

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

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

14 March 2019 (14.03.2019)



(10) International Publication Number

WO 2019/048375 A1

(51) International Patent Classification:

C01B 39/30 (2006.01) B01J 29/56 (2006.01)
B01D 53/94 (2006.01) C01B 39/02 (2006.01)
B01J 29/50 (2006.01) C07C 1/20 (2006.01)

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- of inventorship (Rule 4.17(iv))

(21) International Application Number:

PCT/EP2018/073601

Published:

- with international search report (Art. 21(3))

(22) International Filing Date:

03 September 2018 (03.09.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

P201731091 07 September 2017 (07.09.2017) ES

(71) Applicants: HALDOR TOPSØE A/S [DK/DK]; Haldor Topsøes Allé 1, 2800 Kgs. Lyngby (DK). UNIVERSITAT POLITÈCNICA DE VALÈNCIA [ES/ES]; Ctro. de Apoyo a la Innovación, la Investigación y la Transferencia de Tecnología, CCT, Edif. Nexus (6G), 3a planta. Camino de Vera, s/n, 46022 Valencia (ES).

(72) Inventors: BORUNTEA, Cristian-Renato; Oude Durme 2, 0204, 9160 Lokeren (BE). VENNESTRØM, Peter N. R.; Abildgaardsvej 131, 2830 Virum (DK). LUNDEGAARD, Lars Fahl; Toppen 207, 4000 Roskilde (DK). CANÓS, Avelino Corma; c/o AGENCIA ESTATAL CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS (CSIC), CALLE SERRANO 117, 28006 Madrid (ES).

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

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

(54) Title: CATALYST COMPRISING A NOVEL MOLECULAR SIEVE BELONGING TO THE ERI FAMILY AND USE OF THE CATALYST

(57) Abstract: Catalyst comprising a molecular sieve with the ERI framework type having a mole ratio of silica to alumina from about 8 to about 100 and a crystal morphology defined by the ratio between the dimensions r_c along and r_d orthogonal to the unique c-axis between 0.5 and 2.0 and use of the catalyst in catalytic reactions.

WO 2019/048375 A1

Title: Catalyst comprising a novel molecular sieve belonging to the ERI family and use of the catalyst.

5 The present invention relates to catalyst comprising a novel molecular sieve with the ERI framework type and the use of the catalyst in catalytic reactions.

In particular, the invention provides a catalyst comprising a crystalline zeolite molecular sieve material belonging to the ERI framework family essentially without intergrowth of
10 OFF zeolite, with a high Si/Al ratio and a tabular to prismatic crystal morphology.

Zeolites are crystalline microporous materials formed by corner-sharing TO_4 tetrahedra ($\text{T} = \text{Si}, \text{Al}, \text{P}, \text{Ge}, \text{B}, \text{Ti}, \text{Sn}, \text{etc.}$), interconnected by oxygen atoms to form pores and cavities of uniform size and shape precisely defined by their crystal structure. Zeolites
15 are also denoted “molecular sieves” because the pores and cavities are of similar size as small molecules. This class of materials has important commercial applications as absorbents, ion-exchangers and catalysts.

Zeolite molecular sieves are classified by the International Zeolite Association (IZA) according to the rules of the IUPAC Commission on Molecular Sieve Nomenclature. Once
20 the topology of a new framework is established, a three letter code is assigned. This code defines the atomic structure of the framework, from which a distinct X-ray diffraction patterns can be described.

25 The term framework type or framework topology as used herein, refers to the unique atomic structure of a specific molecular sieve, named by a three letter code devised by the International Zeolite Association [Atlas of Zeolite Framework Types, 6th revised edition, 2007, Ch. Baerlocher, L.B. McCusker and D.H. Olson, ISBN: 978-0-444-53064-6].

30 Erionite (ERI) is a naturally occurring aluminosilicate zeolite [Staples, L.W. and Gard, J.A., *Mineral. Mag.*, **32**, 261-281 (1959)] with a Si/Al ratio around 3. It is often found as an intergrowth with OFF [Schlenker, J.L., Pluth, J.J. and Smith, J.V., *Acta Crystallogr.*, **B33**, 3265-3268 (1977)].

Several ways of preparing ERI by synthetic methods have been disclosed.

US Patent 2,950,952 discloses preparation of molecular sieve type T, which has been shown to be an intergrowth of ERI and OFF [J.M. Bennet et al., Nature, 1967, 214, 1005-1006. US Patent 3,699,139 discloses synthesis of ERI/OFF using trimethylbenzylammonium. US Patent 4,086,186 discloses synthesis of ZSM-34, which is also an intergrowth of ERI and OFF. US Patent 4,503,023 discloses synthesis of LZ-220, which is a slightly more siliceous form of molecular sieve type T and also an intergrowth. The use of DABCO(I) and DABCO(II) has also been reported to give intergrowths of ERI and OFF [M. L. Ocelli et al., Zeolites, 1987, 7, 265-271].

As illustrated by the above references, preparation of ERI typically leads to intergrowths with OFF. These intergrowths cannot be considered pure ERI topologies and leads to different channel systems and distribution of cages within the zeolite materials compared to pure ERI, which all-together will influence the properties of this class of materials.

Only a few publications relate to the synthesis of ERI essentially free of OFF intergrowths. US Patent 7,344,694 reports the preparation of UZM-12, which is proposed to have a Si/Al ratio above 5.5 ($= \text{SiO}_2/\text{Al}_2\text{O}_3 > 11$). Practically carrying out the invention to achieve silica-to-alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3$) ratios higher than 12.6 where not given in the examples. Furthermore, UZM-12 is prepared using a density-mismatch approach where nanocrystalline material with crystallites of 15 to 50 nm with a spheroidal to "rice-grain" crystal morphologies can be obtained. Especially nanocrystallites are difficult to separate from the crystallization liquor.

Recently, another ERI molecular sieve designated SSZ-98 was reported in US Patent 9,409,786, 9,416,017 and US patent application 2016/0001273. This material is also essentially free of OFF intergrowth.

SSZ-98 is claimed to have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between 15 and 50 with a *rod-like* or *plate* crystal morphology and it is prepared using N,N'-dimethyl-1,4-diazobicyclo[2.2.2]octane dication as a structure directing agent.

Later patent applications also claim N,N-dimethylpiperidinium cations, 1,3-dicclohexylimidizalium cations and their combination in US Patent applications 2017/0088432, 2017/0073240 and 2016/0375428 respectively.

5 It is commonly acknowledged in the art that the hydrothermal stability of aluminosilicate molecular sieves become higher when the SiO₂/Al₂O₃ molar ratio is increased. Consequently, there is a need to increase the SiO₂/Al₂O₃ molar ratios of the known ERI molecular sieve materials, in particular for applications where hydrothermal stability is an issue. Furthermore, it is also commonly acknowledged in the art that the crystal morphology has a large impact on the performance of the molecular sieve in catalytic applications. A description of the behavior of different crystal morphologies in zeolite catalysis can be found in [S. Teketel, L. F. Lundegaard, W. Skistad, S. M. Chavan, U. Olsbye, K. P. Lillerud, P. Beato, S. Svelle, *J. Catal.* **2015**, 327, 22–32]. Thus, there is also a need to prepare materials with specific morphologies for specific catalytic applications.

To distinguish different crystal morphologies a parameter (r_c / r_a) is defined, which describes the ratio between the different dimensions along (r_c) and orthogonal (r_a) to the unique c-axis of the prepared crystallites e.g. determined by electron microscopy methods (for hexagonal crystals the unique c-axis is parallel to the six-fold symmetry axis). Crystallite morphologies will be described using the words plate, tabular, prismatic, needle and rod-like. The relationship between these descriptions and r_c / r_a values is defined in the Table below

Morphology	Plate	Tabular	Isotropic	Prismatic	Needle or rod-like
r_c/r_a	<0.2	0.2-1	1	1-5	>5

25 It is thus a general object of this invention, to provide an ERI-crystalline molecular sieve essentially free of OFF intergrowths, high SiO₂/Al₂O₃ molar ratios and crystal morphologies different to what is already known.

30 We have found that the use of a cyclohexane-1,4-bis(trialkylammonium) dication as an organic structure directing agent (OSDA) results in the successful achievement of pure

ERI with high silica-to-alumina ratios of up to 100 and with crystal morphologies different to that of SSZ-98.

- 5 Pursuant to the above finding, the present invention is in a first aspect a catalyst comprising a molecular sieve with the ERI framework type having a mole ratio of silica-to-alumina from about 8 to about 100 and a crystal morphology defined by the ratio between the dimensions r_c along and r_a orthogonal to the unique c-axis between 0.5 and 2.0.
- 10 The crystal morphology of the novel ERI-molecular sieve with an r_c/r_a ratio of between 0.5 and 2 has a prismatic to tabular crystal morphology as shown in Figure 2 and 4 in the drawings, which is different to a *rod-like* or *plate* crystal morphology of the known ERI-molecular sieve SSZ-98.
- 15 Specific features and embodiments of the invention are described below.

In an embodiment, the calcined form of the ERI molecular sieve has a powder X-ray diffraction pattern collected in Bragg-Brentano geometry with a variable divergence slit using Cu K-alpha radiation essentially as shown in the following Table:

2-Theta (°)	d-spacing (Å)	Relative peak area
7,81	11,31	M
9,79	9,03	W
11,79	7,50	W
13,55	6,53	S
14,16	6,25	W
15,66	5,65	W
16,75	5,29	W
18,00	4,92	W
19,40	4,57	W
19,65	4,51	W-M
20,77	4,27	S-VS
21,61	4,11	M-S
23,59	3,77	M-S
23,74*	3,74	W-M
23,72*	3,75	W-M
23,95*	3,71	S-VS
24,33	3,65	W
25,01	3,56	VS

26,45	3,37	W
27,30	3,26	VS
27,44*	3,25	W-M
27,41*	3,25	W-M
28,44	3,14	M
28,55	3,12	S-VS
29,07	3,07	W
29,67	3,01	W
29,83	2,99	W

*Peak intensities and letter assignment is uncertain because of significant peak overlap

where the relative areas of the observed peaks in the 2-Theta range 7-19 degrees are shown according to: W = weak: 0-20%; M = medium: 20-40%; S = strong: 40-60% and VS = very strong: 60-100%. 2-Theta values are $\pm 0.20^\circ$

5

In a further embodiment, the silica-to-alumina mole ratio is between 8 and 100, preferably between 10 and 60.

10 In a further embodiment, at least a part of the aluminum and/or silicon in the molecular sieve is substituted by one or more metals selected from tin, zirconium, titanium, hafnium, germanium, boron, iron, indium and gallium.

In another embodiment, the molecular sieve further contains copper and/or iron.

15 The one or more metals can be introduced into and/or on the molecular sieve product by ion-exchange, impregnation, solid-state procedures and precipitation on surface of the ERI-molecular sieve.

20 A further aspect of the present invention is a method for the conversion of nitrogen oxides to nitrogen in the presence of a reductant comprising the step of contacting the nitrogen oxides and the reductant with the catalyst according to any one of the above disclosed embodiments.

25 In a specific embodiment of the method for the conversion of nitrogen oxides to nitrogen, the reductant comprises hydrocarbons and/or ammonia or a precursor thereof.

In still an embodiment of the method for the conversion of nitrogen oxides to nitrogen, the nitrogen oxides are contained in engine exhaust.

5 In further an embodiment of the method for the conversion of nitrogen oxides to nitrogen, the nitrogen oxides are contained in exhaust from a gas turbine.

In another embodiment of the method for the conversion of nitrogen oxides to nitrogen, the nitrogen oxides comprise nitrous oxide.

10 Another aspect of the invention is a method for the selective oxidation of ammonia to nitrogen comprising the step of contacting the ammonia or a gas comprising the ammonia with the catalyst according to any one of the above disclosed embodiments.

15 In an embodiment of the method for the selective oxidation of ammonia to nitrogen, the catalyst comprises an oxidation functionality or an oxidation catalyst.

In still an embodiment of the method for the selective oxidation of ammonia to nitrogen, the catalyst is arranged downstream of a selective catalytic reduction catalyst and wherein an excess of ammonia is used to reduce nitrogen oxides.

20 A further aspect of the invention method for the simultaneous oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides comprising the step of contacting the hydrocarbons, carbon monoxide and the nitrogen oxides with a catalyst according to any one of the above disclosed embodiments.

25 In an embodiment of the method for the simultaneous oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides, the catalyst further comprises one or more platinum group metals.

30 A further aspect of the invention is a method for the conversion of oxygenates to hydrocarbons comprising the step of contacting the oxygenates with a catalyst according to any one of the above disclosed embodiments.

In an embodiment of method for the conversion of oxygenates to hydrocarbons, the produced hydrocarbons comprise olefins.

5 A further aspect of the invention is a method for partial oxidation of methane to methanol and/or dimethyl ether comprising the step of contacting the methane with a catalyst according to any one of the above disclosed embodiments.

10 A further aspect of the invention is a method for the for the preparation of lower amines by reaction of ammonia with methanol with a catalyst according to any one of the above disclosed embodiments.

The ERI molecular sieve comprised in the catalyst of the invention can be prepared by a method comprising the steps of

15 i) preparing a synthesis mixture comprising at least one source of silica and at least one source of alumina, or a combined source of both silica and alumina, a source of alkali or earth alkali (A), at least one OSDA being a cyclohexane-1,4-bis(trialkylammonium) cation, and water in molar ratios of:

SiO ₂ / Al ₂ O ₃	8-100
OSDA / SiO ₂	0.01-1.0
A / SiO ₂	0.01-1.0
H ₂ O / SiO ₂	2-200

ii) subjecting the mixture to conditions capable of crystallizing the molecular sieve; and

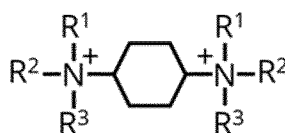
20 iii) separating the molecular sieve product to obtain the as-synthesized molecular sieve.

The source of silica can comprise silica, fumed silica, silicic acid, amorphous or crystalline silicates, colloidal silica, tetraalkyl orthosilicates and mixtures thereof.

The source of alumina can comprise alumina, boehmite, aluminates and mixtures thereof.

5 A combined source of silica and alumina can be co-precipitated amorphous silica-alumina, kaolin, mesoporous materials, crystalline microporous aluminosilicates and mixtures thereof.

The OSDA is a cyclohexane-1,4-bis(trialkylammonium) cation having the structures (R = alkyl group) as shown below.



10

Preferably, the OSDA is selected from the group consisting of cyclohexane-1,4-bis(trimethylammonium), cyclohexane-1,4-bis(triethylammonium), cyclohexane-1,4-bis(ethyl-dimethylammonium), cyclohexane-1,4-bis(diethylmethylammonium).

Presently, the most preferred OSDA is cyclohexane-1,4-bis(trimethylammonium).

15 The OSDA cation is associated with anions, which typically can be hydroxide, chloride, bromide, iodide etc. as long as they are not detrimental to the formation of the molecular sieve.

20 Other tetravalent elements can also be introduced into the synthesis mixture. Such elements include tin, zirconium, titanium, hafnium, germanium and combinations thereof. Trivalent elements can also be included into the synthesis mixture either together with aluminium or without the presence of aluminium. Such trivalent elements include boron, iron, indium, gallium and combinations thereof. Both tetravalent and trivalent elements may be added in the form of metals, salts, oxides, sulphides and combinations thereof.

25

Transition metals may be included in the synthesis mixture either as simple salts or as complexes that protects the transition metal from precipitation under the caustic conditions dictated by the synthesis mixture. Especially, polyamine complexes are useful for protecting transition metal ions of copper and iron during preparation and can also act

30

to direct the synthesis towards specific molecular sieves (see for example the use of polyamines in combination with copper ions in US Patent application 2016271596). In such a way, transition metal ions can be introduced into the interior of the molecular sieve already during crystallization.

5

The synthesis mixture can also contain inexpensive pore-filling agents that can help in the preparation of more siliceous products. Such pore filling agents can be crown-ethers (for example 18-crown-6), simple amines (for example trimethyl- and triethyl-amine) and other uncharged molecules.

10

Crystallization of the synthesis mixture to form the novel molecular sieve is performed at elevated temperatures until the molecular sieve is formed. Hydrothermal crystallization is usually conducted in a manner to generate an autogenous pressure at temperatures from 100-200°C in an autoclave and for periods of time between two hours and 20 days. The synthesis mixture can be subjected to stirring during the crystallization.

15

Once the crystallization has completed the resulting solid molecular sieve product is separated from the remaining liquid synthesis mixture by conventional separation techniques such as decantation, (vacuum-)filtration or centrifugation. The recovered solids are then typically rinsed with water and dried using conventional methods (e.g. heating to 75-150°C under atmospheric pressure, vacuum drying or freeze-drying etc.) to obtain the 'as-synthesized' molecular sieve. The 'as-synthesized' product refers herein to the molecular sieve after crystallization and prior to removal of the structure directing agent(s) or other organic additives.

20

25

The typical composition of the molecular sieve, in its anhydrous state, obtained by the process according to the invention, is summarized in the Table beneath.

Component	Broad range	Preferred range
SiO ₂ / Al ₂ O ₃	8-100	10-60
OSDA / SiO ₂	0.01-0.6	0.02-0.2
A / SiO ₂	0.01-0.6	0.02-0.2

30

The organic OSDA cations still retained in the as-synthesized molecular sieve are in most cases, unless used in the as-synthesized form, removed by thermal treatment in the presence of oxygen. The temperature of the thermal treatment should be sufficient to remove the organic molecules either by evaporation, decomposition, combustion or a combination thereof. Typically, a temperature between 150 and 750°C for a period of time sufficient to remove the organic molecule(s) is applied. A person skilled in the art will readily be able to determine a minimum temperature and time for this heat treatment. Other methods to remove the organic material(s) retained in the as-synthesized molecular sieve include extraction, vacuum-calcination, photolysis or ozone-treatment.

10

The calcined form of the molecular sieve has a powder X-ray diffraction pattern collected in Bragg-Brentano geometry with a variable divergence slit using Cu K-alpha radiation essentially as shown in the following Table:

2-Theta (°)	d-spacing (Å)	Relative peak area
7,81	11,31	M
9,79	9,03	W
11,79	7,50	W
13,55	6,53	S
14,16	6,25	W
15,66	5,65	W
16,75	5,29	W
18,00	4,92	W
19,40	4,57	W
19,65	4,51	W-M
20,77	4,27	S-VS
21,61	4,11	M-S
23,59	3,77	M-S
23,74*	3,74	W-M
23,72*	3,75	W-M
23,95*	3,71	S-VS
24,33	3,65	W
25,01	3,56	VS
26,45	3,37	W
27,30	3,26	VS
27,44*	3,25	W-M
27,41*	3,25	W-M
28,44	3,14	M
28,55	3,12	S-VS
29,07	3,07	W
29,67	3,01	W

29,83	2,99	W
-------	------	---

*Peak intensities and letter assignment is uncertain because of significant peak overlap

where the relative areas of the observed peaks in the 2-Theta range 7-19 degrees are shown according to: W = weak: 0-20%; M = medium: 20-40%; S = strong: 40-60% and VS = very strong: 60-100%. 2-Theta values are ± 0.20

Usually it is desirable to remove the remaining alkali or earth alkali ions (e.g. Na^+) from the molecular sieve essentially free of occluded organic molecules by ion-exchange or other known methods. Ion-exchange with ammonium and/or hydrogen are well recognized methods to obtain the NH_4 -form or H-form of the molecular sieve. Desired metal ions may also be included in the ion-exchange procedure or carried out separately. The NH_4 -form of the material may also be converted to the H-form by simple heat treatment in a similar manner as described above.

In certain cases, it may also be desirable to alter the chemical composition of the obtained molecular sieve, such as altering the silica-to-alumina molar ratio. Without being bound by any order of the post-synthetic treatments, acid leaching (inorganic and organic using complexing agents such as EDTA etc. can be used), steam-treatment, desilication and combinations thereof or other methods of demetallation can be useful in this case.

To promote specific catalytic applications certain metals can be introduced into the novel molecular sieve to obtain a metal-substituted, metal-impregnated or metal-exchanged molecular sieve. Metal ions may be introduced by ion-exchange, impregnation, solid-state procedures and other known techniques. Metals can be introduced to yield essentially atomically dispersed metal ions or be introduced to yield small clusters or nanoparticles with either ionic or metallic character. Alternatively, metals can simply be precipitated on the surface and in the pores of the molecular sieve. In the case where nanoparticles are preferred, consecutive treatment in e.g. a reductive atmosphere can be useful. In other cases, it may also be desirable to calcine the material after introduction of metals or metal ions.

As already mentioned above, the molecular sieve according to the invention is particularly useful in heterogeneous catalytic conversion reactions, such when the molecular sieve catalyzes the reaction of molecules in the gas phase or liquid phase. It can also be

formulated for other commercially important non-catalytic applications such as separation of gases. The molecular sieve provided by the invention and from any of the preparation steps described above can be formed into a variety of physical shapes useful for specific applications. For example, the molecular sieve can be used in the powder form or shaped into pellets, extrudates or moulded monolithic forms, e.g. as full body corrugated substrate containing the molecular sieve.

In shaping the molecular sieve, it will typically be useful to apply additional organic or inorganic components. For catalytic applications it is particularly useful to apply a combination with alumina, silica, titania, ceria, zirconia, various spinel structures or other oxides or combinations thereof. It may also be formulated with other active compounds such as active metals or other molecular sieves etc.

The molecular sieve can also be employed coated onto or introduced into a substrate that improves contact area, diffusion, fluid and flow characteristics of the gas stream. The substrate can be a metal substrate, an extruded substrate or a corrugated substrate, the latter being made of ceramic paper. The substrate can be designed as a flow-through or a wall-flow design. In the latter case, the gas flows through the walls of the substrate, and in this way, it can also contribute with an additional filtering effect.

The molecular sieve is typically present on or in the substrate in amounts between 10 and 600 g/L, preferably 100 and 300 g/L, as calculated by the weight of the molecular sieve per volume of the total catalyst article.

The molecular sieve is coated on or into the substrate using known wash-coating techniques. In this approach the molecular sieve powder is suspended in a liquid media together with binder(s) and stabilizer(s). The wash coat can then be applied onto the surfaces and walls of the substrate. The wash coat optionally also contains binders based on TiO_2 , SiO_2 , Al_2O_3 , ZrO_2 , CeO_2 and combinations thereof.

The molecular sieve can also be applied as one or more layers on the substrate in combination with other catalytic functionalities or other zeolite catalysts. One specific combination is a layer with an oxidation catalyst containing for example platinum or palladium

or combinations thereof. The molecular sieve can be additionally applied in limited zones along the gas-flow-direction of the substrate.

5 The molecular sieve according to the invention can be used in the catalytic conversion of oxides of nitrogen, typically in the presence of oxygen. In particular, the molecular sieve can be used in the selective catalytic reduction (SCR) of oxides of nitrogen with a reductant such as ammonia and precursors thereof, including urea, or hydrocarbons. For this type of application, the molecular sieve will typically be loaded with a transition metal such as copper or iron or combinations thereof, using any of the procedures described
10 above, in an amount sufficient to catalyse the specific reaction.

In certain aspects of the invention a certain amount of alkali or earth alkali can be beneficial. See for example a description of alkali and earth alkali effects on copper promoted CHA in [F. Gao, Y. Wang, N. M. Washton, M. Kollár, J. Szanyi, C. H. F. Peden, *ACS Catal.* **2015**, 5, 6780–6791]. In other aspects, it may be preferred to use the molecular
15 sieve essentially free of alkali or earth alkali.

The ERI molecular sieve according to the invention can advantageously be used as catalyst in the reduction of nitrogen oxides in the exhaust coming from a vehicular (i.e. mobile) internal combustion engine. In this application the exhaust system can comprise
20 one or more of the following components: a diesel oxidation catalyst (DOC), a diesel particulate filter (DPF), a selective catalytic reduction catalyst (SCR) and/or an ammonia slip catalyst (ASC). Such a system typically also contains means for metering the reductant as well as the possibility to meter hydrocarbons into the exhaust system upstream the SCR and DOC, respectively.
25

In an embodiment, the ERI catalyst is arranged downstream and/or upstream of a Diesel oxidation catalyst.

30 In another embodiment, the ERI catalyst is arranged upstream of an ammonia slip catalyst.

In further an embodiment, the ERI catalyst is arranged upstream and/or downstream of a diesel particulate filter

The SCR catalyst comprises the ERI molecular sieve of the invention. The SCR catalyst may also contain other active components such as other molecular sieves. When the SCR catalyst is located in such an exhaust system it is exposed to high temperatures either from the engine or during thermal regeneration of one or more of the components in the system.

In the exhaust system as described above, the SCR catalyst, comprising the ERI molecular sieve, can be located between the DPF and the ASC components. Another possibility is to arrange the SCR catalyst up-stream of the DOC, where some tolerance to unburnt hydrocarbons is required. The SCR functionality may also be included in the DPF or combined with the ASC into a single component with a dual function.

The ERI molecular sieve according to the invention can also be part of an ammonia slip catalyst (ASC). The ASC catalyst is used in combination with the SCR article, and its function is to remove excess amount of ammonia, or a precursor thereof, that is needed in the SCR stage to remove high amounts of nitrogen oxides from the exhaust gas.

ASC-type catalysts are bifunctional catalysts. The first function is oxidation of ammonia with oxygen, which produces NO_x, and the second function is NH₃-SCR, in which NO_x and residual amounts of ammonia react to nitrogen.

Hence, ASC catalysts consist of a combination of a component active for the oxidation of ammonia by oxygen and a component active for NH₃-SCR.

The most commonly applied components for the oxidation of ammonia by oxygen are based on metals like Pt, Pd, Rh, Ir, Ru, but transition metal oxides or a combination of metal oxides, for example oxides Ce, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, Ta, W can also be used for this purpose. When such materials are combined with metal-loaded form of the molecular sieve of the invention having SCR activity, an ammonia slip catalyst is obtained.

Ammonia slip catalysts based on the molecular sieve of the invention may also contain auxiliary materials, for example, and not limited to binders, support materials for the noble metal components, such as Al_2O_3 , TiO_2 , SiO_2 . Such combinations can have different forms, such as a mixture of the ammonia oxidation component with the SCR-active form of the molecular sieve of the invention, reactors or catalyst items in series (See examples US patent 4,188,364).

In particular, the ammonia slip catalyst can be a washcoated layer of a mixture of the ammonia oxidation component with the SCR-active form of the ERI molecular sieve of the invention on a monolith, or a multi-layered arrangement washcoated on a monolith, in which the different layers contain different amounts of the ammonia oxidation component, or of the SCR-active form of the molecular sieve of the invention, or of any combination of the ammonia oxidation component and the SCR-active form of the molecular sieve of the invention (JP3436567, EP1992409).

In another embodiment, the ammonia oxidation component or the SCR-active form of the ERI molecular sieve of the invention or any combination of the ammonia oxidation component and the SCR-active form of the molecular sieve of the invention is present in walls of a monolith. This configuration can further be combined with different combinations of washcoated layers.

Another embodiment of the ASC catalyst is a catalyst article with a gas inlet end and a gas outlet end, in which the outlet end contains an ammonia oxidation component and the SCR-active form of the molecular sieve of the invention. The inlet end of the catalyst article may then contain other functionalities.

The ERI molecular sieve of the invention is useful as catalyst in the reduction of nitrogen oxides in the exhaust gas from a gas turbine using ammonia as a reductant. In this application, the catalyst may be arranged directly downstream from the gas turbine. It may also be exposed to large temperature fluctuations during gas turbine start-up and shut-down procedures.

In certain applications, the molecular sieve catalyst is used in a gas turbine system with a single cycle operational mode without any heat recovery system downstream of the

turbine. When placed directly after the gas turbine the molecular sieve is able to withstand exhaust gas temperatures up to 650°C with a gas composition containing water.

5 Further applications of the molecular sieve of the invention are in a gas turbine exhaust treatment system in combination with a heat recovery system such as a Heat Recovery System Generator (HRSG). In such a process design, the molecular sieve catalyst is arranged between the gas turbine and the HRSG. The molecular sieve can be also arranged in several locations inside the HRSG.

10 Still an application of the ERI molecular sieve according to invention is the employment as catalyst in combination with an oxidation catalyst for the abatement of hydrocarbons and carbon monoxide in exhaust gas.

15 The oxidation catalyst, typically composed of precious metals, such as Pt and Pd, can e.g. be arranged either up-stream or down-stream of the molecular sieve and both inside and outside of the HRSG. The oxidation functionality can also be combined with the molecular sieve catalyst into a single catalytic unit.

20 The oxidation functionality may be combined directly with the molecular sieve by using the molecular sieve as support for the precious metals. The precious metals can also be supported onto another support material and physically mixed with the molecular sieve.

25 The molecular sieve of to the invention is capable of removing nitrous oxide. It can for example be arranged in combination with a nitric acid production loop in a primary, secondary or a tertiary abatement setup. In such an abatement process, the molecular sieve can be used to remove nitrous oxide as well as nitrogen oxides as separate catalytic articles or combined into a single catalytic article. The nitrogen oxide may be used to facilitate the removal of the nitrous oxide. Ammonia or lower hydrocarbons, including methane, may also be added as a reductant to further reduce nitrogen oxides and/or
30 nitrous oxide.

The ERI molecular sieve of the invention can also be used in the conversion of oxygenates into various hydrocarbons. The feedstock of oxygenates is typically lower alcohols

and ethers containing one to four carbon atoms and/or combinations thereof. The oxygenates can also be carbonyl compounds such as aldehyde, ketones and carboxylic acids. Particularly suitable oxygenate compounds are methanol, dimethyl ether, and mixtures thereof. Such oxygenates can be converted into hydrocarbons in presence of the molecular sieve. In such a process the oxygenate feedstock is typically diluted and the temperature and space velocity is controlled to obtain the desired product range.

A further use of the molecular sieve of the invention is as catalyst in the production of lower olefins, in particular olefins suitable for use in gasoline or as catalyst in the production of aromatic compounds.

In the above applications, the ERI molecular sieve is typically used in its acidic form and will be extruded with binder materials or shaped into pellets together with suitable matrix and binder materials as described above.

Other suitable active compounds such as metals and metal ions may also be included to change the selectivity towards the desired product range.

The ERI molecular sieve according to the invention can further be used in the partial oxidation of methane to methanol or other oxygenated compounds such as dimethyl ether.

One example of a process for the direct conversion of methane into methanol at temperatures below 300°C in the gas phase is provided in WO11046621A1. In such a process, the molecular sieve of the invention is loaded with an amount of copper sufficient to carry out the conversion. Typically, the molecular sieve will be treated in an oxidizing atmosphere where-after methane is subsequently passed over the activated molecular sieve to directly form methanol. Subsequently, methanol can be extracted by suitable methods and the active sites regenerated by another oxidative treatment.

Another example is disclosed in [K. Narsimhan, K. Iyoki, K. Dinh, Y. Román-Leshkov, *ACS Cent. Sci.* **2016**, 2, 424–429] where an increase or a continuous production of meth-

anol is achieved by addition of water to the reactant stream to continuously extract methanol without having to alter the conditions between oxidative treatments and methanol formation.

5 The ERI molecular sieve of the invention can be used to separate various gasses. Examples include the separation of carbon dioxide from natural gas and lower alcohols from higher alcohols. Typically, the practical application of the molecular sieve will be as part of a membrane for this type of separation.

10 The ERI molecular sieve of the invention can further be used in isomerization, cracking hydrocracking and other reactions for upgrading oil.

The ERI molecular sieve of the invention may also be used as a hydrocarbon trap e.g. from cold-start emissions from various engines.

15

Furthermore, the molecular sieve can be used for the preparation of small amines such as methyl amine and dimethylamine by reaction of ammonia with methanol.

In all of the above embodiments, the ERI catalyst can be coated on a monolith or on a corrugated substrate or be in form of an extrudate.

20

EXAMPLES

25 Example 1: Synthesis of cyclohexane-1,4-bis(trimethylammonium hydroxide) OSDA

A mixture of 30 mL formic acid (89.5 wt. % aqueous solution), 6.1 g NaHCO₃, 5 g trans-1,4-diaminocyclohexane (98% purity powder) and 14 mL formaldehyde (37 wt. % aqueous solution) was refluxed until no visible evolution of CO₂ was noticed. The synthesis mixture was vacuum distilled after 50 mL HCl (2 mol/L aqueous solution) was added, followed by the addition of an excess of NaOH and extraction 3 times with chloroform. The chloroform portions were combined and 8 mL of methyl iodide (99 wt. %) was added followed by mixing overnight. The obtained solid was dissolved in water and ion exchange to hydroxide form, using an ion exchange resin

30

Example 2: Synthesis of ERI

A mixture of 1.87 g cyclohexane-1,4-bis(trimethylammonium hydroxide)(12.7 wt. % aqueous solution), 1.7 g KOH (10 wt. % aqueous solution), 0.48 g distilled water and 0.94 g co-precipitated amorphous silica-alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 12$) was prepared. The mixture was heated in a closed Teflon lined autoclave at 135°C for 7 days and the solid product separated by filtration and washing with deionized water. By X-ray powder diffraction analysis, the as-synthesized product is seen to be phase-pure ERI.

Example 3: Synthesis of ERI

A mixture of 1.97 g cyclohexane-1,4-bis(trimethylammonium hydroxide)(12.7 wt. % aqueous solution), 1.79 g KOH (10 wt. % aqueous solution), 0.46 g distilled water and 0.79 g FAU zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 12$) was prepared. The mixture was heated in a closed Teflon lined autoclave at 135°C for 7 days and the solid product separated by filtration and washing with deionized water.

The dried solid product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 9.8 determined by ICP-AES analysis. By X-ray powder diffraction analysis, the as-synthesized product is seen to be phase-pure ERI. SEM analysis further reveals a tabular to prismatic crystal morphology.

Example 4: Synthesis of ERI

A mixture of 1.95 g cyclohexane-1,4-bis(trimethylammonium hydroxide)(12.7 wt. % aqueous solution), 1.77 g KOH (10 wt. % aqueous solution), 0.5 g distilled water and 0.79 g co-precipitated amorphous silica-alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) was prepared. The mixture was heated in a closed Teflon lined autoclave at 135°C for 7 days and the solid product separated by filtration and washing with deionized water.

By X-ray powder diffraction analysis, the as-synthesized product is seen to be phase-pure ERI. The measured diffractogram for the as-synthesized product is shown in Figure 1. SEM analysis further reveals a tabular crystal morphology (see Figure 2).

Figure 1 XRPD of the as-prepared molecular sieve prepared in Example 4.

Figure 2 SEM micrograph of the as-prepared molecular sieve prepared in Example 4.

Example 5: Synthesis of ERI

A mixture of 1.99 g cyclohexane-1,4-bis(trimethylammonium hydroxide)(12.7 wt. % aqueous solution), 1.81 g KOH (10 wt. % aqueous solution), 0.45 g distilled water and 0.74 g FAU zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) was prepared. The mixture was heated in a closed Teflon lined autoclave at 135°C for 7 days and the solid product separated by filtration and washing with deionized water.

The dried solid product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 22.0 determined by ICP-AES analysis. By X-ray powder diffraction analysis, the as-synthesized product is seen to be phase-pure ERI. The measured diffractogram for the as-synthesized product is shown in Figure 3. SEM analysis further reveals a prismatic crystal morphology (see Figure 4).

Figure 3 XRPD of the as-prepared molecular sieve prepared in Example 5.

Figure 4 SEM micrograph of the as-prepared molecular sieve prepared in Example 5.

Calcination of the dried as-prepared molecular sieve was carried out at 550°C for 3h. Afterwards the calcined product was ion-exchanged with NH_4^+ . The measured X-ray diffractogram for the calcined product is shown in Figure 5. Furthermore, N_2 -physisorption revealed a multipoint BET surface area of 559 m^2/g and a micropore volume of 0.19 cm^3/g , clearly indicating the microporous nature of the prepared material.

Figure 5 XRPD of the calcined molecular sieve prepared in Example 5.

Claims

1. Catalyst comprising a molecular sieve with the ERI framework type having a mole ratio of silica-to-alumina from about 8 to about 100 and a crystal morphology defined by the ratio between the dimensions r_c along and r_a orthogonal to the unique c-axis between 0.5 and 2.0.
2. The catalyst of claim 1, wherein the calcined form of the ERI molecular sieve has a powder X-ray diffraction pattern collected in Bragg-Brentano geometry with a variable divergence slit using Cu K-alpha radiation essentially as shown in the following Table:

2-Theta (°)	d-spacing (Å)	Relative peak area
7,81	11,31	M
9,79	9,03	W
11,79	7,50	W
13,55	6,53	S
14,16	6,25	W
15,66	5,65	W
16,75	5,29	W
18,00	4,92	W
19,40	4,57	W
19,65	4,51	W-M
20,77	4,27	S-VS
21,61	4,11	M-S
23,59	3,77	M-S
23,74*	3,74	W-M
23,72*	3,75	W-M
23,95*	3,71	S-VS
24,33	3,65	W
25,01	3,56	VS
26,45	3,37	W
27,30	3,26	VS
27,44*	3,25	W-M
27,41*	3,25	W-M
28,44	3,14	M
28,55	3,12	S-VS
29,07	3,07	W
29,67	3,01	W
29,83	2,99	W

*Peak intensities and letter assignment is uncertain because of significant peak overlap

where the relative areas of the observed peaks in the 2-Theta range 7-19 degrees are shown according to: W = weak: 0-20%; M = medium: 20-40%; S = strong: 40-60% and VS = very strong: 60-100%. 2-Theta values are $\pm 0.20^\circ$.

3. The catalyst of claim 1 or 2, wherein the ERI molecular sieve has a silica-to-alu-
5 mina mole ratio between 8 and 100.
4. The catalyst of claim 1 or 2, wherein the ERI molecular sieve has a silica-to-alu-
mina mole ratio between 10 and 60.
5. The catalyst of any one of claim 1 to 4, wherein at least a part of the aluminum
and/or silicon of the ERI molecular sieve is substituted by one or more metals selected
10 from tin, zirconium, titanium, hafnium, germanium, boron, iron, indium and gallium.
6. The catalyst of any one of claims 1 to 5, wherein the ERI molecular sieve con-
tains copper and/or iron.
7. A method for the conversion of nitrogen oxides to nitrogen in presence of a re-
ductant comprising the step of contacting the nitrogen oxides and the reductant with
15 the catalyst according to any one of claims 1 to 6.
8. The method of claim 7, wherein the reductant comprises hydrocarbons and/or
ammonia or a precursor thereof.
9. The method of claim 7 or 8, wherein the nitrogen oxides are contained in engine
20 exhaust.
10. The method of claim 7 or 8, wherein the nitrogen oxides are contained in ex-
haust from a gas turbine.
25
11. The method of any one of claim 7 to 10, wherein the nitrogen oxides comprise
nitrous oxide.
12. A method for the selective oxidation of ammonia to nitrogen comprising the step
30 of contacting the ammonia or a gas comprising the ammonia with the catalyst accord-
ing to any one of claims 1 to 6.

13. The method of claim 12, wherein the catalyst is arranged downstream and/or upstream of a Diesel oxidation catalyst.

5 14. The method of claim 12 or 13, wherein the catalyst is arranged upstream of an ammonia slip catalyst.

15. The method of any one of claims 12 to 14, wherein the catalyst is arranged upstream and/or downstream of a diesel particulate filter

10 16. The method of claim 12, wherein the catalyst further comprises an oxidation functionality or an oxidation catalyst.

15 17. The method of claim 16, wherein the catalyst is arranged downstream of a selective catalytic reduction catalyst and wherein an excess of ammonia is used to reduce nitrogen oxides.

20 18. A method for the simultaneous oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides comprising the step of contacting the hydrocarbons, carbon monoxide and the nitrogen oxides with a catalyst according to any one of claims 1 to 6.

19. The method of any one of claim 15 to 18, wherein the catalyst further comprises one or more platinum group metals.

25 20. The method of any one of claim 12 to 19, wherein catalyst is coated on a monolith or on a corrugated substrate or in form of an extrudate.

30 21. A method for the conversion of oxygenates to hydrocarbons the comprising the step of contacting the oxygenates with a catalyst according to any one of claims 1 to 6.

22. The method according to claim 21, wherein the produced hydrocarbons comprise olefins.

23. A method for partial oxidation of methane to methanol and/or dimethyl ether comprising the step of contacting the methane with a catalyst according to any one of claims 1 to 6.
- 5 24. A method for the for the preparation of lower amines by reaction of ammonia with methanol in presence of a catalyst according to any one of claims 1 to 6.

Fig. 1

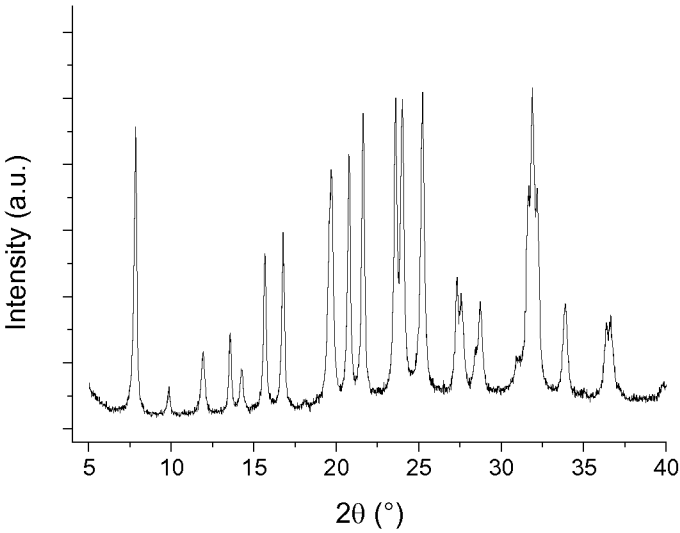
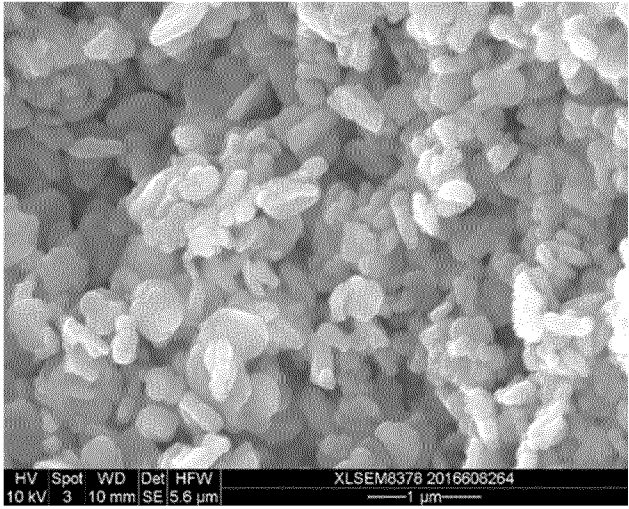


Fig. 2



2/3

Fig. 3

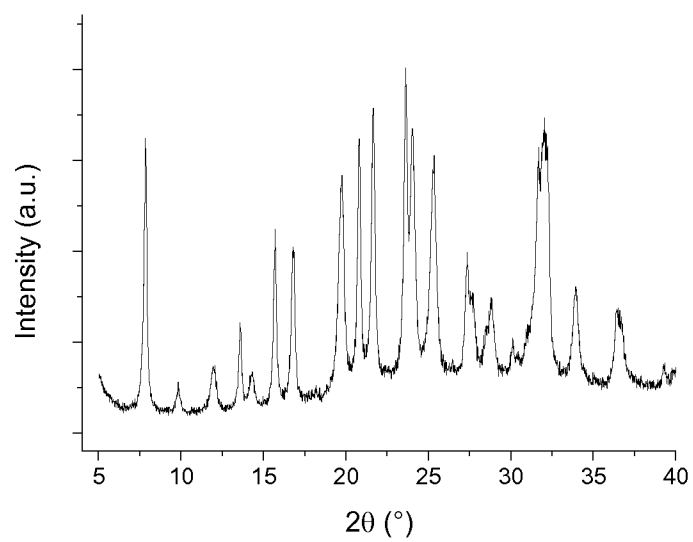
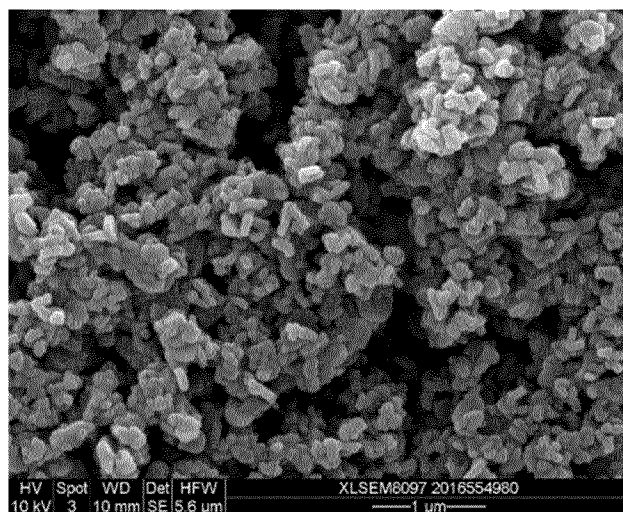
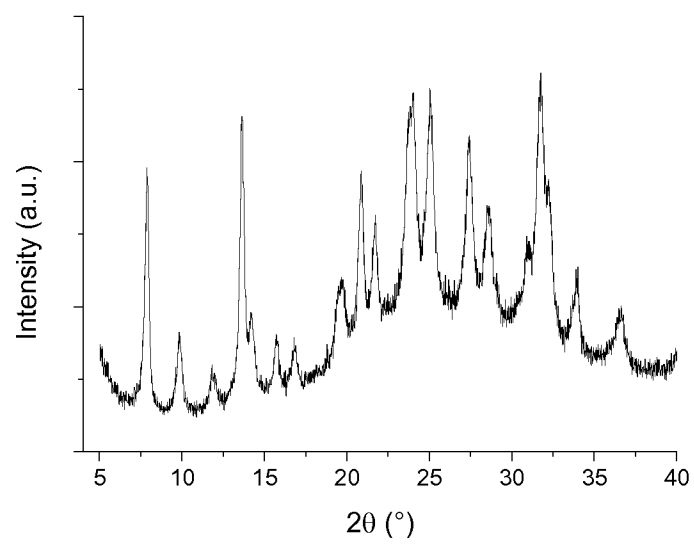


Fig. 4



3/3

Fig. 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/073601

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B39/30 B01D53/94 B01J29/50 B01J29/56 C01B39/02 C07C1/20 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 B01D B01J C07C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, COMPENDEX, INSPEC											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> JOO HYUCK LEE ET AL: "Synthesis and Characterization of ERI-Type UZM-12 Zeolites and their Methanol-to-Olefin Performance", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, US, vol. 132, no. 7, 22 September 2010 (2010-09-22), pages 12971-12982, XP002668581, ISSN: 0002-7863, DOI: 10.1021/JA105185R [retrieved on 2010-08-25] </td> <td style="text-align: center; vertical-align: top;"> 1-4,21, 22 </td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y A</td> <td style="vertical-align: top;"> Experimental section; page 12972, right-hand column; figures 1,3; tables 1,3 page 12974 - page 12975 Catalysis; page 12973, right-hand column, paragraph third page 12977 - page 12978, left-hand column, -/-- </td> <td style="text-align: center; vertical-align: top;"> 5,6 7-20,23, 24 </td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	JOO HYUCK LEE ET AL: "Synthesis and Characterization of ERI-Type UZM-12 Zeolites and their Methanol-to-Olefin Performance", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, US, vol. 132, no. 7, 22 September 2010 (2010-09-22), pages 12971-12982, XP002668581, ISSN: 0002-7863, DOI: 10.1021/JA105185R [retrieved on 2010-08-25]	1-4,21, 22	Y A	Experimental section; page 12972, right-hand column; figures 1,3; tables 1,3 page 12974 - page 12975 Catalysis; page 12973, right-hand column, paragraph third page 12977 - page 12978, left-hand column, -/--	5,6 7-20,23, 24
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
X	JOO HYUCK LEE ET AL: "Synthesis and Characterization of ERI-Type UZM-12 Zeolites and their Methanol-to-Olefin Performance", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, US, vol. 132, no. 7, 22 September 2010 (2010-09-22), pages 12971-12982, XP002668581, ISSN: 0002-7863, DOI: 10.1021/JA105185R [retrieved on 2010-08-25]	1-4,21, 22									
Y A	Experimental section; page 12972, right-hand column; figures 1,3; tables 1,3 page 12974 - page 12975 Catalysis; page 12973, right-hand column, paragraph third page 12977 - page 12978, left-hand column, -/--	5,6 7-20,23, 24									
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.											
<table style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> * 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 </td> <td style="width: 50%; vertical-align: top;"> "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 </td> </tr> </table>			* 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							
* 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 11 October 2018		Date of mailing of the international search report 18/10/2018									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Follens, Lana									

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/073601

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	paragraph first; table 5 page 12979, right-hand column, last paragraph - page 12980, left-hand column, paragraph first; figures 7-10 the whole document & JOO HYUCK LEE ET AL: "Supporting info for Synthesis and Characterization of ERI-Type UZM-12 Zeolites and their Methanol-to-Olefin Performance", Asia-Pacific Journal of Chemical Engineering, 22 September 2010 (2010-09-22), pages 596-605, XP055513517, Chichester, UK DOI: 10.1002/apj.453 Retrieved from the Internet: URL:https://pubs.acs.org/doi/suppl/10.1021/ /ja105185r/suppl_file/ja105185r_si_001.pdf [retrieved on 2018-10-09] figures S1,S3, S5 the whole document	
X	----- JIE ZHU ET AL: "Ultrafast synthesis of high-silica erionite zeolites with improved hydrothermal stability", CHEMICAL COMMUNICATIONS, vol. 53, no. 50, 24 May 2017 (2017-05-24), pages 6796-6799, XP055513320, ISSN: 1359-7345, DOI: 10.1039/C7CC03166A	1-4,7-24
A	page 6797, left-hand column, paragraph third; figures 1-2,5 page 6798, right-hand column, last paragraph page 6796, right-hand column, paragraph second page 6798, right-hand column, paragraph third - page 6799, left-hand column, paragraph first page 6799, right-hand column, paragraph first the whole document -/--	5,6

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/073601

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& Jie Zhu ET AL: "Supporting information for Ultrafast synthesis of high-silica erionite zeolites with improved hydrothermal stability", Chemical communications (Cambridge, England), 24 May 2017 (2017-05-24), pages 6796-6799, XP055513700, England DOI: 10.1039/C7CC03166A Retrieved from the Internet: URL: http://www.rsc.org/suppdata/c7/cc/c7cc03166a/c7cc03166a1.pdf [retrieved on 2018-10-09] figures S3,S6; table S2 -----	
X	MARTÍN NURIA ET AL: "Cage-based small-pore catalysts for NH₃-SCR prepared by combining bulky organic structure directing agents with modified zeolites as reagents", APPLIED CATALYSIS B: ENVIRONMENTAL, ELSEVIER, AMSTERDAM, NL, vol. 217, 29 May 2017 (2017-05-29), pages 125-136, XP085112832, ISSN: 0926-3373, DOI: 10.1016/J.APCATB.2017.05.082	1-4,6-24
Y A	Point 2. Experimental; page 127 - page 128; figures 2,4; tables 1,3,4 page 125, right-hand column, paragraph first 2.5 Catalytic testing; page 129, left-hand column 3.2 Catalytic performance in NH₃-SCR of NO; page 131, left-hand column - page 135, left-hand column the whole document -----	6 5
X	US 2006/073094 A1 (MILLER MARK A [US] ET AL) 6 April 2006 (2006-04-06)	1-24
Y	paragraphs [0006], [0015] - [0018], [0020] - [0022], [0042] - [0049]; examples 1-14 the whole document -----	5
A	US 2016/001273 A1 (XIE DAN [US] ET AL) 7 January 2016 (2016-01-07) cited in the application paragraphs [0053] - [0087]; examples 22,23 the whole document -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/073601

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2006073094	A1	06-04-2006	CN 101072728 A	14-11-2007
			EP 1797005 A2	20-06-2007
			JP 5498658 B2	21-05-2014
			JP 2008515760 A	15-05-2008
			RU 2377181 C2	27-12-2009
			US 2006073094 A1	06-04-2006
			WO 2006137900 A2	28-12-2006

US 2016001273	A1	07-01-2016	AU 2015284750 A1	08-12-2016
			CA 2949762 A1	07-01-2016
			CN 106470945 A	01-03-2017
			EP 3164362 A1	10-05-2017
			JP 2017530006 A	12-10-2017
			US 2016001273 A1	07-01-2016
			WO 2016003504 A1	07-01-2016
