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(54) Title: METHOD FOR THE DIRECT SYNTHESIS OF CU-CONTAINING SILICOALUMINATE MATERIAL WITH THE AEI ZEOLITE STRUCTURE, AND THE CATALYTIC APPLICATIONS THEREOF

(57) Abstract: The main object of the present invention is to provide a new method for preparing the copper-containing silicoaluminate form of the AEI zeolite structure by means of a direct synthesis methodology. This new process involves combining an organometallic copper-complex with an additional organic molecule capable of directing the crystallisation of the silicoaluminate form of the AEI zeolite structure as organic structure-directing agents (OSDAs).



WO 2016/166247 A1

**METHOD FOR THE DIRECT SYNTHESIS OF CU-CONTAINING SILICOALUMINATE
MATERIAL WITH THE AEI ZEOLITE STRUCTURE, AND THE CATALYTIC
APPLICATIONS THEREOF**

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DESCRIPTION

Technical Field

The present invention relates to a new method for preparing the silicoaluminate form of
10 the AEI zeolite structure, containing copper atoms introduced therein, by means of a
direct synthesis methodology. This new methodology requires the combination of a
copper organometallic complex and an organic molecule capable of directing the
crystallisation of the AEI zeolite structure as organic co-structure-directing agents
(OSDAs). The present invention also relates to the application of said Cu-containing
15 silicoaluminate materials with the AEI zeolite structure as catalysts in the selective
catalytic reduction (SCR) of NO_x, amongst others.

Background

20 Zeolites are microporous materials formed by TO₄ tetrahedra (T = Si, Al, P, Ti, Ge, Sn,
etc.) interconnected by oxygen atoms creating pores and cavities of uniform size and
shape within the molecular range (3-15 Å).

These microporous crystalline materials may be used as catalysts in numerous
25 chemical processes. The use of a zeolite with specific physico-chemical properties in a
given chemical process is directly dependent on the nature of the reagents and
products involved in the process (such as size, shape, hydrophobicity, etc.), as well as
the reaction conditions. On the one hand, the nature of the reagents and products will
affect the diffusion of these molecules in the pores and cavities of the zeolite and,
30 consequently, the choice of a zeolite with a suitable pore topology for the products
involved in the reaction is essential. On the other hand, the zeolite must be chemically
and structurally stable under the required reaction conditions.

The formation of nitrogen oxides (NO_x) during the combustion of fossil fuels has
35 become a problem for society, since they are amongst the main air pollutants. The

selective catalytic reduction (SCR) of NO_x using ammonia as the reducing agent has become an efficient method for controlling said emissions (Brandenberger, et al. *Catal. Rev. Sci. Eng.*, 2008, 50, 492).

- 5 Recently, it has been disclosed that silicoaluminates with the AEI structure and Cu atoms introduced therein present high catalytic activity and hydrothermal stability in the SCR reduction of NO_x (Moliner et al. WO2013159825; Moliner et al. *Chem. Commun.*, 2012, 2012, 48, 8264).
- 10 The AEI zeolite structure presents a tri-directional system of small pores (< 4 Å) interconnected by large cavities, and also double six-membered rings (DA6) as secondary building units (Wagner, et al. *J. Am. Chem. Soc.*, 2000, 122, 263).

The silicoaluminate form of the AEI zeolite structure can be synthesised using cyclic ammonium cations with alkyl substituents (Zones et al. U.S. Patent 5958370; Cao et al. WO 2005/063624; Moliner et al. WO2013159825) or tetraalkylphosphonium cations (Sano et al. WO/2015/005369) as OSDAs.

15

In order to prepare the copper-containing silicoaluminate form of the AEI zeolite structure, the incorporation of the copper species is preferably performed by means of post-synthetic metal ion exchange processes on the previously synthesised and calcined AEI material (Moliner et al. WO2013159825; Sonoda, et al. *J. Mater. Chem. A.*, 2015, 3, 857). When using this methodology, several steps are required to obtain the final material, including the hydrothermal synthesis of the silicoaluminate, calcination in order to eliminate the OSDA, transformation into the ammonium form, metal ion exchange and, finally, calcination, to obtain the material in the desired Cu-silicoaluminate form. All these steps contribute to increase the total cost of the material preparation process.

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Therefore, the possibility of directly synthesising the material with the copper-containing silicoaluminate form of the AEI zeolite structure may considerably decrease the costs associated with the preparation thereof, since it would avoid most of the steps described above, making these directly prepared materials very attractive for industry.

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Description of the invention

The main object of the present invention is to provide a new method for preparing the copper-containing silicoaluminate form of the AEI zeolite structure by means of a direct synthesis methodology. This new process involves combining a copper organometallic complex with an additional organic molecule capable of directing the crystallisation of the silicoaluminate form of the AEI zeolite structure as organic structure-directing agents (OSDAs). The additional organic molecule may be, amongst others, any cyclic ammonium cation with alkyl substituents, such as N,N-dimethyl-3,5-dimethylpiperidinium.

Following this synthesis process, it is possible to synthesise the copper-containing silicoaluminate form of the AEI zeolite structure directly, thus avoiding the steps required to obtain said material by means of the traditional post-synthetic metal ion exchange processes.

The present invention also relates to the use as catalysts of the materials with the copper-containing silicoaluminate form of the AEI zeolite structure obtained according to the present methodology.

Therefore, the present invention relates to a process for the direct synthesis of the material with the copper-containing silicoaluminate form of the AEI zeolite structure with high synthesis yields, which comprises, at least, the following steps:

- (i) Preparation of a mixture containing, at least, one source of water, one source of copper, one polyamine to form the Cu organometallic complex, one source of tetravalent element Y, one source of trivalent element X, one cyclic ammonium cation with alkyl substituents as the OSDA and one source of alkaline or alkaline-earth cations (A), where the synthesis mixture has the following molar composition:

$$YO_2 : a X_2O_3 : b OSDA : c A : d H_2O : e Cu : f Polyamine$$

where

a ranges between 0.001 and 0.2, preferably between 0.005 and 0.1, and, more preferably, between 0.01 and 0.07,

- b* ranges between 0.01 and 2; preferably between 0.1 and 1, and, more preferably, between 0.1 and 0.6;
- c* ranges between 0 and 2; preferably between 0.001 and 1, and, more preferably, between 0.01 and 0.8;
- 5 *d* ranges between 1 and 200; preferably between 1 and 50, and, more preferably, between 2 and 20;
- e* ranges between 0.001 and 1; preferably between 0.001 and 0.6, and, more preferably, between 0.001 and 0.5;
- 10 *f* ranges between 0.001 and 1; preferably between 0.001 and 0.6, and, more preferably, between 0.001 and 0.5.
- (ii) Crystallisation of the mixture obtained in (i) in a reactor.
 - (iii) Recovery of the crystalline material obtained in (ii).

According to the present invention, Y is a tetravalent element that may be preferably
15 selected from Si, Sn, Ti, Ge and combinations thereof; more preferably, it is Si.

The source of Si used may be selected from silicon oxide, silicon halide, colloidal silica, fumed silica, tetraalkyl orthosilicate, silicate, silicic acid, a previously synthesised
20 crystalline material, a previously synthesised amorphous material and combinations thereof, and, more preferably, it is a material selected from a previously synthesised crystalline material, a previously synthesised amorphous material and combinations thereof; more preferably, it is a previously synthesised crystalline material.

According to the present invention, X is a trivalent element that may be preferably
25 selected from Al, B, Fe, In, Ga and combinations thereof; more preferably, it is Al.

The source of Al used may be selected from any aluminum salt, any hydrated aluminum oxide, any aluminum alkoxide, a previously synthesised crystalline material, a previously synthesised amorphous material and combinations thereof, and, more
30 preferably, it is a material selected from a previously synthesised crystalline material, a previously synthesised amorphous material and combinations thereof; more preferably, it is a previously synthesised crystalline material.

According to a particular embodiment of the present invention, the crystalline material
35 with the FAU zeolite structure may be used in (i) as the only source of Y and X,

preferably silicon and aluminum, and may preferably present a Si/Al ratio greater than 7.

Therefore, according to a particular embodiment of the present invention, Y is Si and X is Al, for which reason the process for the direct synthesis of the material with the copper-containing silicoaluminate form of the AEI zeolite structure with high synthesis yields would comprise, at least, the following steps:

- (i) Preparation of a mixture containing, at least, one source of water, one source of copper, one polyamine to form the Cu organometallic complex, one zeolite with the FAU crystal structure, such as zeolite Y, as the only source of silicon and aluminum, one cyclic ammonium cation with alkyl substituents as the OSDA and one source of alkaline or alkaline-earth cations (A), where the synthesis mixture has the following molar composition:



where

- a ranges between 0.001 and 0.2, preferably between 0.005 and 0.1, and, more preferably, between 0.01 and 0.07;
- b ranges between 0.01 and 2; preferably between 0.1 and 1, and, more preferably, between 0.1 and 0.6;
- c ranges between 0 and 2; preferably between 0.001 and 1, and, more preferably, between 0.01 and 0.8;
- d ranges between 1 and 200; preferably between 1 and 50, and, more preferably, between 2 and 20;
- e ranges between 0.001 and 1; preferably between 0.001 and 0.6, and, more preferably, between 0.001 and 0.5;
- f ranges between 0.001 and 1; preferably between 0.001 and 0.6, and, more preferably, between 0.001 and 0.5.
- (ii) Crystallisation of the mixture obtained in (i) in a reactor.
- (iii) Recovery of the crystalline material obtained in (ii).

According to the present invention, any source of Cu may be used in (i). Preferably, the source of copper may be selected from nitrate, sulfate and oxalate salts, and combinations thereof, amongst others.

- 5 According to the present invention, the mixture formed in (i) is free from any source of phosphorous.

According to a preferred embodiment of the present invention, the mixture formed in (i) may be free from any source of fluorine.

10

According to a preferred embodiment of the present invention, the source of alkaline or alkaline-earth cations may be any source of these elements, and may be preferably selected from a source of Na, K, and combinations thereof.

- 15 According to the present invention, the OSDA required in step (i) may be any cyclic ammonium cation with an alkyl substituent, preferably a quaternary ammonium selected from N,N-dimethyl-3,5-dimethylpiperidinium (DMDMP), N,N-diethyl-2,6-dimethylpiperidinium (DEDMP), N,N-dimethyl-2,6-dimethylpiperidinium, N-ethyl-N-methyl-2,6-dimethylpiperidinium and combinations thereof, preferably N,N-dimethyl-
20 3,5-dimethylpiperidinium.

- According to a particular embodiment, the process of the present invention may further comprise another OSDA, called co-operative OSDA, which may also be present in step (i), and may be selected from any cyclic quaternary ammonium or any other organic
25 molecule, such as, for example, any amine or quaternary ammonium.

- According to the present invention, any polyamine or mixture of different polyamines capable of forming a copper complex may be used in (i), regardless of the form (cyclic, linear, branched, etc.), and regardless of the nature of the amine (primary, secondary
30 or tertiary). Preferably, said polyamine may be selected from tetraethylenepentamine, triethylenetetramine, 1,4,8,11-tetraazacyclotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, and combinations thereof, amongst others. Preferably, the polyamine is tetraethylenepentamine.

According to the present invention, the crystallisation process described in (ii) is preferably performed in autoclaves, under static or dynamic conditions (for example, by stirring the mixture) at a temperature selected from 100°C and 200°C, preferably between 130°C and 200°C, and, more preferably, between 130°C and 175°C; with a
5 crystallisation time that may range between 6 hours and 50 days, preferably between 1 and 20 days, and, more preferably, between 2 and 15 days. It must be borne in mind that the components of the synthesis mixture may originate from different sources, which may modify the crystallisation conditions described.

10 According to a particular embodiment of the process of the present invention, it is possible to add AEI crystals to the synthesis mixture, which act as seeds that favour the synthesis described, in a quantity of up to 25% by weight with respect to the total quantity of oxides. These crystals may be added before or during the crystallisation process.

15

According to the process described, following the crystallisation described in (ii), the resulting solid is separated from the mother liquors and recovered. The recovery step (iii) may be performed by means of any well-known separation technique, such as, for example, decantation, filtration, ultrafiltration, centrifugation or any other solid-liquid
20 separation technique, and combinations thereof.

The process of the present invention may further comprise the elimination of the organic content retained inside the material by means of an extraction process.

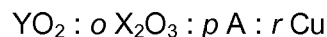
25 According to a particular embodiment, the elimination of the organic compound retained inside the material may be performed by means of a heat treatment at temperatures greater than 25°C, preferably between 100°C and 1000°C, for a period of time preferably ranging between 2 minutes and 25 hours.

30 According to a particular embodiment of the present invention, in the process for obtaining the material described above, at least one metal may be further introduced by means of post-synthetic processes, such as impregnation, ion exchange or combinations thereof. These metals are preferably selected from precious metals and, more preferably, from Pt, Pd and combinations thereof, and they are preferably located
35 at extra-lattice positions.

According to another particular embodiment of the present invention, during the process for obtaining the material described above, any metal oxide may be further introduced which contains, at least, one precious metal, preferably selected from Pt, Pd, and combinations thereof.

According to another particular embodiment, the material produced according to the present invention may be pelletised using any well-known technique.

According to a preferred embodiment, the material obtained according to the present invention may be calcined. Therefore, the zeolite material with the AEI structure may have the following molar composition after being calcined:

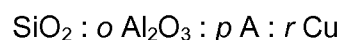


where o ranges between 0.001 and 0.2, preferably between 0.005 and 0.1, and, more preferably, between 0.01 and 0.07;

where p ranges between 0 and 2, preferably between 0.001 and 1, and, more preferably, between 0.01 and 0.8;

where r ranges between 0.001 and 1, preferably between 0.001 and 0.6, and, more preferably, between 0.001 and 0.5.

According to a particular embodiment, Y is Si and X is Al; therefore, the zeolite material with the AEI structure may present the following molar composition after being calcined:



where o ranges between 0.001 and 0.2, preferably between 0.005 and 0.1, and, more preferably, between 0.01 and 0.07;

where p ranges between 0 and 2, preferably between 0.001 and 1, and, more preferably, between 0.01 and 0.8;

where r ranges between 0.001 and 1, preferably between 0.001 and 0.6, and, more preferably, between 0.001 and 0.5.

According to a preferred embodiment, the material obtained is Cu-SSZ-39.

According to a particular embodiment of the present invention, the zeolite material with the AEI structure obtained may further comprise a precious metal, preferably selected from Pd, Pt and combinations thereof.

- 5 The present invention also relates to the use of the materials described above, obtained according to the process of the present invention, as catalysts in the conversion of feeds formed by organic compounds into higher-added-value products, or as molecular sieves for the elimination/separation of streams (for example, gas mixtures), by placing the feeds in contact with the material obtained.

10

- According to a preferred embodiment, the material obtained in the present invention may be used as a catalyst in the selective catalytic reduction (SCR) of NO_x (nitrogen oxides) in a gas stream. In particular, the SCR of NO_x will be performed in the presence of reducing agents, preferably selected from ammonium, urea, hydrocarbons, and combinations thereof. According to this particular embodiment, the selective catalytic reduction (SCR) of NO_x (nitrogen oxides) may be performed using a monolith as the substrate, and applying a layer of the zeolite material obtained according to the present invention thereto, such that the gas stream may go through it to perform the desired reaction. Likewise, a layer of the zeolite material obtained according to the present invention may be applied to other substrates, such as, for example, a filter through which the gas stream may pass.

- According to another particular embodiment of the present invention, the material synthesised according to the present invention, which contains a precious metal, such as Pt or Pd, may be used as a catalyst in the selective oxidation of ammonia to nitrogen. According to this particular embodiment, the selective catalytic oxidation of ammonia to nitrogen may be performed using a monolith as the substrate, and applying a layer of the zeolite material obtained according to the present invention thereto, such that the gas stream may go through it to perform the desired reaction. Likewise, a layer of the zeolite material obtained according to the present invention may be applied to other substrates, such as, for example, a filter, amongst others, through which the gas stream may pass.

According to another particular embodiment, the material described according to the present invention may be used in the conversion of methane into methanol (Wulfers, et al. Chem. Commun. 2015, 51, 4447).

5 Throughout the description and the claims, the word "comprises" and variants thereof are not intended to exclude other technical characteristics, additives, components or steps. For persons skilled in the art, other objects, advantages and characteristics of the invention will arise, partly from the description and partly from the practice of the invention.

10

Brief description of the figures

Figure 1: PXRD patterns of the Cu-silicoaluminate materials with the AEI structure synthesised according to the present invention.

15

Figure 2: UV-Vis spectrum of the Cu-silicoaluminate material with the AEI structure synthesised according to Example 2 of the present invention.

EXAMPLES

20

Example 1: Synthesis of N,N-dimethyl-3,5-dimethylpiperidinium (DMDMP)

10 g of 3,5-dimethylpiperidine (Sigma-Aldrich, $\geq 96\%$ by weight) is mixed with 19.51 g of potassium bicarbonate (KHCO_3 , Sigma-Aldrich; 99.7% by weight), and dissolved in
25 140 ml of methanol. Subsequently, 54 ml of methyl iodide (CH_3I , Sigma-Aldrich, $\geq 99\%$ by weight) is added, and the resulting mixture is kept under stirring for 5 days at room temperature. Once this time has elapsed, the reaction mixture is filtered in order to eliminate the potassium bicarbonate. The filtrated solution is partially concentrated by means of a rotary evaporator. Once the methanol has been partially evaporated, the
30 solution is washed with chloroform several times and magnesium sulfate is added (MgSO_4 , Sigma-Aldrich, $\geq 99.5\%$ by weight). Subsequently, the mixture is filtered in order to eliminate the magnesium sulfate. The ammonium salt is obtained by precipitation with diethyl ether and subsequent filtration. The final yield of N,N-dimethyl-3,5-dimethylpiperidinium iodide is 85%.

35

In order to prepare the hydroxide form of the preceding organic salt: 10.13 g of the organic salt is dissolved in 75.3 g of water. Subsequently, 37.6 g of an anion-exchange resin (Dower SBR) is added, and the resulting mixture is kept under stirring for 24 hours. Finally, the solution is filtered, to obtain N,N-dimethyl-3,5-dimethylpiperidinium hydroxide (with a 94% exchange).

Example 2: Direct synthesis of the Cu-silicoaluminate with the AEI structure

154.0 mg of a 20% by weight aqueous solution of copper sulfate (II) (CuSO_4 , Alfa Aesar, 98%) is mixed with 31.2 mg of tetraethylenepentamine (TEPA, 98%, Sigma Aldrich), in order to prepare the organometallic copper-complex *in situ*, keeping the resulting mixture under stirring for 2 hours. Once this time has elapsed, 3216.0 mg of a 7.4% by weight aqueous solution of N,N-dimethyl-3,5-dimethylpiperidinium hydroxide and 163.1 mg of a 20% by weight aqueous solution of sodium hydroxide are added, keeping the resulting mixture under stirring for 15 minutes. Finally, 235.3 mg of a zeolite with the FAU structure (CBV-720, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 21) is introduced into the synthesis mixture and kept under stirring for the period of time required to evaporate the excess water and achieve the desired gel concentration. The final composition of the gel is $\text{SiO}_2 : 0.047 \text{ Al}_2\text{O}_3 : 0.046 \text{ Cu(TEPA)}^{2+} : 0.2 \text{ DMDMP} : 0.2 \text{ NaOH} : 23 \text{ H}_2\text{O}$. The resulting gel is transferred to a teflon-lined autoclave. The crystallisation is performed at 135°C for 7 days under static conditions. The solid product is filtered, washed abundantly with water, dried at 100°C and, finally, calcined in air at 550°C for 4 h in order to eliminate the organic remainders. The yield of the solid obtained is greater than 90% (without taking the organic remainders into account).

25

The solid is characterised by means of powder X-ray diffraction, and the characteristic peaks of the AEI structure are obtained (see Figure 1). Chemical analyses of the sample indicate a Si/Al ratio of 9.95 and a copper content of 3.3% by weight.

30 The uncalcined crystalline material obtained is characterised by UV-VIS spectroscopy in order to study the stability of the molecules of the organometallic copper-complex after the crystallisation of the zeolite. As can be observed in Figure 2, the UV-VIS spectrum shows a single band centred at $\sim 265 \text{ nm}$, which has been assigned to the presence of the intact Cu-TEPA complex inside the zeolite structure (Franco, et al. 2013/159828, 2012).

35

Example 3: Direct synthesis of the Cu-silicoaluminate with the AEI structure

75.1 mg of a 20% by weight aqueous solution of copper sulfate (II) (CuSO_4 , Alfa Aesar, 98%) is mixed with 18.0 mg of tetraethylenepentamine (TEPA, 98%, Sigma Aldrich), in order to prepare the organometallic copper-complex *in situ*, keeping the resulting mixture under stirring for 2 hours. Once this time has elapsed, 4049.0 mg of a 5.9% by weight aqueous solution of N,N-dimethyl-3,5-dimethylpiperidinium hydroxide and 159.1 mg of a 20% by weight aqueous solution of sodium hydroxide are added, keeping the resulting mixture under stirring for 15 minutes. Finally, 285.2 mg of a zeolite with the FAU structure (CBV-720, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 21) is introduced into the synthesis mixture, and kept under stirring for the period of time required to evaporate the excess water and achieve the desired gel concentration. The final composition of the gel is $\text{SiO}_2 : 0.047 \text{ Al}_2\text{O}_3 : 0.019 \text{ Cu}(\text{TEPA})^{2+} : 0.3 \text{ DMDMP} : 0.2 \text{ NaOH} : 18 \text{ H}_2\text{O}$. The resulting gel is transferred to a teflon-lined autoclave. The crystallisation is performed at 135°C for 7 days under static conditions. The solid product is filtered, washed abundantly with water, dried at 100°C and, finally, calcined in air at 550°C for 4 h in order to eliminate the organic remainders. The yield of the solid obtained is greater than 90% (without taking the organic remainders into account). The solid is characterised by means of powder X-ray diffraction, and the characteristic peaks of the AEI structure are obtained (see Figure 1).

Example 4: Direct synthesis of the Cu-silicoaluminate with the AEI structure

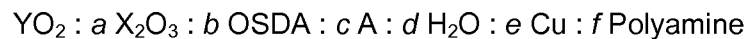
112.2 mg of a 20% by weight aqueous solution of copper sulfate (II) (CuSO_4 , Alfa Aesar, 98%) is mixed with 27.0 mg of tetraethylenepentamine (TEPA, 98%, Sigma Aldrich), in order to prepare the organometallic copper-complex *in situ*, keeping the resulting mixture under stirring for 2 hours. Once this time has elapsed, 2416.0 mg of a 7.4% by weight aqueous solution of N,N-dimethyl-3,5-dimethylpiperidinium hydroxide and 66.2 mg of a 20% by weight aqueous solution of sodium hydroxide are added, keeping the resulting mixture under stirring for 15 minutes. Finally, 196.2 mg of a zeolite with the FAU structure (CBV-720, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 21) is introduced into the synthesis mixture, and kept under stirring for the period of time required to evaporate the excess water and achieve the desired gel concentration. The final composition of the gel is $\text{SiO}_2 : 0.047 \text{ Al}_2\text{O}_3 : 0.041 \text{ Cu}(\text{TEPA})^{2+} : 0.3 \text{ DMDMP} : 0.1$

Example 2	71.7	98.4	99.6	99.8	97.1	96.9	85.1
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CLAIMS

1. Process for the direct synthesis of a material with the copper-containing silicoaluminate form of the AEI zeolite structure, which comprises, at least, the following steps:

(i) Preparation of a mixture containing, at least, one source of water, one source of copper, one polyamine, one source of tetravalent element Y, one source of trivalent element X, one cyclic ammonium cation with alkyl substituents as the OSDA and one source of alkaline or alkaline-earth cations (A), where the synthesis mixture has the following molar composition:



where

a ranges between 0.001 and 0.2;

b ranges between 0.01 and 2;

c ranges between 0 and 2;

d ranges between 1 and 200;

e ranges between 0.001 and 1;

f ranges between 0.001 and 1.

(ii) Crystallisation of the mixture obtained in (i) in a reactor.

(iii) Recovery of the crystalline material obtained in (ii).

25

2. Process for the direct synthesis of a material according to claim 1, wherein *c* ranges between 0.001 and 1.

3. Process for the direct synthesis of a material according to any of claims 1 or 2, wherein Y is a tetravalent element selected from Si, Sn, Ti, Ge and combinations thereof.

4. Process for the direct synthesis of a material according to claim 3, wherein Y is Si and originates from a source selected from silicon oxide, silicon halide, colloidal silica, fumed silica, tetraalkyl orthosilicate, silicate, silicic acid, a previously synthesised

35

crystalline material, a previously synthesised amorphous material and combinations thereof.

5 5. Process for the direct synthesis of a material according to claim 4, wherein the source of Y is a previously synthesised crystalline material.

6. Process for the direct synthesis of a material according to any of claims 1 to 5, wherein X is selected from Al, B, Fe, In, Ga and combinations thereof.

10 7. Process for the direct synthesis of a material according to claim 6, wherein X is Al and originates from a source selected from aluminum salt, any hydrated aluminum oxide, any aluminum alkoxide, a previously synthesised crystalline material, a previously synthesised amorphous material and combinations thereof.

15 8. Process for the direct synthesis of a material according to claim 7, wherein the source of X is a previously synthesised crystalline material.

9. Process for the direct synthesis of a material according to the preceding claims, wherein a zeolite with the FAU structure is the only source of Y and X.

20

10. Process for the direct synthesis of a material according to any of claims 1 to 9, wherein any source of copper may be used in step (i).

25 11. Process for the direct synthesis of a material according to claim 10, wherein the source of copper is selected from nitrate, sulfate and oxalate salts, and combinations thereof.

30 12. Process for the direct synthesis of a material according to any of claims 1 to 11, wherein the cyclic ammonium cation used as the OSDA is a quaternary ammonium selected from N,N-dimethyl-3,5-dimethylpiperidinium (DMDMP), N,N-diethyl-2,6-dimethylpiperidinium (DEDMP), N,N-dimethyl-2,6-dimethylpiperidinium, N-ethyl-N-methyl-2,6-dimethylpiperidinium and combinations thereof.

35 13. Process for the direct synthesis of a material according to claim 12, wherein the OSDA selected is N,N-dimethyl-3,5-dimethylpiperidinium.

14. Process for the direct synthesis of a material according to any of claims 1 to 13, wherein the polyamine of step (i) comprises primary, secondary or tertiary amines, or mixtures thereof.

5

15. Process for the direct synthesis of a material according to claim 14, wherein the polyamine required in step (i) is selected from tetraethylenepentamine, triethylenetetramine, 1,4,8,11-tetraazacyclotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, or mixtures thereof.

10

16. Process for the direct synthesis of a material according to claim 15, wherein the polyamine used in step (i) is tetraethylenepentamine.

17. Process for the direct synthesis of a material according to claims 1 to 16, wherein
15 the crystallisation process described in (ii) is performed in autoclaves, under static or dynamic conditions.

18. Process for the direct synthesis of a material according to claims 1 to 17, wherein
20 the crystallisation process described in (ii) is performed at a temperature ranging between 100°C and 200°C.

19. Process for the direct synthesis of a material according to claims 1 to 18, wherein
the crystallisation time for the process described in (ii) ranges between 6 hours and 50
days.

25

20. Process for the direct synthesis of a material according to claims 1 to 19, further comprising the addition of AEI crystals, as seeds, to the synthesis mixture in a quantity of up to 25% by weight with respect to the total quantity of oxides.

30 21. Process for the direct synthesis of a material according to any of claims 1 to 20, wherein the recovery step (iii) is performed by means of a separation technique selected from decantation, filtration, ultrafiltration, centrifugation and combinations thereof.

22. Process for the direct synthesis of a material according to claims 1 to 21, further comprising the elimination of the organic content retained inside the material by means of an extraction process.

5 23. Process for the direct synthesis of a material according to claims 1 to 22, further comprising the elimination of the organic content retained inside the material by means of a heat treatment at temperatures ranging between 100°C and 1000°C, for a period of time ranging between 2 minutes and 25 hours.

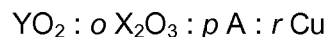
10 24. Process for the direct synthesis of a material according to claims 1 to 23, wherein the material obtained is pelletised.

25. Process for the direct synthesis of a material according to claims 1 to 24, further comprising the introduction of at least one precious metal.

15

26. Process for the direct synthesis of a material according to claim 25, wherein the precious metal is selected from Pd, Pt and combinations thereof.

20 27. Zeolite material with the AEI structure obtained according to the process described in claims 1 to 26, characterised by the following molar composition after being calcined:



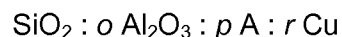
where o ranges between 0.001 and 0.2;

where p ranges between 0 and 2;

25 where r ranges between 0.001 and 1.

28. Zeolite material with the AEI structure obtained according to claim 27, wherein Y is Si and X is Al, and which has the following molar composition:

30



where o ranges between 0.001 and 0.2;

where p ranges between 0 and 2;

where r ranges between 0.001 and 1.

29. Zeolite material with the AEI structure obtained according to claims 27 and 28, wherein the material is Cu-SSZ-39.
30. Zeolite material with the AEI structure obtained according to claims 27 to 29, further
5 comprising a precious metal.
31. Zeolite material with the AEI structure obtained according to claim 30, wherein the precious metal is selected from Pd, Pt and combinations thereof.
- 10 32. Use of the zeolite material with the AEI structure described in claims 27 to 31, obtained according to the process described in claims 1 to 26, in processes for converting feeds formed by organic compounds into higher-value-added products, or for the elimination/separation of the reactive stream by placing said feed in contact with the material described.
- 15 33. Use of the zeolite material with the AEI structure according to claim 32, as a catalyst in the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) in a gas stream.
- 20 34. Use of the zeolite material with the AEI structure according to claim 33, as a catalyst in the SCR of NO_x, which is performed in the presence of a reducing agent selected from ammonia, urea, hydrocarbons, and combinations thereof.
- 25 35. Use of the zeolite material with the AEI structure according to claim 32, as a catalyst in the conversion of methane into methanol.
36. Use of the zeolite material with the AEI structure according to claims 30 and 31, as a catalyst in the selective oxidation of ammonia to nitrogen.

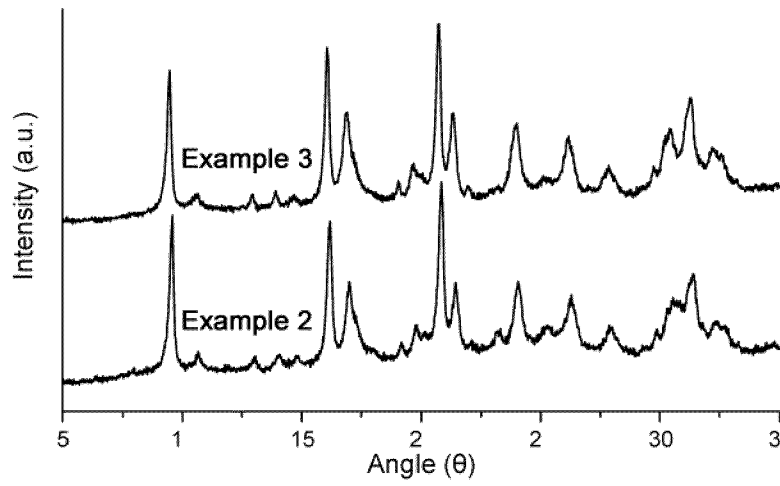


FIG. 1

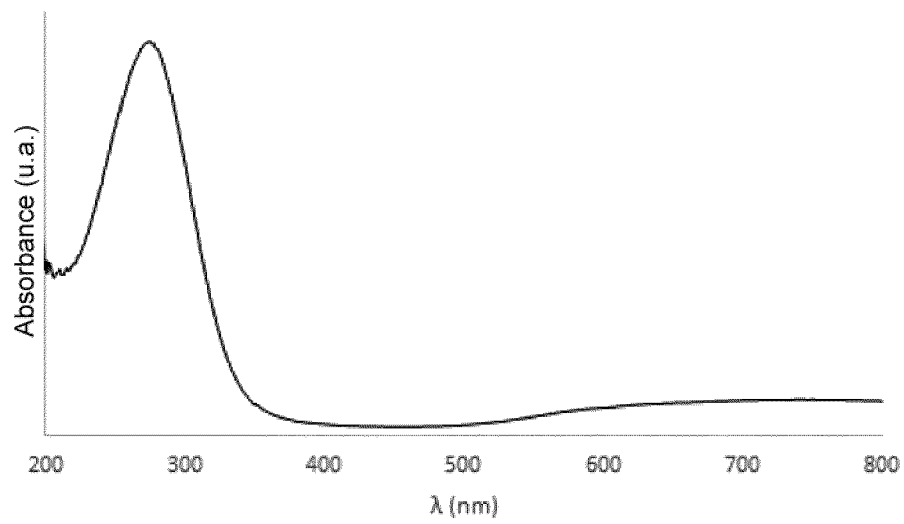


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058278

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B39/02 B01J29/70 B01J29/72 C01B39/48
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 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, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TAKUSHI SONODA ET AL: "Synthesis of high-silica AEI zeolites with enhanced thermal stability by hydrothermal conversion of FAU zeolites, and their activity in the selective catalytic reduction of NO x with NH 3", JOURNAL OF MATERIALS CHEMISTRY A, vol. 3, no. 2, 13 November 2014 (2014-11-13), pages 857-865, XP055179309, ISSN: 2050-7488, DOI: 10.1039/C4TA05621C cited in the application	27-36
Y	Hydrothermal conversion of FAU to AEI zeolites; page 858 Sample 28; table 2 Preparation of the Cu-loaded AEI zeolite catalyst; -/--	1-26

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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 20 June 2016	Date of mailing of the international search report 12/07/2016
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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
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058278

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>page 858 NH3-SCR of the NOx activity test; page 859 page 862, left-hand column, lines 46-54 Catalyst n° 6; table 3 page 863, left-hand column, line 27 - right-hand column, line 37 figure 9 the whole document</p> <p style="text-align: center;">-----</p>	
X	<p>MANUEL MOLINER ET AL: "Cu-SSZ-39, an active and hydrothermally stable catalyst for the selective catalytic reduction of NOx", CHEMICAL COMMUNICATIONS, vol. 48, no. 66, 27 June 2012 (2012-06-27) , page 8264, XP055120043, ISSN: 1359-7345, DOI: 10.1039/c2cc33992g cited in the application</p>	27-36
A	<p>page 8264, right-hand column, lines 11-30 page 8265, left-hand column, line 44 - right-hand column, line 11; figure 3; table 1 the whole document</p>	1-26
X	<p>& Manuel Moliner ET AL: "Electronic Supplementary Information (ESI) Cu-SSZ-39, an active and hydrothermally stable catalyst for the selective catalytic reduction of NOx", 27 June 2012 (2012-06-27), XP055179612, Retrieved from the Internet: URL:http://www.rsc.org/suppdata/cc/c2/c2cc33992g/c2cc33992g.pdf [retrieved on 2015-03-26] cited in the application</p>	27-36
A	<p>1.1.2.2. SSZ-39 experimental study 1.2. Cu-exchanged zeolites 1.3. Catalytic test; page 2; figure S1; tables S1,S5 the whole document</p>	1-26
X	<p style="text-align: center;">-----</p> <p>US 2014/271426 A1 (CASCI JOHN LEONELLO [GB] ET AL) 18 September 2014 (2014-09-18)</p>	27-36
A	<p>paragraphs [0018], [0024], [0025], [0061], [0062], [0067], [0072] claims 1-27; example 6 the whole document</p> <p style="text-align: center;">-----</p>	25,26
	-/--	

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058278

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	MARTÍNEZ-FRANCO RAQUEL ET AL: "Direct synthesis design of Cu-SAPO-18, a very efficient catalyst for the SCR of NOx", JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 319, 6 September 2014 (2014-09-06), pages 36-43, XP029082389, ISSN: 0021-9517, DOI: 10.1016/J.JCAT.2014.08.005	1-26
A	page 36, right-hand column, line 4 - page 37, right-hand column, line 15 page 37, right-hand column, lines 54-65 figures 6,7,8,10,11; table 1 the whole document	27-36
X,P	----- WO 2015/084834 A1 (JOHNSON MATTHEY PLC [GB]; FEDEYKO JOSEPH MICHAEL [US]) 11 June 2015 (2015-06-11)	1-34,36
A,P	page 5, line 10 - page 7, line 30 page 9, lines 1-18 page 11, lines 15-23 page 17, lines 4-18; claims 1-21 the whole document -----	35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/058278

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2014271426	A1	18-09-2014	CN 104703694 A
			DE 102014103626 A1
			EP 2983819 A1
			GB 2532342 A
			JP 2016516565 A
			KR 20150132498 A
			US 2014271426 A1
			US 2015238947 A1
			WO 2014141200 A1

WO 2015084834	A1	11-06-2015	CN 104801338 A
			DE 102014117671 A1
			GB 2522753 A
			US 2015151285 A1
			WO 2015084834 A1
