium source.

The invention therefore relates to a method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles, the method comprises the steps of:

- 1) Adding one or more metal precursors to a silica or alumina source;
- 2) Reducing the one or more metal precursors to form metal nanoparticles on the surface of the silica or alumina source;
- 3) Passing a gaseous hydrocarbon, alkyl alcohol or alkyl ether over the silica or alumina supported metal nanoparticles to form a carbon template coated zeolite, zeolite-like or zeotype precursor composition;

- 4a) Adding a structure directing agent to the carbon template coated zeolite, zeolite-like or zeotype precursor composition thereby creating a zeolite, zeolite-like or zeotype gel composition;
- 5 4b) Crystallising the zeolite, zeolite-like or zeotype gel composition by subjecting said composition to a hydrothermal treatment;
- 5) Removing the carbon template and structure directing agent and isolating the resulting zeolite, zeolite-like or zeotype encapsulated metal nanoparticles.

10 The metal nanoparticles are still present within each single crystal of the zeolite after synthesis. When the carbon template has been removed by calcinations from the zeolite structure the nanoparticles are individually encapsulated within the created pores or cavities of the zeolite structure, so that the individual nanoparticles are protected from contact with other nanoparticles, thereby preventing sintering of the nanoparticles when these are subjected to elevated temperatures.

15

The zeolite, zeolite-like or zeotype encapsulated metal nanoparticles are preferably sinter stable or sinter resistant.

20 By encapsulating metal nanoparticles in a zeolite matrix, shape selective catalysis is possible.

By encapsulation, the metal nanoparticles are immobilised and sustained in the entire zeolite crystals, and thus more stable towards sintering. The nanoparticles are accessible through the framework of pores which act as molecular sieves.

25

The novel method can be used to synthesize sintering stable heterogeneous nanoparticle catalysts useful for environmental protection and production of chemicals. The zeolite-based catalysts containing metal nanoparticles are synthesized according to the approach depicted in figure 2b. The hydrocarbon gas 30 alkyl alcohol or alkyl ether which is employed in step 3 decomposes on the metal surface to leave a protective layer of carbon around the metal nanoparticles. It is expected that this novel synthesis method can improve the current synthesis of encapsulated metal nanoparticles in zeolites.

The encapsulation of metal nanoparticles within the zeolite structure inhibits sintering, thereby preserving their high surface area required for the effective catalytic activity. This novel approach for preparation of sintering stable heterogeneous nanoparticle catalysts is rather simple and can be used to develop novel automotive exhaust catalyst. Moreover, it is also the more general method for the stabilization of metal nanoparticles against sintering which could find use in the chemical and pharmaceutical industry. For example, the heterogeneous gold, silver and platinum nanoparticle catalysts are active and selective catalysts for several oxidation reactions.

10

The method of the invention is based on carbon templating and originates from the desire to develop a fast, efficient and cheap alternative method that can be scaled up for industrial application more easily than the known sucrose method [41]. An overview of this synthesis is presented in Figure 2b.

15

Different zeolite structures (framework) are suitable for the above method of production. The zeolite structure can be zeolite beta (BEA), Y (FAU), ZSM-5 (MFI), ZSM-11 (MEL) or ZSM-12 (MTW).

20 Throughout the description, when zeolites are mentioned this is meant to comprise zeolites, zeolite-like materials and zeotypes unless otherwise specifically mentioned.

By the term zeolite-like is meant non-silicon comprising material. Examples of zeolite-like materials are non-silicon comprising materials such as aluminium phosphate (AlPO₄) molecular sieves, known as AIPO's. The phosphorous compound can be selected from the group consisting of phosphoric acid, phosphate salts and mixtures thereof. By the term "phosphate salts" is meant salts of phosphates, monohydrogen phosphates and dihydrogen phosphates.

30 By zeolite, zeolite-like and zeotype particle is meant zeolite, zeolite-like and zeotype crystal or zeolite, zeolite-like and zeotype material.

"Metal nanoparticles" also comprises mixtures of metals nanoparticles.

By metal nanoparticles is also meant metal oxide nanoparticles and metal nitrate nanoparticles. The metal or mixture of metal precursors might form into the respective oxides or nitrates. This can happen either during the manufacturing process or in the end product.

5

Possible silica sources for zeolites may be bulk silica of different quality and alumina contamination, including pure silica, fumed silica, sodium silicate or other soluble silicate salts, precipitated silica, tetraethyl orthosilicate and other alkoxy-silicates, silicic acid, etc.

10

Possible aluminium sources for zeolites may be aluminum nitrate, aluminum sulphate, aluminum phosphate, sodium aluminate ect.

The inherent micropores in the zeolite structure are also here called primary porosity whereas the ekstra pores created by the method of the present invention are referred to as secondary porosity. This secondary porosity can both be micropores or mesopores.

The first step in the process is to add a metal or a mixture of metal precursors to a silica/alumina precursor. In one embodiment the first step is performed at elevated temperatures such as from 50°C to 150°C, such as around 80°C.

The metal precursors can be added by grinding, impregnation, co-precipitation, deposition-precipitation or chemical vapor deposition.

25

Impregnation: a solution, e.g. an aqueous or alcoholic solution of one or several transition metal precursors is applied to a silica/alumina source. The solution is dried, e.g. in an oven at 80°C overnight, whereby water is evaporated and left is the metal on the surface of the silica/alumina source.

30

Deposition Precipitation: silica and the metal or mixture of metals is mixed together in a solution. By changing pH or adding chemicals, e.g. H₂O₂, the character of the metal change to another compound and deposit on the silica.

Chemical Vapour Deposition: The metal or mixture of metals can be in a gas phase or liquid phase. If the metal is in a liquid phase the liquid is heated to the boiling point and lead over the silica where it is deposited. If the metal is in the gas phase, the gas is lead over the silica where it is deposited.

5

In one embodiment nickelparticles are made volatile by CO and carbonyl compound are created, which are deposited on the silica and creates carbon nanotubes.

10 In one embodiment of the method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles the one or more metal(s) is selected from the group consisting of group 4 elements, group 6 elements, group 7 elements, group 8 elements, group 9 elements, group 10 elements, group 11 elements or group 12 elements or mixtures thereof. The group elements are defined by the new IUPAC numbering.

15

In one embodiment of the method the one or more metal(s) is selected from the group consisting of titanium, osmium, iridium, platinum, ruthenium, palladium, rhodium, rhenium, copper, nickel, iron, cobalt, silver, gold, cadmium, molybdenium or mixtures thereof. In one embodiment the metal is nickel.

20

In one embodiment of the method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles **the first step** is performed in a liquid phase, e.g. in an aqueous or alcoholic solution, in a gas phase or in a solid phase. The aqueous or alcoholic solution of of the one or more metal precursors could comprise
25 nitrates, carbonates, acetates sulphates orchlorides.

In another embodiment, **the first step** in the process involves impregnating a silica or alumina precursor with an aqueous or alcoholic solution of one or more transition metal precursors. The possible metals especially include Fe, Co, Ni, Cu, Ru, Rh, Pd,
30 Ag, Pt, Au, Mo, and mixtures thereof. The possible metal precursor could be nitrates, carbonates, acetates, sulfates, chlorides, carbonyls, and several other cheap and readily available chemicals.

The possible metal can also be a metal alloy such as gold-platinum, copper-palladium, ruthenium-copper, platinum-iridium, platinum-palladium, platinum-ruthenium, cobalt-molybdenum, nickel-molybdenum, or palladium-gold, where one of the metals in the metal alloy can be present in an amount of from 1 to 50%. The optimal weight ratio between the metals in the alloy depends on the metal alloy.

The second step in the process involves reducing the one or more metal precursors to form metal nanoparticles on the surface of the silica or alumina source. The metal precursors is reduced in a reducing atmosphere, for instance in a stream of hydrogen gas, or decomposed by a thermal treatment to give the corresponding transition metal nanoparticles. The transition metal nanoparticles can also be in the form of metal oxide nanoparticles or metal nitrate nanoparticles. This reduction step is in one embodiment performed at elevated temperatures, e.g. from 200 to 800 °C such as from 200 to 700 °C, or such as from 200 to 600 °C.

The third step in the process involves passing a gaseous hydrocarbon, alkyl alcohol or alkyl ether over the silica or alumina source with the impregnated metal nanoparticles, forming a zeolite precursor composition comprising carbon coated metal nanoparticles. The physical shape of the carbon (also called the carbon template) coating the nanoparticles can vary depending on the process conditions. In one embodiment the carbon is in the form of whiskers (nanotubes). In another embodiment the carbon is in the form of nanofibers. In another embodiment the carbon is in the form of spheres encircling the metal nanoparticles.

In one embodiment the flow of gaseous hydrocarbon, alkyl alcohol or alkyl ether is in the range of 20 to 500 ml/min, 20 to 400 ml/min, 100 to 400 ml/min, 30 to 100 ml/min, 50 to 90 ml/min, 50 to 70 ml/min or 60 to 70 ml/min.

In one embodiment, the third step of the process involves heating the silica or alumina and metal nanoparticles to 200-1100°C, such as from 200-800°C. or from 300-1100°C.

In separate embodiments the hydrocarbon is selected from aliphatic hydrocarbons having 1 to 8 carbon atoms, having 1 to 3 carbon atoms, alkenes having 2 to 6

carbon atoms, aromatic hydrocarbons having 6 to 10 carbon atoms and cyclic hydrocarbons having 3 to 8 carbon atoms.

5 In one embodiment the hydrocarbon gas is selected from methane, propene, xylene, methane or benzene.

In other separate embodiments the alkyl alcohol is selected from aliphatic alcohols having 1 to 8 carbon atoms, or having 1 to 3 carbon atoms.

10 In other separate embodiments the alkyl ether is selected from aliphatic ethers having 2 to 8 carbon atoms, or having 2 to 4 carbon atoms.

In a specific embodiment the alkyl ether is DME (dimethylether).

15 In one embodiment the flow of gaseous hydrocarbon, alkyl alcohol or alkyl ether is applied for around 1-5 hours, e.g. 2 hours.

20 In one embodiment, the third step of the process involves that the silica or alumina and metal nanoparticles is heated (maybe 300-1100°C) in a stream of a simple hydrocarbon gas (1-8 carbon atoms or cyclic hydrocarbons) that decomposes on the metal surface to leave the carbon template on the zeolite precursor composition. The layer of carbon protects the nanoparticles in the relatively harsh reaction (temperature, pressure, alkaline) that are necessary to grow the zeolite.

25 **The fourth step** involves two steps; step 4a is adding a structure directing agent to the carbon template coated zeolite, zeolite-like or zeotype precursor composition thereby creating a zeolite, zeolite-like or zeotype gel composition; and step 4b is crystallization of the zeolite, zeolite-like or zeotype gel composition by subjecting the zeolite, zeolite-like or zeotype gel composition to a hydrothermal treatment.

30 During this step 4, the silica/aluminium is dissolved in an aqueous alkaline media creating a supersaturated solution from which the zeolite is formed around the carbon template in the presence of a structure directing agent (SDA), preferably a quaternary ammonium salt such as TPAOH (tetrapropylammonium hydroxide) or

TBAOH (tetrabutylammonium hydroxide). This creates an initial, amorphous zeolite gel, which in a subsequent hydrothermal step is transformed into the crystalline zeolite. The hydrothermal process is often performed under elevated temperatures between 70 and 300 °C, preferably at 180 °C, and autogeneous pressure in an
5 autoclave or open flask for 24 hours or more.

A hydrothermal process is a technique of crystallizing substances from high-temperature aqueous solutions at high vapour pressure.

10 In one or more embodiments, the carbon template coated zeolite, zeolite-like or zeotype precursor composition of step 3 is used directly in step 4a without removing the silica or alumina source. In this way, the silica or alumina source is reused in the following process, which reduces the production cost compared to alternative
15 processes, where it is removed and only the carbon skeleton is used in the further process as seen in e.g. A. H. Janssen et al, Microporous and Mesoporous Materials 65 (2003), page 59-75. Further, by reusing the silica or alumina source, the method is simplified.

In a specific embodiment, the fourth step comprises a hydrothermal treatment of the
20 initially formed zeolite gel wherein the gel is heated to temperatures between 70 and 300 °C, preferably at 180 °C. In addition it may be under an autogeneous pressure in an autoclave or open flask for 24 hours or more.

In one embodiment the method of producing zeolite or zeotype encapsulated metal
25 nanoparticles comprises adding an Al, Sn, Ti, Zr or Ge source during step 4a. The source may be an Al³⁺, Sn²⁺, Sn⁴⁺, Ti⁴⁺, Zr or Ge source. Sources of Titanium could be e.g. titanium chlorides, titanium sulphates, titanium alkoxides e.g. TEOT (tetraethyl orthotitanate) and TBOT (tetrabutyl orthotitanate). Sources of aluminium could be aluminium nitrate, aluminium sulphate, aluminium phosphate, sodium
30 aluminate ect. Sources of tin could be tin chlorides, tin oxides or splid tin dissolved in hydrochloric acid. Sources of zirconia could be zirconia chloride or zirconia oxide. If an aluminium source was used in step 1 in the process instead of a silica source, then a silica source should be applied at this step. The source of silica is bulk silica

of different quality and alumina contamination, including pure silica, fumed silica, sodium silicate or precipitated silica, tetraethyl orthosilicate ect.

5 The source of Al^{3+} , Sn^{2+} , Sn^{4+} , Ti^{4+} , Zr or Ge will be part of the framework in the crystal structure. Therefore, Ti-zeotype particles, Sn-zeotype particle, Zr-zeotype particle or Ge-zeotype particles can be manufactured by the present method.

In the fifth step the catalyst is washed, dried and calcined in air at above 300 °C, preferably between 300-700 °C, preferably between 400-700 °C to remove the structure directing agent and the carbon template. More preferably a controlled combustion is conducted by calcination the crystalized zeolite in air at 550 °C. The combustion is conducted for e.g. 24 hours or 20 hours. Upon removal of the carbon template, by calcination, the zeolite crystals obtain a secondary porosity, in addition to the inherent zeolite microporous system. The porosity can be modified by changing the type and amount of carbon.

20 According to the present invention, the metal nanoparticles previously supporting the growth of carbon templates (whiskers, nanotubes etc) during the third step of the process are left behind in the secondary porosity of the zeolites after the fifth step has been carried out. These metal nanoparticles are homogeneously distributed throughout the crystalline zeolite structure and are further individually shielded from physical contact with other metal nanoparticles hosted in the zeolite by the walls of the formed pores. The metal nanoparticles remain accessible through the porous structure of the zeolites, however, but are thus protected from sintering with other nanoparticles at elevated temperatures due to said physical separation.

30 The calcination procedure conducted in step 5 is expected to remove the carbon template and remaining amounts of the structure directing agent. However, under certain combinations of reaction parameters the isolated encapsulated metal nanoparticles may still contain traces of carbon trapped in the zeolite structure which may influence the eventual activity and/or selectivity of the metal nanoparticles.

In the following one possible method is outlined. The first step involves that an aqueous solution of a metal nitrate is impregnated on the silica. The metal nitrate is

then reduced in a hydrogen stream to form metal nanoparticles. Subsequently, the gas flow is exchanged and a carbon gas, e.g. propene gas is passed over the sample. Depending on the nature of the metal nanoparticles, the time of exposure to the hydrocarbon gas, the temperature, the carbon gas, e.g. propene may cover and encapsulate the metal nanoparticles or deposit as carbon [42, 43]. After this procedure, the zeolite precursor is mixed with a structuring directing agent (SDA) and OH⁻ and put in a Teflon beaker inside a Teflon-lined autoclave containing a sufficient amount of water to generate saturated steam and heated to e.g. 180 °C for e.g. 72 hours. After the hydrothermal treatment, the carbon template is removed by combustion. This will lead to uniformed micropores or mesopores in the zeolite, which are modifiable by increasing or decreasing the nanoparticle size.

In one embodiment of the method the carbon template is shaped as carbon nanotubes.

Carbon formation in the form of whisker carbon is a very common phenomenon with e.g. nickel nanoparticles [42, 43]. This might resort to a larger amount of carbon formation than expected if the nanoparticles where simply encapsulated. The length, width and amount of carbon, e.g. in the form of whiskers, can be tuned by changing the different parameters, such as gas, temperature and time.

In one embodiment of the method the one or more metal precursors is loaded to the silica or alumina in an amount of 0.5 to 20 wt %, from 0.5 to 5 wt %, from 0.5 to 2 wt %, or around 1 wt % during step 1.

In one embodiment of the method the zeolite precursor has a carbon-to-silica ratio of from 0.30 to 2.00 w/w, 0.30 to 1.00 w/w, 1.00 to 2.00 w/w or from 0.34 to 0.75 w/w.

In one embodiment of the method the zeolite precursor has a carbon-to-alumina ratio of from 0.30 to 2.00 w/w, 0.30 to 1.00 w/w, 1.00 to 2.00 w/w or from 0.34 to 0.75 w/w.

EDS analysis of the calcined zeolite showed presence of nickel, titanium, oxygen and silicon.

5 The present invention also relates to a zeolite, zeolite-like or zeotype encapsulated metal nanoparticles manufactured by the method according to the present invention.

The physical and chemical properties of the zeolite material are modified by having the encapsulated nanoparticles within the pore system of the zeolite crystal.

10 In one embodiment, the encapsulated metal nanoparticles are sinter-resistant.

In one embodiment the particle is a hierarchical mesoporous zeolite, zeolite-like or zeotype particle.

15 In one embodiment the particles comprises mesopores in the range from 2 to 50 nm, from 5 to 30 nm, from 10 to 25 nm, from 15 to 25 nm, from 18 to 22 nm, from 19 to 21 nm or around 20 nm. In one embodiment the particles comprises mesopores having sizes around 10 nm.

20 In one embodiment the zeolite particles comprises micropores in the range from 0.1 to 2 nm, from 1 to 2 nm or around 2 nm.

In one embodiment the encapsulated metal nanoparticles comprise one or more metal(s) selected from the group consisting of group 4 elements, group 6 elements,
25 group 7 elements, group 8 elements, group 9 elements, group 10 elements, group 11 elements or group 12 elements or mixtures thereof. The group elements are defined by the new IUPAC numbering.

In one embodiment the encapsulated metal nanoparticles comprise one or more
30 metal(s) selected from the group consisting of titanium, osmium, iridium, platinum, ruthenium, palladium, rhodium, rhenium, copper, nickel, iron, cobalt, silver, gold, cadmium, molybdenum or mixtures thereof. In one embodiment the metal is nickel.

In one embodiment the size of the crystal structure are in the range of 1.0 to 2.5 μm .

In one embodiment the metal nanoparticles are immobilized in the zeolite or zeotype.

- 5 In one embodiment the zeolite, zeolite-like or zeotype encapsulated metal nanoparticles comprise an Al, Sn, Ti, Zr or Ge source in the framework of the crystal structure. The source may be an Al³⁺, Sn²⁺, Sn⁴⁺, Ti⁴⁺, Zr or Ge source. The source of Al³⁺, Sn²⁺, Sn⁴⁺, Ti⁴⁺, Zr or Ge will be part of the framework in the crystal structure. Therefore, the invention also comprise Ti-zeotype particles, Sn-zeotype particle, Zr-
10 zeotype particle or Ge-zeotype particles manufactured by the present method.

In one embodiment the amount of metal nanoparticles are in the range of 0.1 to 25 wt%, in the range from 0.5 to 20 wt%, from 0.5 to 10 wt%, from 0.5 to 5%, from 1.0 to 5 wt %, from 1 to 2 wt %, or around 1 wt %.

- 15 The amount of metal nanoparticles in the crystallised zeolite structure is preferably more than 80% of the metal loading.

- 20 In one embodiment the zeolite, zeolite-like or zeotype particle has a Vp value in the range of 0.300 to 0.500 cm³/g, 0.300 to 0.400 cm³/g or around 0.320 cm³/g, or around 0.450 cm³/g.

- 25 In one embodiment the zeolite, zeolite-like or zeotype particle has an external surface area in the range of 100-400 m²/g, or around 170 to 200 m²/g or around 190 m²/g.

In one embodiment the zeolite, zeolite-like or zeotype particle has a BET surface area of 300 to 500 m²/g or 350 to 400 m²/g.

- 30 The zeolite, zeolite-like or zeotype encapsulated nanoparticles of the invention can be used as catalytic material for chemical reactions.

The invention also relates to the use of the zeolite, zeolite-like or zeotype encapsulated metal nanoparticles of the present invention in shape-selective catalysis.

5 **Experimental details**

Methods for characterisation – X-ray Powder Diffraction

XRPD is a widely used analytic method for structural characterization of crystalline materials. It is used to identify crystal structure and detect impurity phases. The method is based on diffraction, which occurs when an incident radiation interacts
10 with an ordered solid and the wavelength of the electron magnetic radiation is in the same order as the distance between the crystal planes. Most often, the zeolite is analysed in the form of a powder and the obtained powder X-ray diffractogram can be used as a fingerprint unique to the particular crystalline phase. Due to the small amount of titanium in the sample, it will be difficult to discern by XRPD, whether TiO₂
15 has formed. X-ray powder diffraction patterns (XRPD) was measured in transmission mode using Cu-K α radiation from a focusing quartz monochromator and a HUBER G670 Guinier camera.

Methods for characterisation – Scanning Electron Microscopy (SEM)

20 This analytic technique uses a finely focused high energy beam of electrons are is directed onto the surface of a sample. The electrons which are reflected by the surface and emitted secondary electrons, are detected to give a map of the surface topography of the sample. The samples may need to be applied with a conductive coating such as gold or graphite, to hinder local surface charging which leads to a
25 decreased quality of SEM images [79].

Methods for characterisation – Transmission Electron Microscopy (TEM)

TEM is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image
30 is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

Methods for characterisation – Energy Dispersive X-ray Spectroscopy

In electron microscopy, the elements present in the sample emit characteristic X-rays due to the incident electron beam. These X-rays can be analysed to give a spectrum, and from there give both qualitative and quantitative results of the elements present [79]. Several precautions must however be made, as it is nigh impossible to get accurate quantitative results with this method on samples such as zeolites. This is because the accuracy of the spectrum is affected by the nature of the sample. X-rays are generated by any atom in the sample that is sufficiently excited by the incident electron beam. The X-rays are emitted in any direction, and so they may not all escape the sample. The likelihood of a X-ray escaping the sample, depends on the energy of the X-ray and the amount and density of material it has to pass through. This can result in reduced accuracy in porous and rough samples. As zeolites present are porous, the EDS results must be interpreted with caution, and are therefore only used qualitatively. SEM and EDS analysis were performed on a Quanta 200 ESEM FEG. The calcined zeolite samples were placed on a carbon film.

Methods for characterisation – Nitrogen Physisorption

Key parameters for a solid catalyst is the accessibility of the active sites for reactants. A conventional way of measuring this is by physisorption of nitrogen gas at 77 K. This method provides information on both surface area and pore size distribution in the micro-, meso- and macroporous range. The method is a stepwise adsorption of N₂ which first forms a monolayer, as the pressure of N₂ increases multilayers begin to form. The N₂ physisorption isotherms generated are very distinct, and classified into six types by IUPAC [80] which are presented in Figure 3. Nitrogen physisorption of microporous solids, such as zeolites, result typically in Type I isotherms. They are characterised by the limiting uptake, which happens at relative low pressure and is controlled by the accessible micropore volume, and not the internal surface area. Type IV isotherms are most common when analysing mesoporous materials. The hysteresis loop between the adsorption and desorption branches, is a very characteristic feature for this type of isotherm, and is attributed to capillary condensation taking place in mesopores. Type II, III, V and VI are not commonly observed for zeolite materials, since they are typical for non-porous, macroporous or materials with weak forces of adsorption [80].

Nitrogen adsorption and desorption measurements were performed at liquid nitrogen temperature (77 K) on a Micromeritics ASAP 2420. The samples were outgassed in vacuum at 300 °C, 16 hours prior to measurement. The total surface areas were calculated according to the BET method. Pore size distributions were calculated with BJH method. External surface area, micropore area and micropore volume were determined by t-plot methods in the desorption branch. Total pore volume was calculated for pores around 80 nm width at $p/p_0 = 0.97$.

10 Methods for characterisation – Diffuse Reflectance UV-Vis Spectroscopy

By exposing molecules to radiation in the ultraviolet-visible (UV-Vis) spectral region, spectroscopy can be applied to determine the concentration of an analyte. However, important characteristics of the sample are obtainable. It is possible to detect and determine the coordination environment of d-d transitions in the sample, and metal-ligand complexes due to the specific energy required to excite them. However, in the case of powdered catalyst samples, the incident light can not penetrate the sample and is almost completely diffused. It is therefore not possible to use transmission spectroscopy, instead diffuse reflectance (DR) spectroscopy has to be applied. Overall, this method can serve as a great asset in determining which titanium species is present in the produced catalysts. DR UV-Vis spectra were obtained with a CARY 5000 spectrometer employing spectralon® as internal standard.

Materials

Mesoporous silica (Merck, silica gel 100, particle size 0.063–0.200mm, pore diameter 15 nm, pore volume 1.15 ml/g), was used for the synthesis of mesoporous zeolites involving metal nanoparticles. The silica were dried at 80 °C for 24 hours prior to use. All other reagents were of reagent grade and used without further purifications: tetraethylorthosilicate (TEOS, 98 wt%, Aldrich), tetraethylorthotitanate (TEOT, 98 wt%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 40 wt%, Fluka), hydrogen peroxide (H₂O₂, 40 wt%, Aldrich).

Synthesis – propene based method

The zeolites prepared by the new synthesis method disclosed in this application may be prepared by the following method using propene to form the carbon

- template coated zeolite, zeolite-like or zeotype precursor composition: First, 2.5 grams of silica is impregnated to incipient wetness with a metal nitrate solution, eg. nickel nitrate. This is allowed to stand at 80 °C overnight. The solid is subsequently placed in a tube oven and heated to 600 °C in argon flow. A gas mixture of 10% hydrogen in nitrogen is then led over for a total of 4 hours. The temperature is afterwards reduced to 550 °C under argon atmosphere. As an alternative to reducing the temperature to 550 °C under argon atmosphere, it may be increased to 700 °C still under argon atmosphere.
- 5
- 10 Propene gas is subsequently applied for 2 hours, afterwards a low flow of argon is led over, while the sample is allowed to cool off. Pure silica did not change colour during the procedure, while both nickel- and iron nitrate on silica were completely black after the treatment.
- 15 A mixture of 16.915 g 20% TPAOH, 4.25 ml water, 0.265 g NaOH and 0.095 g TEOT is prepared and stirred until a clear solution was obtained. The silica-carbon composite is added and left for 1 hour. The gel is then introduced into a stainless steel autoclave which is heated to 180 °C for 72 hours. Afterwards it is filtrated until the rinse water is neutral. The solid is left overnight at room temperature, followed
- 20 by calcination at 550 °C for 24 hours. Zeolites made by this method are nominated Metal-C/SiO₂ ratio-TS-1, e.g. Ni-0.74-TS-1.

The above synthesized zeolite is in the following compared to other mesoporous catalysts prepared through carbon templating and desilication (results presented in figures 4-6 and 8-14). This is done to determine the influence the synthesis method has on active species in the catalyst, as well as the effect on the external surface area, and the ability to introduce mesoporosity in addition to the microporosity found in conventional zeolites.

25

- 30 In the following, conventional TS-1 catalysts are denoted TS-1 and mesoporous carbon-templated TS-1 (1% Ti) are denoted cTS-1. A conventional TS-1 that has been desilicated is denoted dTS-1 and TS-1 that has been prepared with BP-2000 and desilicated is named cdTS-1.

Characterization of Catalysts – Carbon Uptake with Propene Method

Several experiments were done to test the carbon loading with different parameters. After the carbon loading, several were synthesised to either HZSM-5, TS-1 or both. Table 1 shows the carbon uptake in a carbon-to-silica ratio (on weight basis) with different metals and parameters. Pure silica took up no amount of carbon, which also was proven by the absence of colour change after the propene procedure. The following zeolite synthesis was abandoned, as this would only create a conventional zeolite. The carbon uptake on nickel-SiO₂ was proven to be modifiable by both changing the metal loading and the flow of propene. An increase in nickel loading, also increased the carbon uptake, with a linear correlation. By changing the flow of propene, it was possible to modify the carbon uptake to some extent. An increase in flow from 51 ml/min to 67 ml/min resulted in a raise of C/SiO₂ ratio from 0.34 to 0.74. This was not increased further by another raise in flow speed. Iron showed a very limited uptake with a C/SiO₂ ratio of 0.03. The silica was black after the propene treatment, confirming the uptake of carbon.

Samples	Metal Loading [wt%]	Propene Flow [ml/min]	C/SiO ₂ Ratio [w/w]
SiO ₂	-	67	0
Ni-SiO ₂	1%	51	0.34
Ni-SiO ₂	1%	67	0.74
Ni-SiO ₂	1%	85	0.75
Ni-SiO ₂	2%	67	1.18
Ni-SiO ₂	5%	67	2.13
Fe-SiO ₂	1%	67	0.03

Table 1: Carbon uptake of silica with different metal loading and propene flow.

20 Characterization of Catalysts – XRPD

For comparison of crystallinity of the zeolite catalysts, XRPD patterns were recorded after synthesis and subsequent calcination. Patterns for all synthesised TS-1 catalysts are presented in Figure 4. It is clear that the zeolite samples contain highly crystalline structure, with no impurities or amorphous phase present. It is difficult to discern if titanium is present in other confirmations than inside the framework, as the titanium content is very low. In addition, all patterns match the pattern of silicalite-1, confirming the MFI structure. The Ni-0.74-TS-1 catalyst produced by the synthesis

method disclosed in this application (nickel-propene method), also underwent XRPD analysis. The result is present in Figure 5. The catalyst exhibit the same characteristic pattern as samples with MFI structure. In addition, no amorphous phase or impurities were found present, and the sample was highly crystalline.

5

Characterization of Catalysts – Scanning Electron Microscopy (SEM)

All synthesised catalyst underwent analysis by SEM. This was done to investigate the morphology of the produced catalysts. In Figure 6 conventional and mesoporous TS-1 are compared to the desilicated counterparts. Conventional TS-1, Figure 6a, shows clearly defined cubic coffin shaped crystals with sizes of 0.2-0.4 μm . With crystals in this size range, the diffusion limitations have been decreased to a minimum, without introducing mesopores. Desilicated TS-1 are shown in Figure 6b. It shows an agglomerate of smaller crystals, with no clear consistent structure or size. Compared to the conventional TS-1, the mesoporous sample in Figure 6c is much bigger, with crystal sizes in the range of 1.5-2.5 μm . While the surface for the conventional TS-1 is very smooth, the mesoporous sample exhibits a more "sponge"-like shape. The desilicated mesoporous TS-1, Figure 6d, shows some of the same characteristics as the other desilicated sample. These similarities are the agglomeration of smaller crystals, and no clear structure or size. The shape of the original mesoporous sample can however faintly be seen.

10
15
20

SEM images of the propene treated nickel and iron samples are shown in Figure 7. The reason for the higher carbon uptake on the nickel samples are clear here. Several carbon nanofibers are present on the nickel sample, and absent on the iron sample. This was expected as, nickel is known for creating carbon whiskers at high temperatures in the presence of hydrocarbons [42]. To examine whether the iron nanoparticles were unchanged within the zeolite and encapsulated in carbon, TEM analysis will have to be done. TEM analysis will also be interesting, as to determine the size of the produced nanoparticles, both before and after synthesis.

25
30

Figure 8 is a picture of the titanium containing zeolites prepared through the coking of nickel nanoparticles. The sample presented in Figure 8, has a C/SiO₂ ratio = 0.75, and showed mesoporosity visible with SEM. In addition, all silica was also converted to zeolites.

Characterization of Catalysts – Energy Dispersive X-ray Spectroscopy

EDS was used to qualitatively determine the elements present in the samples. All TS-1 catalysts synthesised showed the presence of titanium, silicon and oxygen.

- 5 Furthermore the samples prepared through coking of nickel nanoparticles, also showed presence of nickel. To get an exact value of the nickel present in the sample, a method consisting of dissolution of the zeolite, followed by Inductively Coupled Plasma (ICP) could be applied.

10 Characterization of Catalysts – Nitrogen Physisorption

- The textural properties of the synthesized materials were determined by adsorption-desorption analysis with nitrogen. The observed SBET, external surface areas, S_{ext} , micropore and total pore volumes are collated in Table 2. The BET value is less for cdTS-1 and cTS-1. Logically the samples exhibit increasing external surface area
15 after the introduction of mesoporosity. cTS-1 has the highest external surface, dTS-1 somewhat lower, and cdTS-1 curiously has a value which corresponds with the average of cTS-1 and dTS-1. The same is the case for the micropore volumes. Figure 9 shows the isotherms of the samples. According to the IUPAC classification of physisorption isotherms, the conventional TS-1 has a type I isotherm with a sharp
20 transition in the adsorption branch at $P/P_0 < 0.1$ and almost no adsorption at intermediate relative pressures. This is typical for purely microporous materials such as zeolites.

- At $P/P_0 > 0.9$ further nitrogen uptake takes place due to the interparticle adsorption
25 within the voids between the small zeolitic particles as observed in the SEM analysis for conventional TS-1. cTS-1, dTS-1 and cdTS-1 exhibit the type IV isotherms with clearly visible hysteresis loops, which are typical for mesoporous materials. The mesoporous samples created by carbon templating of TS-1, present hysteresis loops at $P/P_0 > 0.86$ and can be attributed to the interparticle adsorption within the
30 voids formed between the zeolitic particles, or more likely due to creation of some very large pores, which would be in line with observation of large, SEM visible porosity in the cTS-1 sample. dTS-1 (and cdTS-1 to a smaller extent) show smaller hysteresis loop closing at $P/P_0 > 0.42$ with less generation of mesopores compared to micropores. These could be from the voids existing between the nanocrystallites

due to the desilication, but they are more likely to originate from the so-called TSE-effect [81, 82] where capillary evaporation during desorption occurs via a hemispherical meniscus, separating the vapour and the capillary condensed phase [83].

5

Sample	S_{BET} m ² /g	S_{ext} m ² /g	V_{Micro} cm ³ /g	V_{p} cm ³ /g
TS-1	390	166	0.0915	0.224
dTS-1	346	225	0.0498	0.478
cTS-1	367	136	0.0981	0.448
cdTS-1	353	182	0.0731	0.622

Table 2: Nitrogen physisorption data for the investigated catalysts.

Barrett-Joyner-Halenda (BJH) analysis of desorption branch further indicate
 10 secondary a mesopore distributions in the TS-1 derived catalysts. This mesoporosity
 is created at the expense of the decrease of micropore volume as seen in Table 2,
 especially for cTS-1 and cdTS-1, and an increase of the external surface compared
 to the value of TS-1 as mentioned above. For cTS-1 calcination of carbon template
 create mesoporous of around 19 nm and around 59 nm for cdTS-1. The dTS-1
 15 catalyst exhibits mesopores around 60 nm but in lesser amount as shown in figure
 10.

The zeolite prepared trough coking of nickel nanoparticles, Ni-0.74-TS-1, was also
 characterised with nitrogen physisorption. Figure 11 shows the
 20 adsorption/desorption isotherms of the zeolite. The sample shows a clear type IV
 isotherm, with hysteresis loops at $P/P_0 > 0.80$, most likely to originate from
 mesopores. The hysteresis loop around $P/P_0 > 0.18$, has still yet to be assigned to a
 structural property. The BJH pore size distribution, Figure 12, confirms the presence
 of mesopores of the same size (19 nm) as the carbon templated TS-1, but in a much
 25 smaller magnitude. In addition, the size of the micropores are slightly smaller than
 the conventional TS-1, and similar to the TS-1 zeolites prepared by carbon
 templated. The mesoporosity of the Ni-0.74-TS-1 is also confirmed by the V_{p} result
 presented in Table 3. With a value of 0.323 cm³/g, this is nearly 1.5 times greater

than the conventional TS-1 synthesised. In addition, the external surface area of Ni-0.74-TS-1, is also larger, at 189 m²/g compared to 166m²/g of the conventional TS-1.

Sample	S _{BET} m ² /g	S _{ext} m ² /g	V _{Micro} cm ³ /g	V _p cm ³ /g
Ni-0.74-TS-1	400	189	0.0854	0.323

5 Table 3: Nitrogen physisorption data for the synthesised Ni-0.74-TS-1.

Characterization of Catalysts – Diffuse Reflectance UV-Vis spectroscopy

Figure 13 shows the results of the DR-UV-Vis spectroscopy. TS-1 shows a maximum at 47600 cm⁻¹ (210 nm), which is characteristic from the charge transfer of oxygen 2p electron to the empty 3d orbit of framework Ti species in tetrahedral coordination. This band is known as a fingerprint of tetrahedrally coordinated Ti(OSi)₄ species in titanium silicate frameworks. The slightly shift to higher wavelengths. at ca. 45500 cm⁻¹ (220 nm) for the desilicated samples suggests the simultaneous presence of tetrahedral tripodal Ti(OSi)₃OH and tetrapodal Ti(OSi)₄. This might be a due to an increased surface density of Ti⁴⁺, due to the desilication process. This effect is only apparent in the desilicated samples, cdTS-1 and dTS-1.

Furthermore, dTS-1 shows a broad band at 38400-33300 cm⁻¹ (260–300 nm) that can be attributed to the partially polymerized hexacoordinated non-framework Ti species, which contain Ti-O-Ti bonds [84, 85]. This strongly suggest a densitification of titania species, most likely on the outside of the zeolite framework. In addition, cTS-1 and cdTS-1 also shows a broad band between 31250–29400 cm⁻¹ (320–340 nm), which is typical for larger extraframework TiO₂ particles with a structure similar to anatase. This suggest that the carbon-templating technique might also interfere with the active titania sites to some degree, perhaps by provoking some agglomeration of titania species near the mesopore channels, which could be thought to occur from the creation of hotspots during the carbon burnout. Overall, the titania species appear less harmed by the carbon-template method compared to the desilication method.

30

For an easier comparison, TS-1 is also shown in Figure 14. Ni-0.74-TS-1 shows a maximum at around 47600 cm^{-1} (210 nm), just as conventional TS-1. In addition it shows the same tendency to absorb in the broad band between $31250\text{--}29400\text{ cm}^{-1}$ (320–340 nm), just like the other carbon templated zeolites.

5

Synthesis – methane based method

As an alternative to the propene based synthesis shown and discussed above, the zeolites prepared by the new synthesis method disclosed in this application may be prepared by the following method using methane to form the carbon template
10 coated zeolite, zeolite-like or zeotype precursor composition: First, 5 grams of silica are impregnated to incipient wetness with a nickel nitrate solution. The resulting materials typically contained around 2 wt% of Ni metal. This is allowed to stand overnight. The solid is then placed in a tube oven and heated to $600\text{ }^{\circ}\text{C}$ in argon flow, with a subsequent change of gas to 10% hydrogen in nitrogen for 4 hours. The
15 temperature is reduced to $550\text{ }^{\circ}\text{C}$ under argon. As an alternative to reducing the temperature to $550\text{ }^{\circ}\text{C}$ under argon atmosphere, it may be increased to $700\text{ }^{\circ}\text{C}$ still under argon atmosphere.

Methane gas is then applied for between 10 minutes and up to 12 hours. Preferably,
20 methane is added for between 2-8 hours, or approximately 6 hours if the temperature is kept at $550\text{ }^{\circ}\text{C}$. If the temperature is kept at $700\text{ }^{\circ}\text{C}$, methane is normally applied for a shorter time of 10 minutes to 4 hours, or for 2-3 hours. Afterwards, the oven is cooled to room temperature with a flow of Ar.

25 In a 20 ml Teflon beaker 0.5 g of the materials from above are impregnated with 2.95 ml of 20% TPAOH (tetrapropylammonium hydroxide) solution. 10-20 ml of water is introduced to a 300 ml stainless steel autoclave. The Teflon beaker is placed in the water in the bottom of the autoclave. The closed autoclave is heated to $180\text{ }^{\circ}\text{C}$ for 72 hours. Afterwards, the solid is washed with demineralized water. The
30 zeolite/carbon composition is then heated to $550\text{ }^{\circ}\text{C}$ for 24 hours to remove the carbon.

The TEM image of the above zeolite produced using methane, where the material is heated to 550 °C under argon before methane gas is added, is displayed in Figure 15.

- 5 The SEM image of the above zeolite produced using methane, where the material is heated to 700 °C under argon before methane gas is added, is displayed in Figure 16.

10 In Figures 17a and Figures 17b, the XRPD pattern of MFI zeolite synthesized using methane is displayed, where Figure 17a represents a synthesis method, where the material is heated to 550 °C under argon before methane gas is added and Figure 17b represents a synthesis method, where the material is heated to 700 °C under argon before methane gas is added.

- 15 As can be seen when comparing Figure 5 with Figure 17a and Figure 17b, very little variation is observed in the XRPD pattern depending on which gaseous hydrocarbon that is used in the synthesis and at which temperature the sample is heated.

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Claims

1. A method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles, the method comprises the steps of:
 - 1) Adding one or more metal precursors to a silica or alumina source;
 - 5 2) Reducing the one or more metal precursors to form metal nanoparticles on the surface of the silica or alumina source;
 - 3) Passing a gaseous hydrocarbon, alkyl alcohol or alkyl ether over the silica or alumina supported metal nanoparticles to form a carbon template coated zeolite, zeolite-like or zeotype precursor composition;
 - 10 4a) Adding a structure directing agent to the carbon template coated zeolite, zeolite-like or zeotype precursor composition thereby creating a zeolite, zeolite-like or zeotype gel composition;
 - 4b) Crystallising the zeolite, zeolite-like or zeotype gel composition by subjecting said composition to a hydrothermal treatment;
 - 15 5) Removing the carbon template and structure directing agent and isolating the resulting zeolite, zeolite-like or zeotype encapsulated metal nanoparticles.

2. A method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to claim 1, wherein the carbon template coated zeolite, zeolite-like or zeotype precursor composition of step 3 is used directly in step 4a without removing the silica or alumina source.

- 25 3. A method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any preceding claim, wherein the one or more metal(s) is selected from the group consisting of group 4 elements, group 6 elements, group 7 elements, group 8 elements, group 9 elements, group 10 elements, group 11 elements or group 12 elements or mixtures thereof.

- 30 4. A method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any preceding claim, wherein the one or more metal(s) is selected from the group consisting of titanium, osmium, iridium, platinum, ruthenium, palladium, rhodium, rhenium, copper, nickel, iron, cobalt, silver, gold, cadmium, molybdenum or mixtures thereof.

5. A method for producing zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any any preceding claim, wherein the hydrocarbon is selected from aliphatic hydrocarbons having 1 to 8 carbon atoms, having 1 to 3
5 carbon atoms, alkenes having 2 to 6 carbon atoms, aromatic hydrocarbons having 6 to 10 carbon atoms and cyclic hydrocarbons having 3 to 8 carbon atoms.
6. A method for producing zeolite, zeolite-like or zeotype encapsulated metal
10 nanoparticles according to any any preceding claim, wherein the one or more metal precursor is loaded to the silica or alumina in an amount of from 0.5 to 20 wt %, from 0.5 to 5 wt %, from 0.5 to 2 wt %, or around 1 wt % during step 1.
7. A method for producing zeolite, zeolite-like or zeotype encapsulated metal
15 nanoparticles according to any any preceding claim, comprising adding an Al, Sn Ti, Zr or Ge source during step 4a.
8. A method for producing zeolite, zeolite-like or zeotype particles according to any
20 one any preceding claim, wherein the hydrothermal treatment comprise that the zeolite, zeolite-like or zeotype gel composition is heated to temperatures between 70 and 300 °C, preferably at 180 °C, under an autogeneous pressure in an autoclave or open flask for 24 hours or more.
9. Zeolite, zeolite-like or zeotype encapsulated metal nanoparticles manufactured
25 by the method according to any one of the claims 1-8.
10. A zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to
30 claim 9, wherein said metal nanoparticles are located predominantly in the secondary porosity of the zeolite structure, for example more than 70%, more than 80%, more than 90% or more than 95% of the total amount of the encapsulated metal nanoparticles.

11. A zeolite zeolite-like or zeotype encapsulated metal nanoparticles according to claim 9 or 10, wherein the particle is a hierarchical mesoporous zeolite, zeolite-like or zeotype particle.
- 5 12. A zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any one of the claims 9-11, wherein the amount of metal nanoparticles are in the range of 0.1 to 25 wt%, in the range from 0.5 to 20 wt%, from 0.5 to 10 wt%, from 0.5 to 5%, from 1.0 to 5 wt %, from 1 to 2 wt %, or around 1 wt %.
- 10 13. A zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any one of the claims 9-12, wherein the one or more metal(s) is selected from the group consisting of group 4 elements, group 6 elements, group 7 elements, group 8 elements, group 9 elements, group 10 elements, group 11 elements or group 12 elements or mixtures thereof.
- 15 14. A zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any one of the claims 9-13, wherein the one or more metal(s) is selected from the group consisting of titanium, osmium, iridium, platinum, ruthenium, palladium, rhodium, rhenium, copper, nickel, iron, cobalt, silver, gold, cadmium, molybdenum or mixtures thereof.
- 20 15. A zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any one of the claims 9-14, comprising an Al, Sn, Ti, Zr or Ge source in the framework of the crystal structure.
- 25 16. Use of the zeolite, zeolite-like or zeotype encapsulated metal nanoparticles according to any one of the claims 9-15 in shape-selective catalysis.

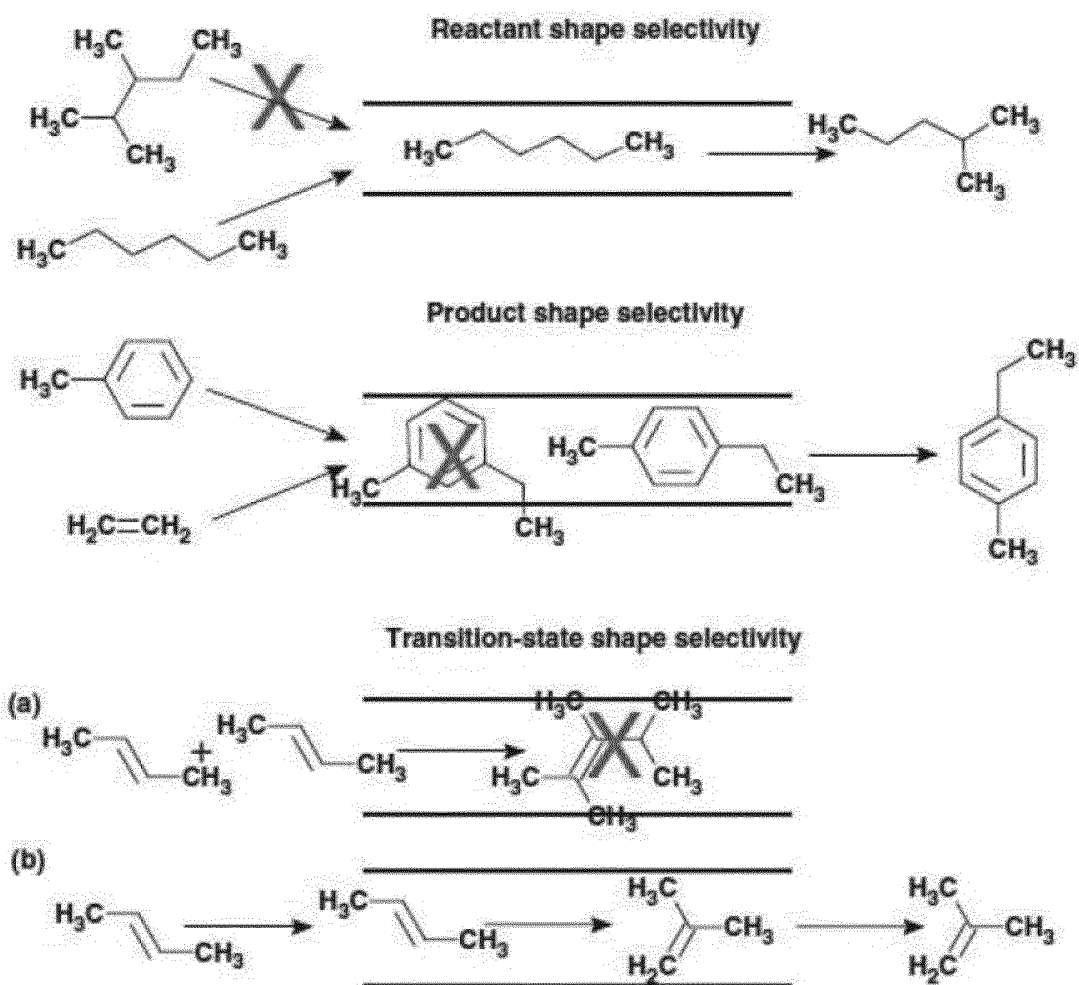


Fig. 1

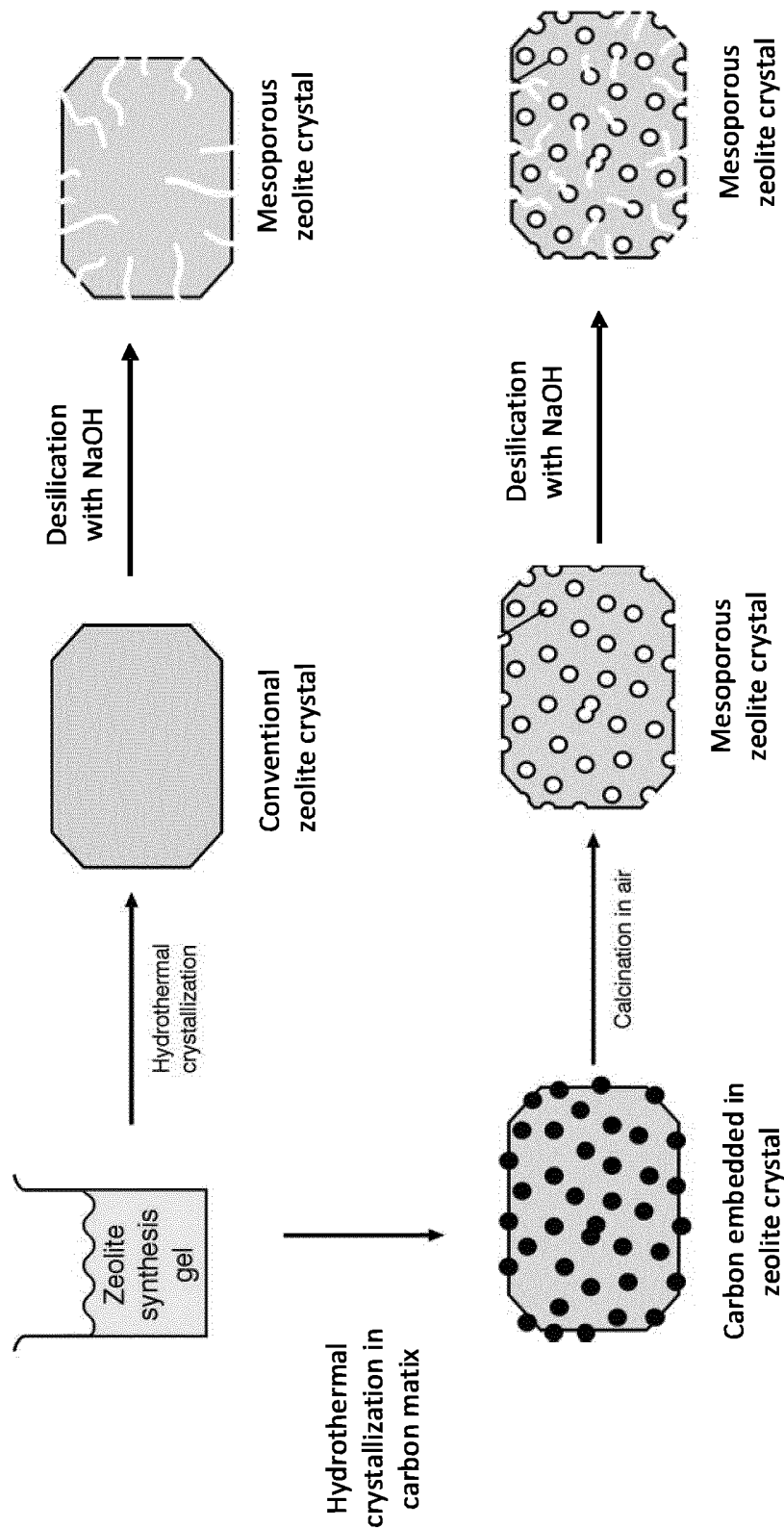


Fig. 2a

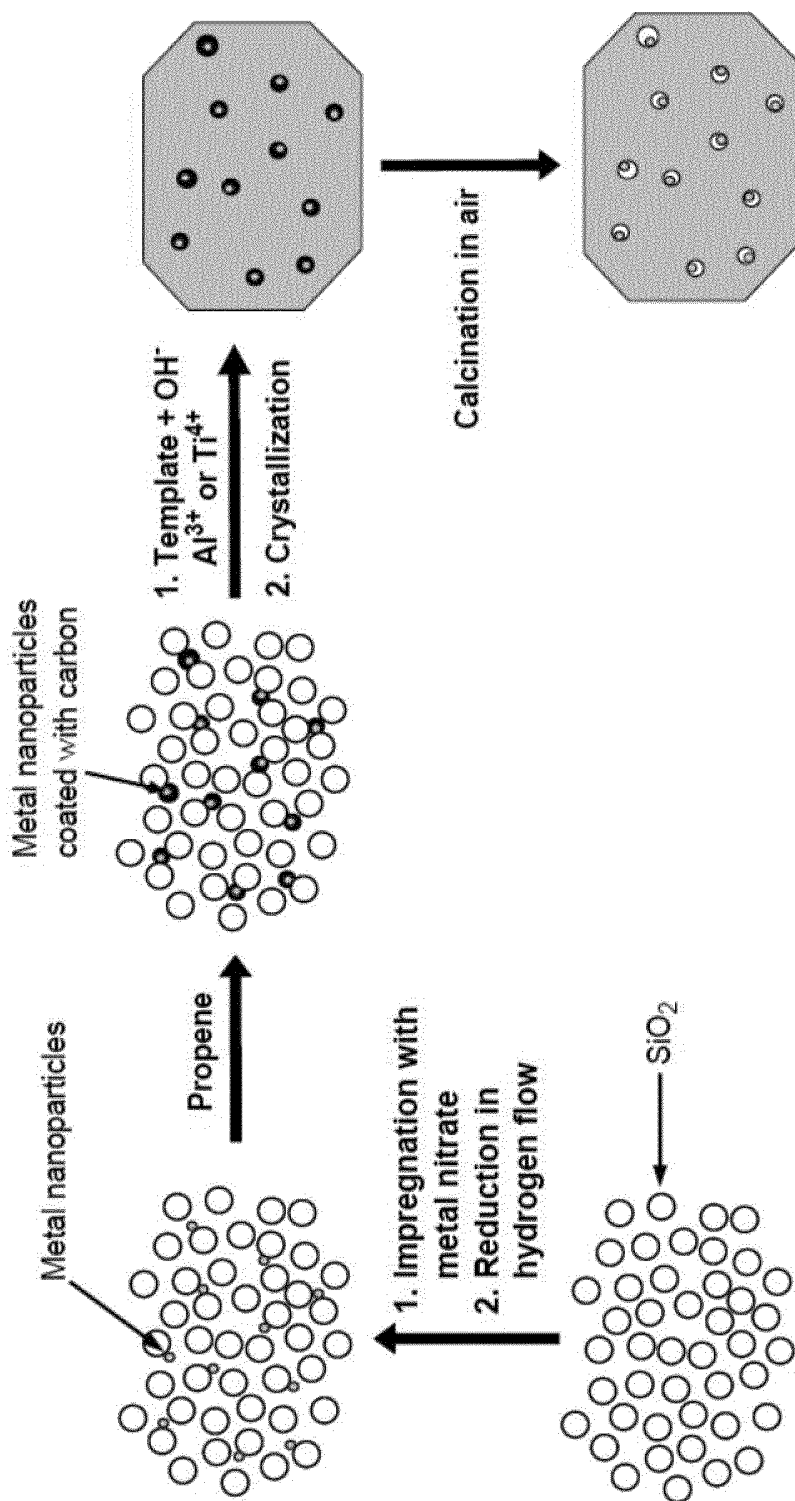


Fig. 2b

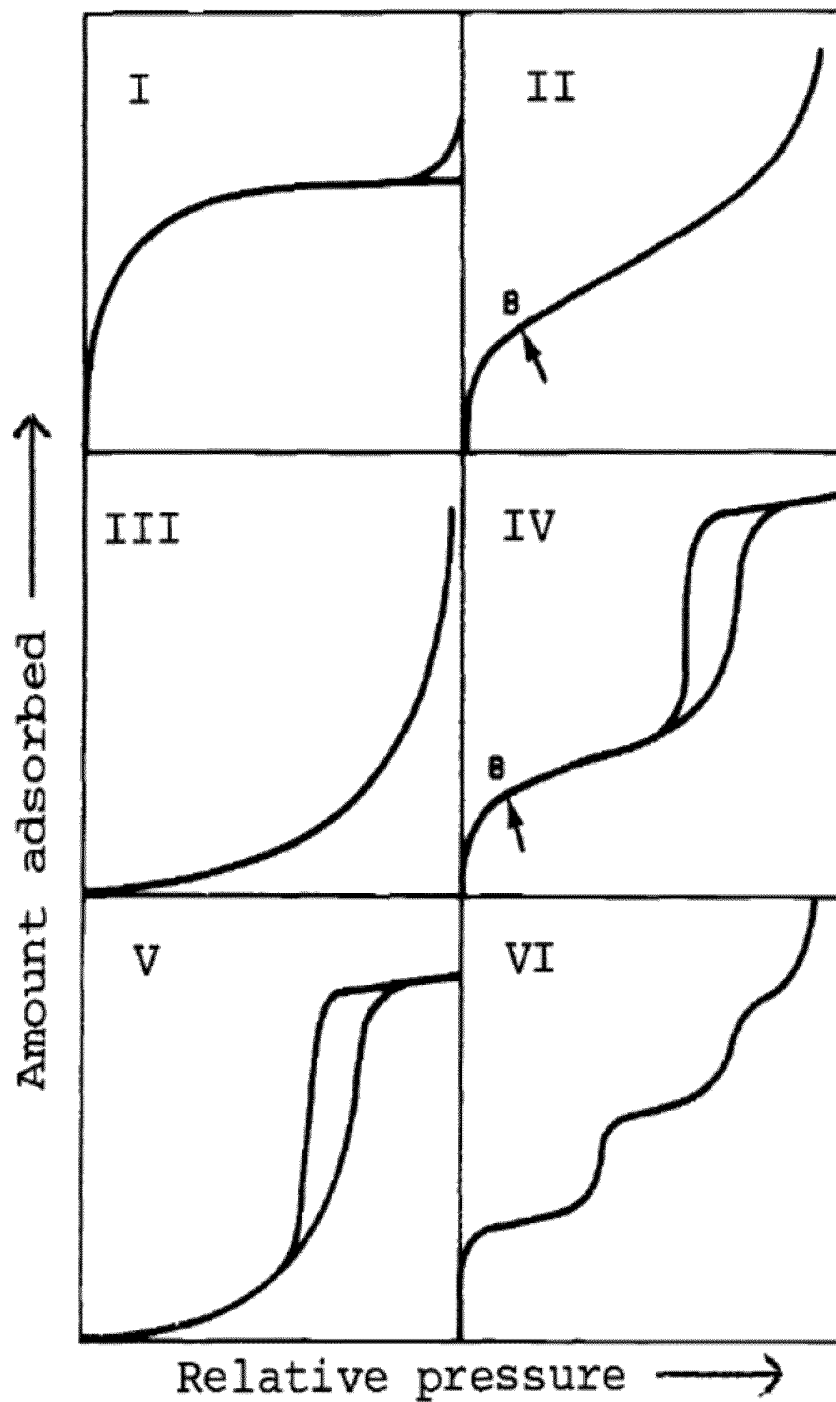


Fig. 3

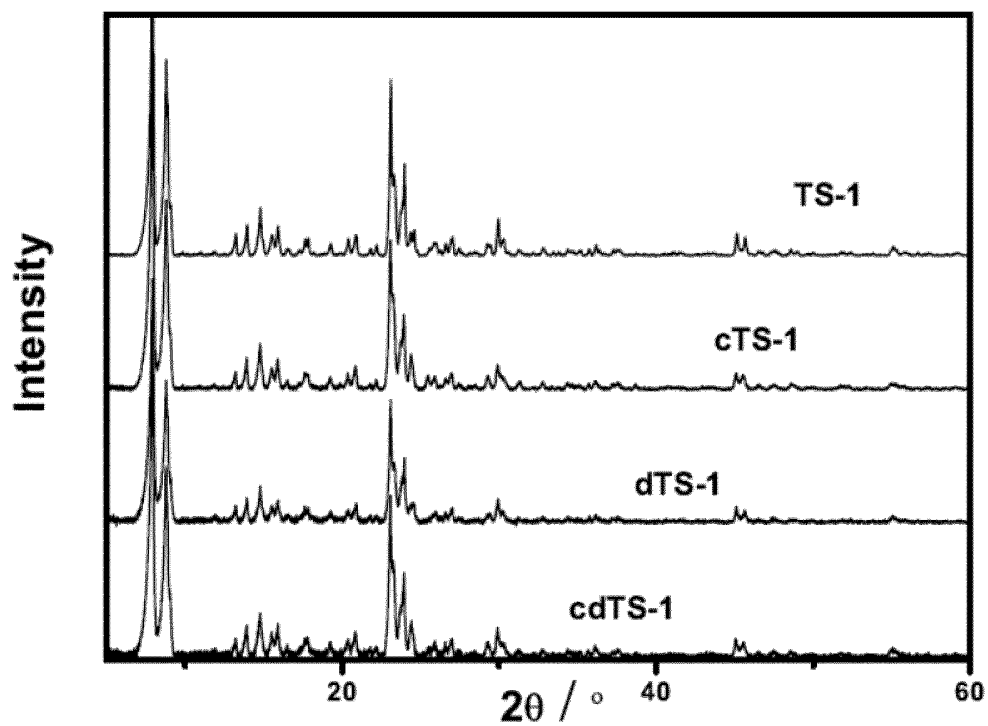


Fig. 4

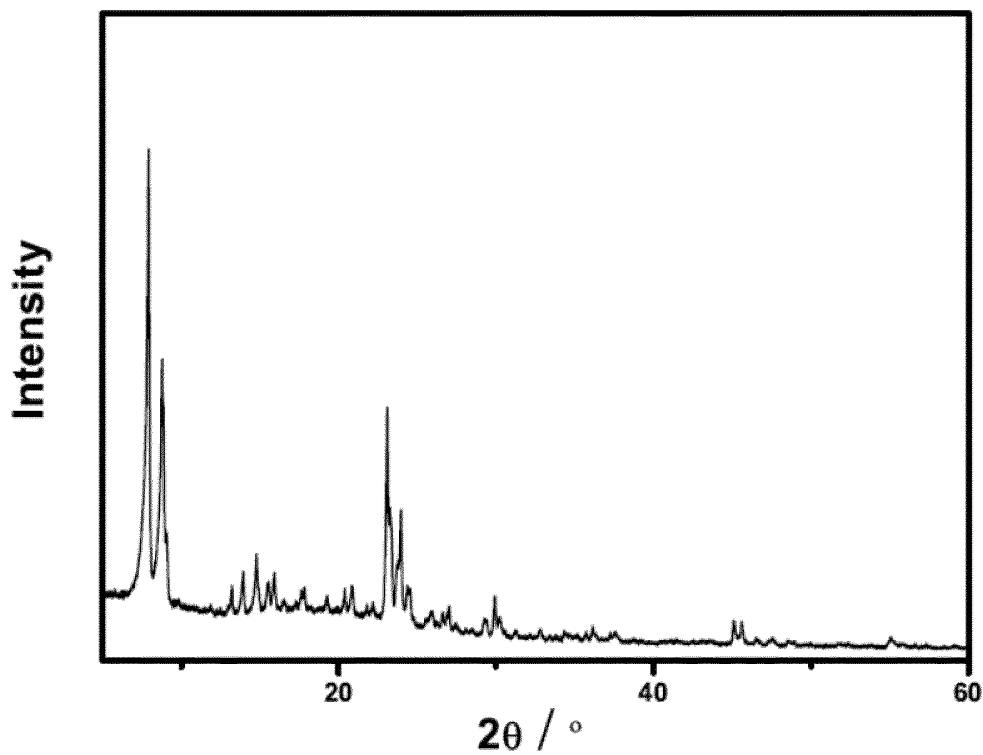
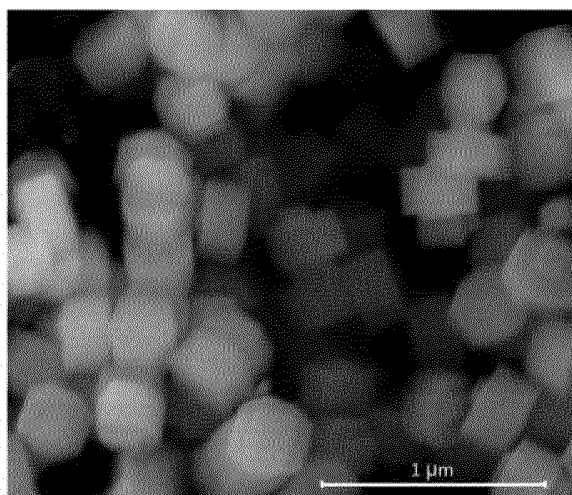
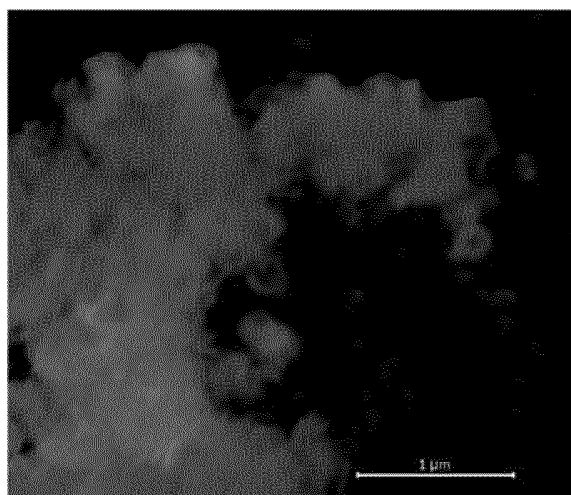


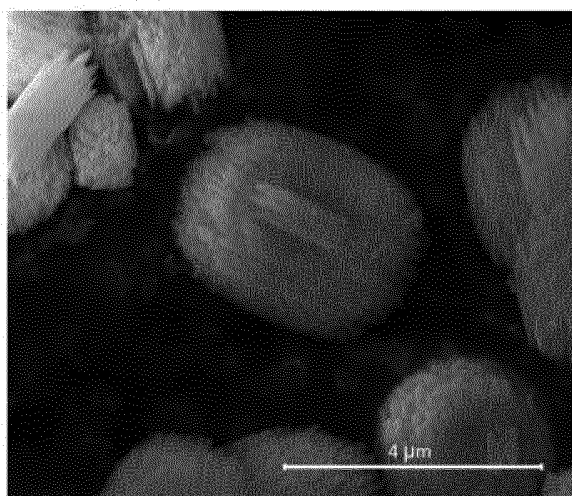
Fig. 5



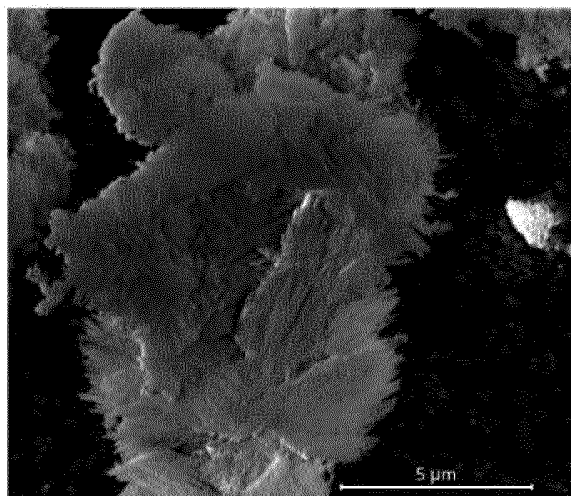
(a) Conventional TS-1



(b) Desilicated conventional TS-1



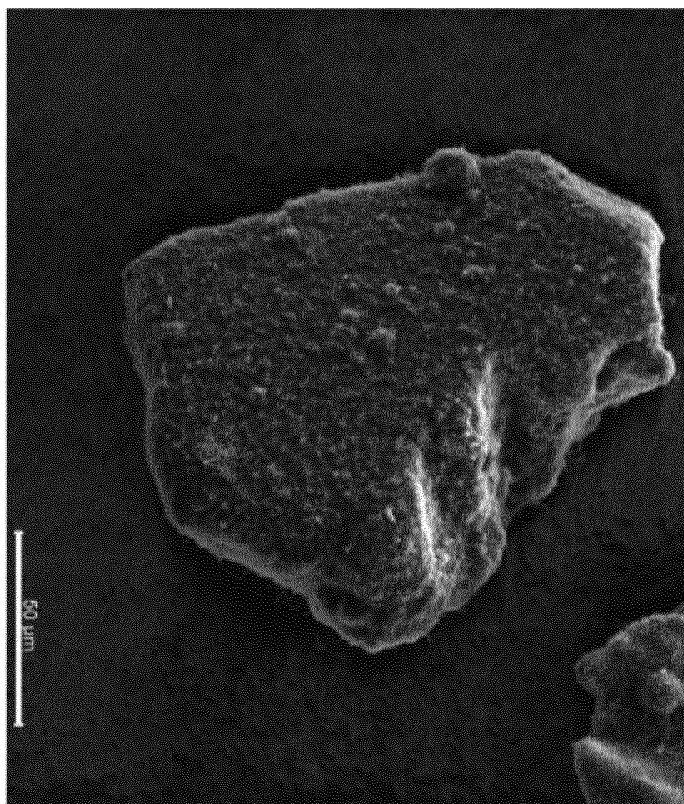
(c) Mesoporous TS-1



(d) Desilicated mesoporous TS-1

Fig. 6

(a) Nickel containing silica after exposure to propene



(b) Iron containing silica after exposure to propene

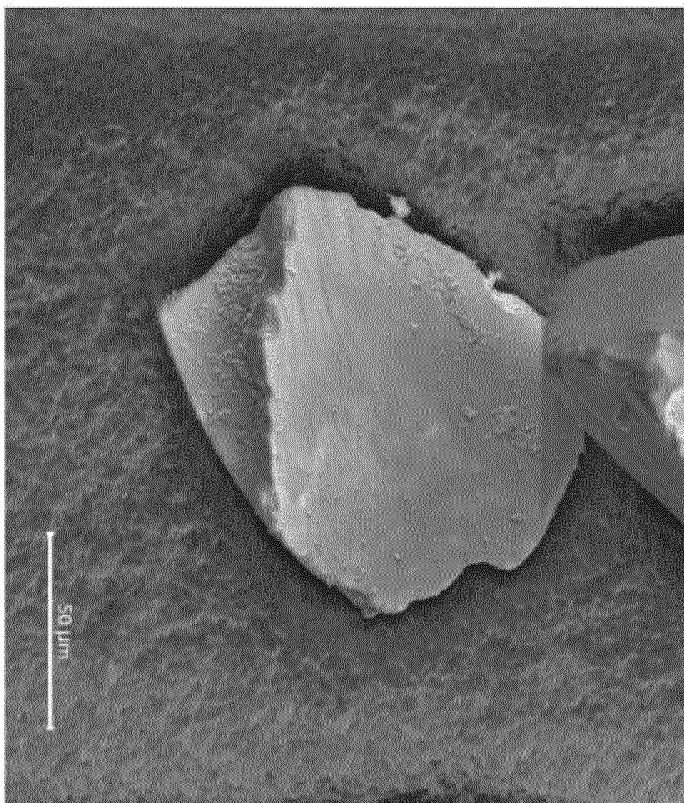


Fig. 7

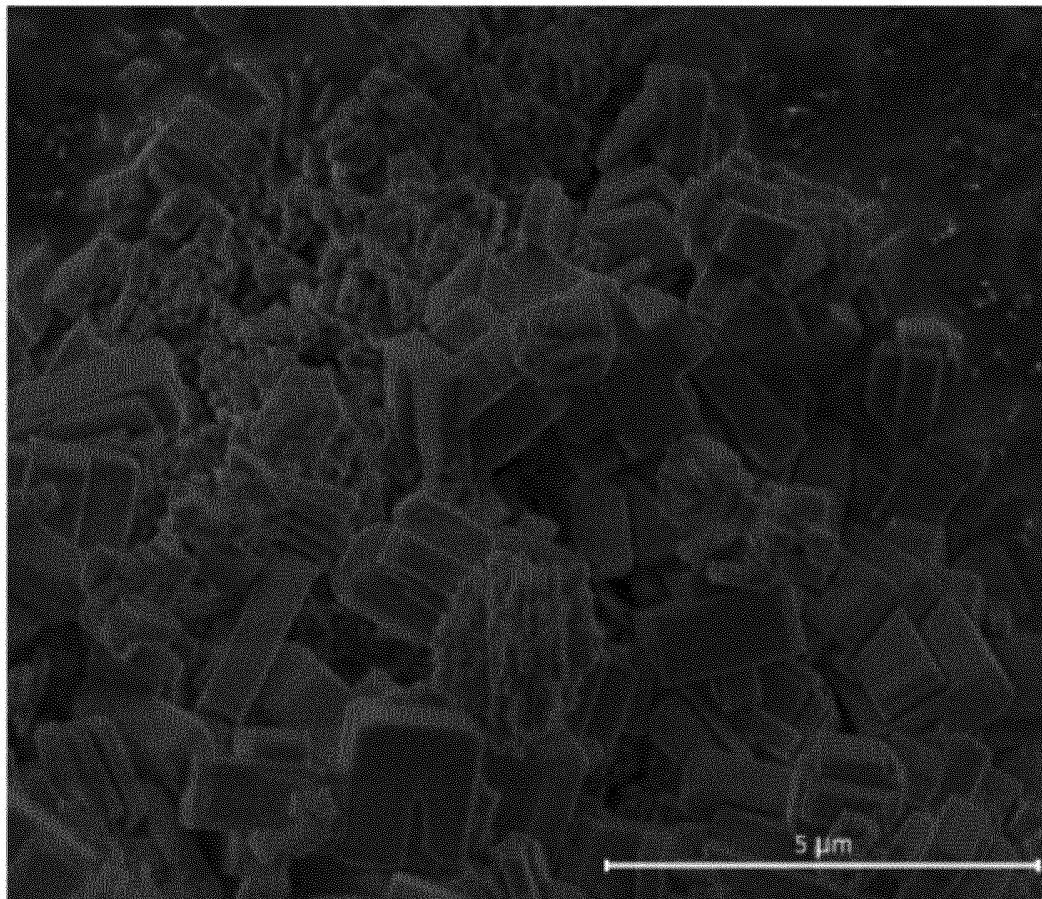


Fig. 8

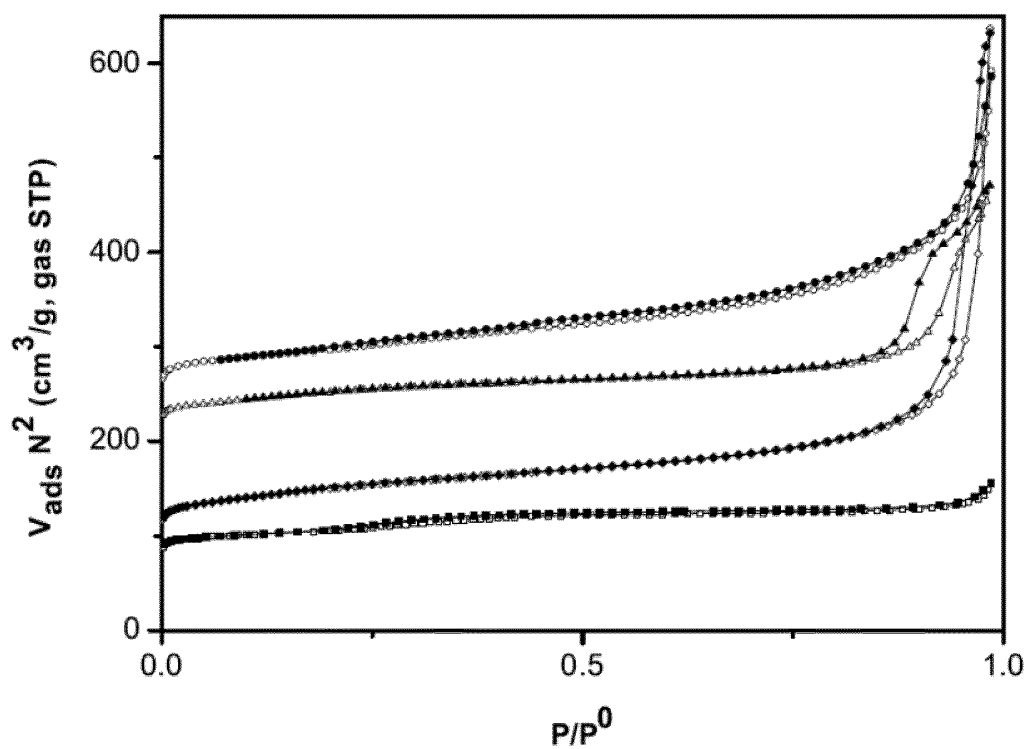


Fig. 9

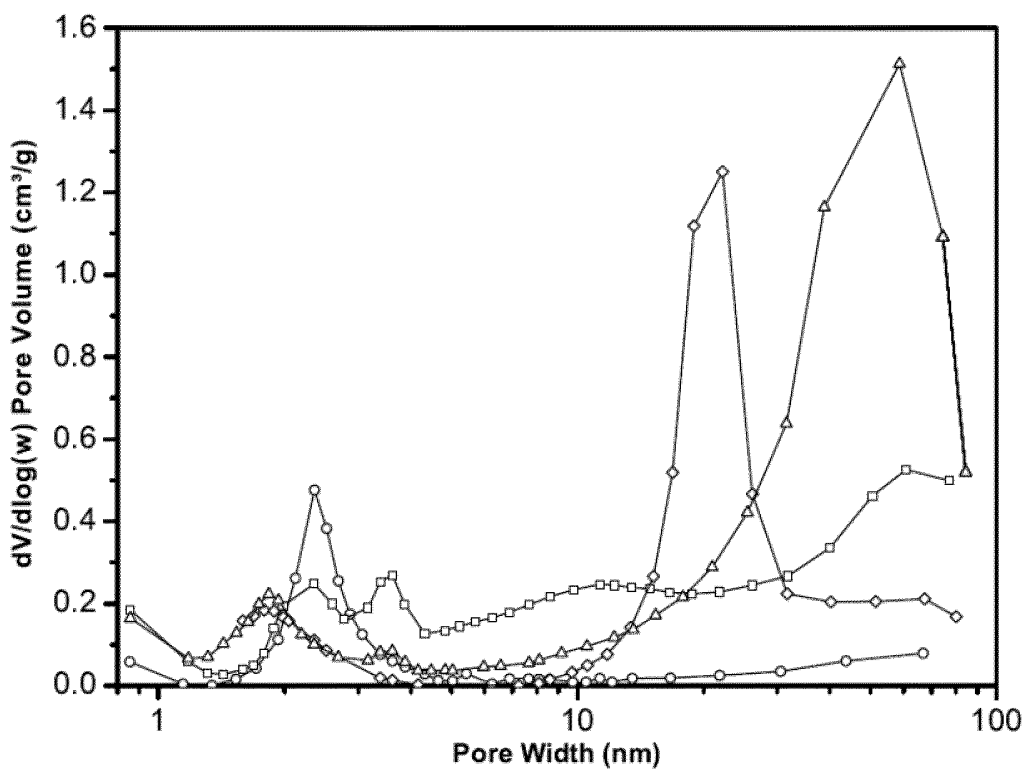


Fig. 10

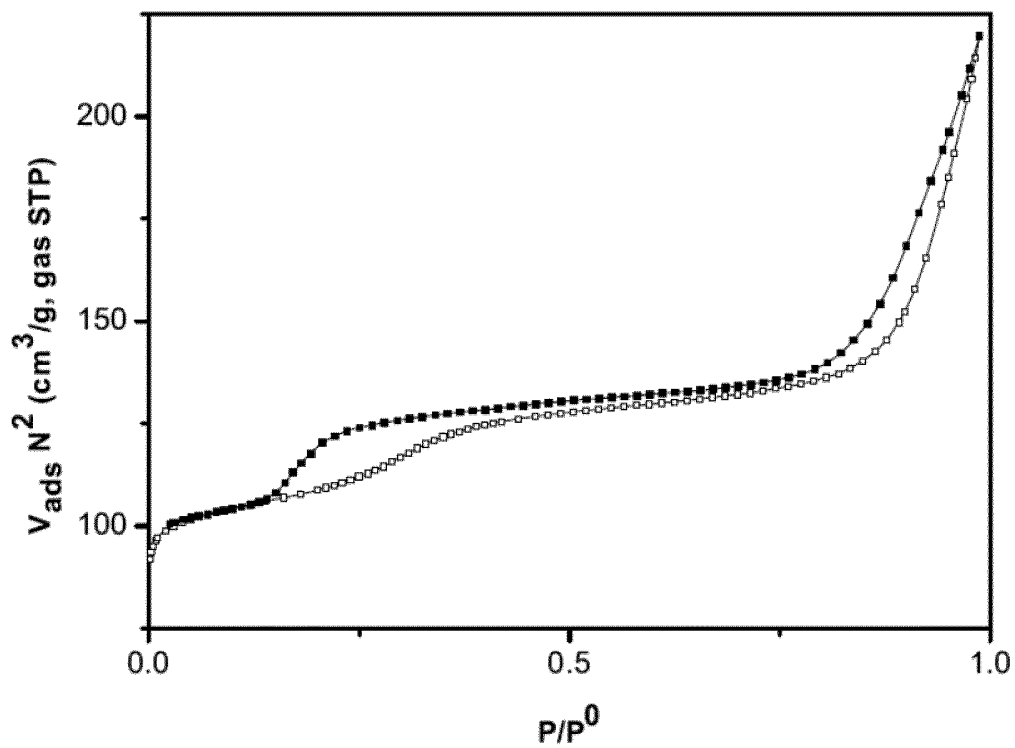


Fig. 11

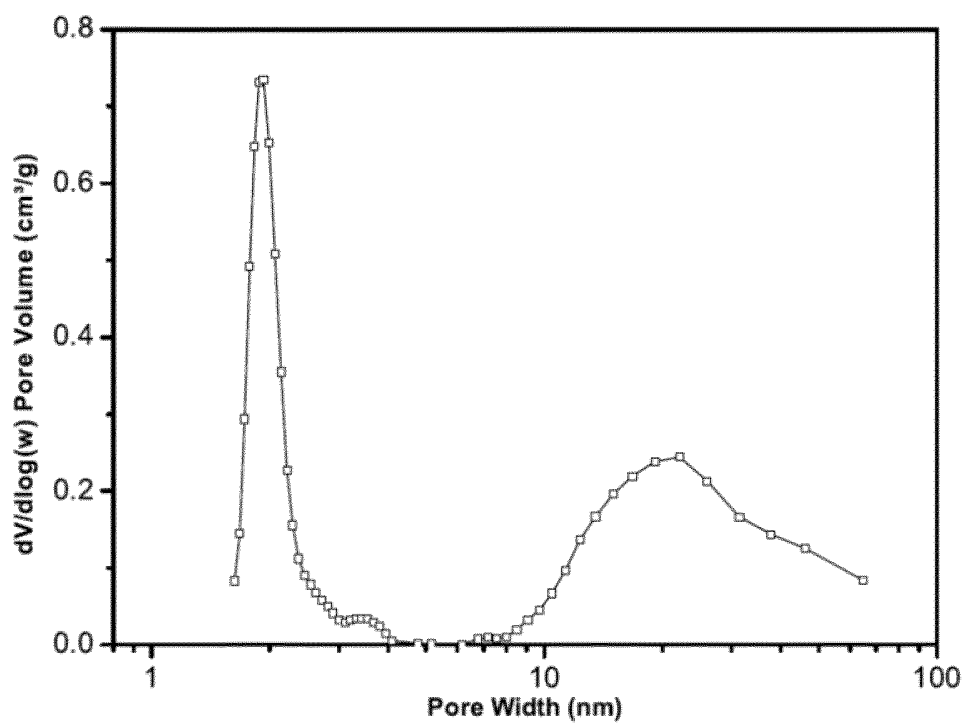


Fig. 12

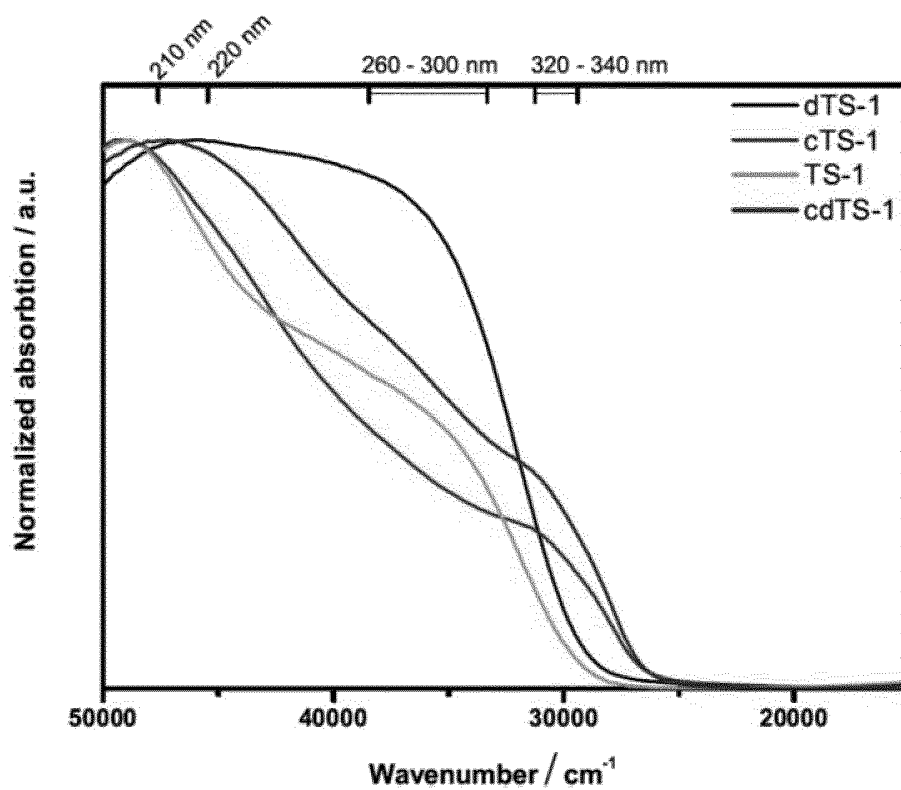


Fig. 13

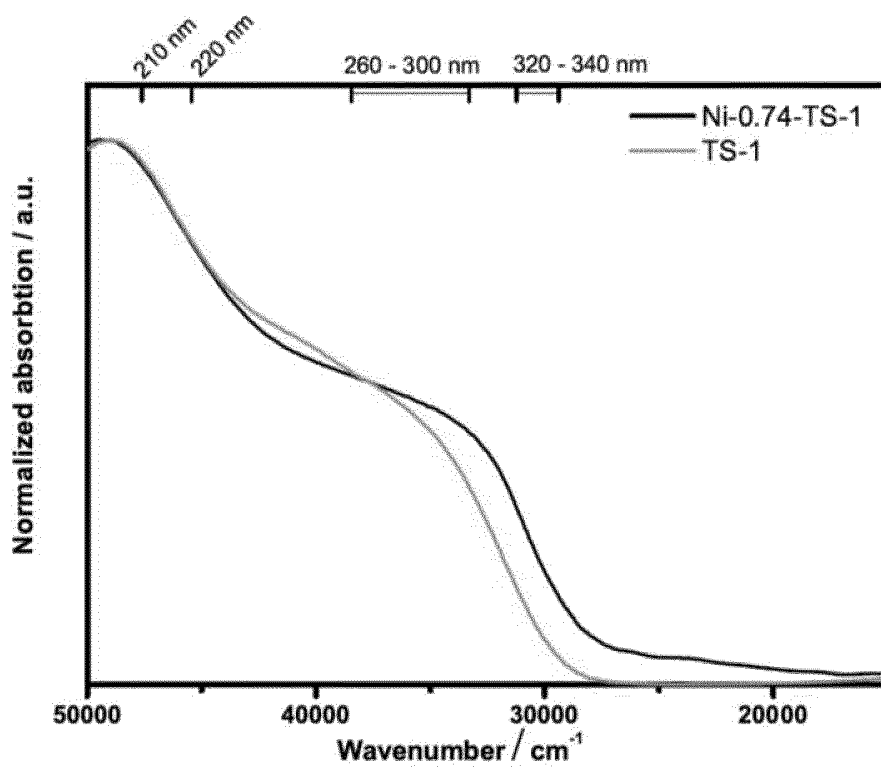


Fig. 14

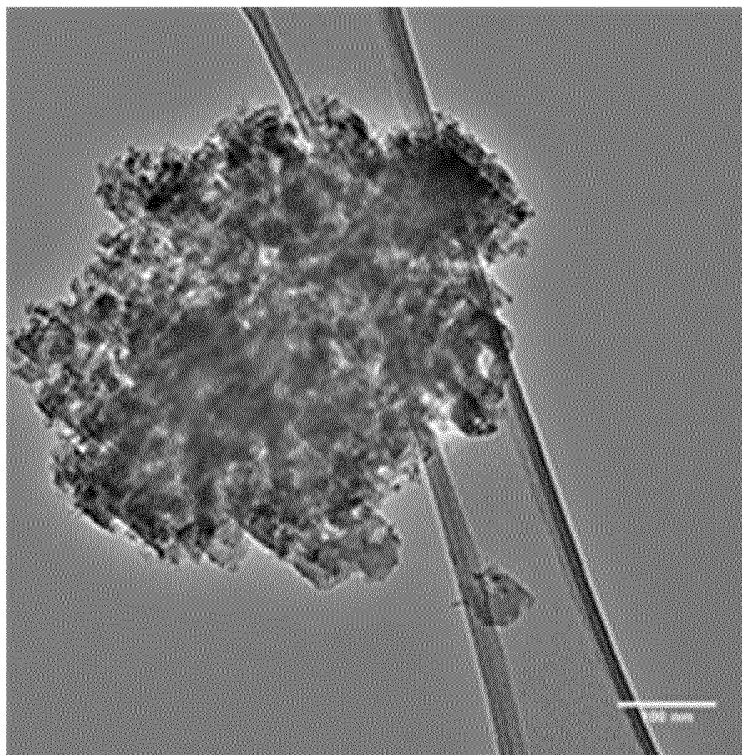


Fig. 15

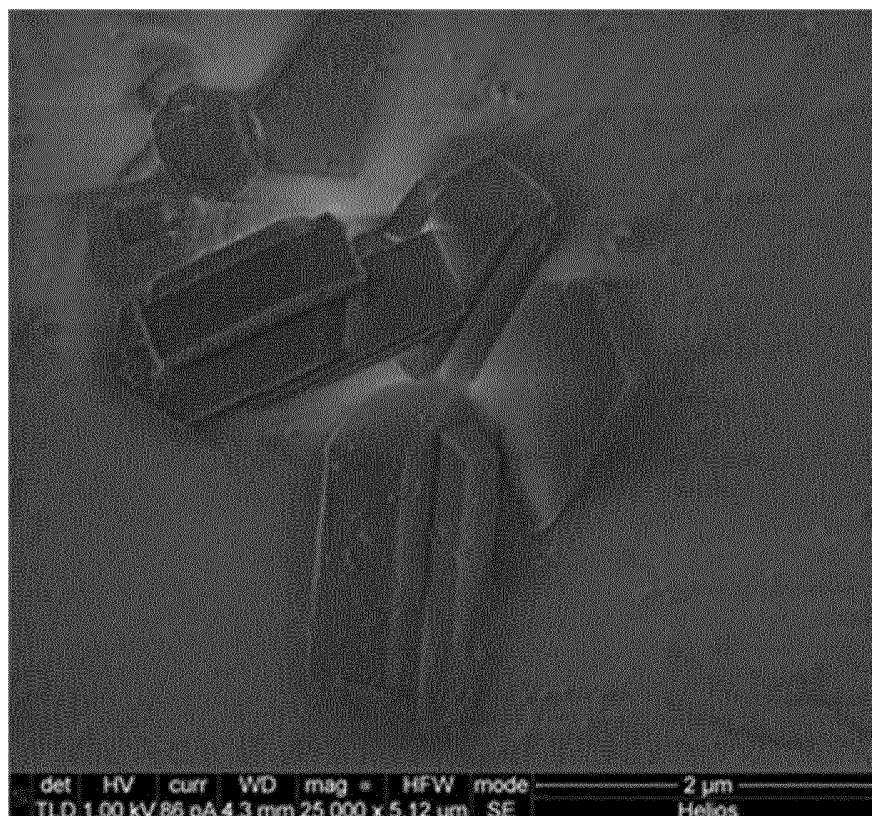


Fig. 16

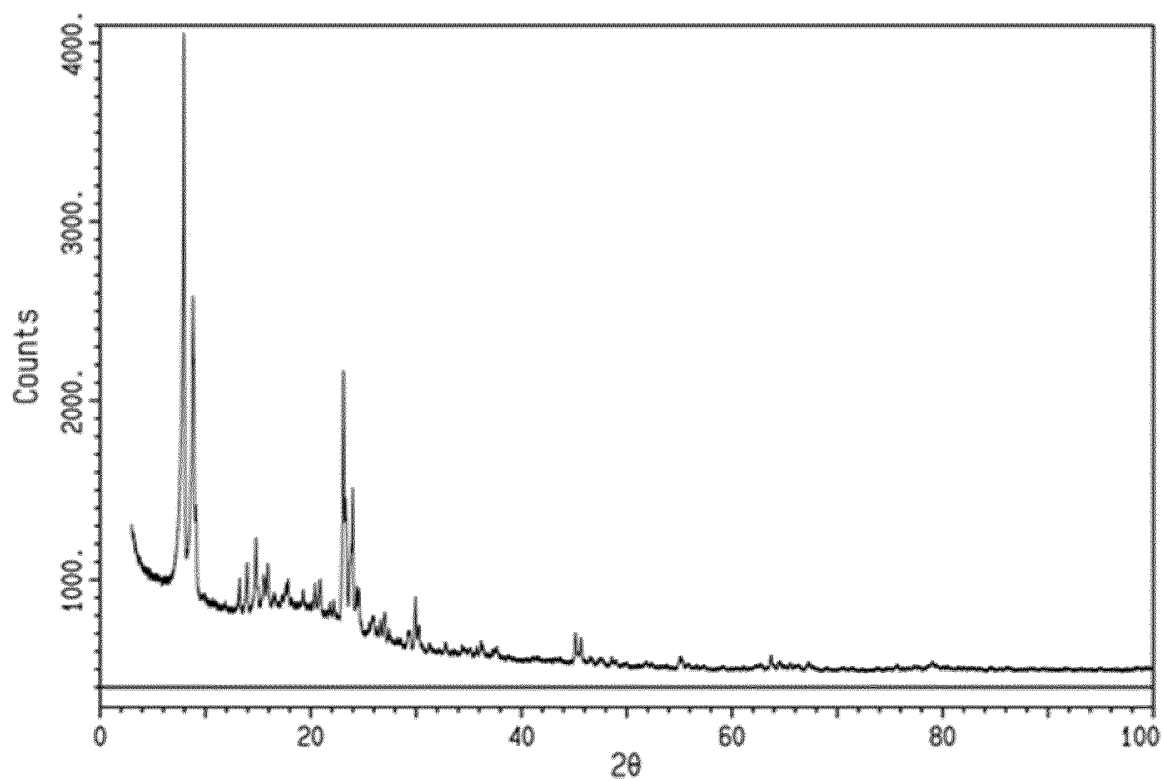


Fig. 17a

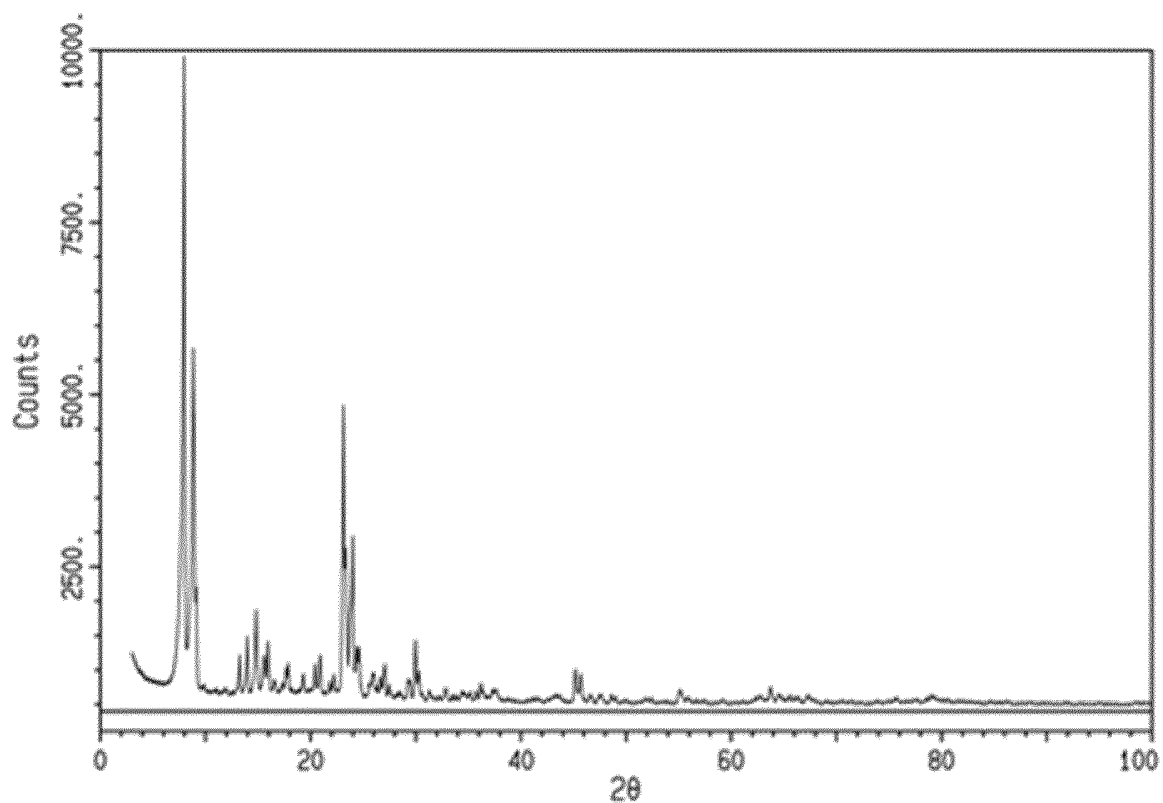


Fig. 17b

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2014/064428

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J29/89 B01J35/10 C01B39/08 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) B01J C01B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JANSSEN A H ET AL: "Exploratory study of mesopore templating with carbon during zeolite synthesis", MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 65, no. 1, 17 October 2003 (2003-10-17), pages 59-75, XP004460960, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2003.07.003 the whole document <div style="text-align: center; margin-top: 10px;">----- -/--</div>	1-16
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search	Date of mailing of the international search report	
1 September 2014	10/09/2014	
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 Schoofs, Bart	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/064428

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>SCHMIDT I ET AL: "CARBON NANOTUBE TEMPLATED GROWTH OF MESOPOROUS ZEOLITE SINGLE CRYSTALS", CHEMISTRY OF MATERIALS, AMERICAN CHEMICAL SOCIETY, WASHINGTON, US, vol. 13, no. 12, 1 December 2001 (2001-12-01), pages 4416-4418, XP001076943, ISSN: 0897-4756, DOI: 10.1021/CM011206H cited in the application the whole document</p> <p style="text-align: center;">-----</p>	1-16
A	<p>JAVIER PÉREZ-RAMÍREZ ET AL: "Hierarchical zeolites: enhanced utilisation of microporous crystals in catalysis by advances in materials design", CHEMICAL SOCIETY REVIEWS, vol. 37, no. 11, 1 January 2008 (2008-01-01), page 2530, XP055078762, ISSN: 0306-0012, DOI: 10.1039/b809030k the whole document</p> <p style="text-align: center;">-----</p>	1-16
A	<p>XIAOXING WANG ET AL: "Synthesis, characterization and catalytic performance of hierarchical TS-1 with carbon template from sucrose carbonization", MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 142, no. 2, 24 December 2010 (2010-12-24), pages 494-502, XP028189853, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2010.12.035 [retrieved on 2010-12-31] the whole document</p> <p style="text-align: center;">-----</p>	1-16