EU-7 zeolite: a synthetic BIK type zeolite with high hydrothermal stability†

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EU-7 zeolite with Si/Al ratio of 15 is identified as a BIK type zeolite. The framework charge is compensated with Cs⁺ cations located in 8-ring channels at regular distances. Even partially exchanged, Cu-loaded EU-7 is active in NH₃-SCR and withstands hydrothermal aging at 900 °C needed for application in diesel particulate filters.

Small-pore zeolites with pore openings limited by 8 corner-sharing tetrahedra such as the LTA type zeolite are frequently used in gas purification and separation, gas and solvent drying and water softening. They are also popular in catalysis, and especially for methanol-to-olefin conversion and selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia (NH₃) in exhaust gas aftertreatment systems.^{1–6} The reagents and products of the NH₃-SCR reaction are small molecules, *viz.* NO, NO₂, O₂, H₂O, NH₃, N₂ which can access the intracrystalline pore volume of small-pore zeolites. The hydrothermal stability requirement for NH₃-SCR catalysts is severe, especially when this catalytic function is to be integrated in the diesel particulate filter where the temperature during regeneration can reach up to 900 °C.^{7,8} Many of the known small-pore zeolites are minerals and for several of them no synthetic counterpart exists. The growing interest in small-pore zeolites for catalysis justifies a search for synthetic versions of natural zeolites expected to have high hydrothermal stability. EU-7 zeolite was first reported by Araya and Lowe in 1986.⁹ According to Dewing *et al.*¹⁰ the zeolite was proposed to be related to EU-13, a 10-ring zeolite with MTT framework type¹¹ and to EU-12 zeolite.¹² Recently, the crystal structure of EU-12 was elucidated by synchrotron powder X-ray diffraction (XRD) and Rietveld analyses as a small-pore zeolite containing a 2-dimensional channel system consisting of 2 types of straight 8-ring channels intersected by a sinusoidal 8-ring channel.¹³ The topology of this framework has been assigned the

3-letter code ETL by the structure commission of the International Zeolite Association in 2016.¹⁴ EU-7 zeolite can be synthesized in presence of Cs cations and butane-1,4-diamine as structure directing agent.⁹ Until now the structure of EU-7 zeolite remained elusive but now is identified as BIK type zeolite, a small-pore zeolite with a straight 1-dimensional channel system and high Si/Al ratio. Here we report the synthesis and structure analysis of EU-7 zeolite and an evaluation of its hydrothermal stability in view of NH₃-SCR catalysis.

Synthesis of EU-7 zeolite was performed similar to example 7 of patent US4581212.⁹ More details on the synthesis and the characterization techniques can be found in the ESI.†

The X-ray powder diffraction pattern of the EU-7 zeolite shown in Fig. 1 indicates the formation of crystalline material corresponding to the EU-7 zeolite reported in the original patent.⁹ SEM revealed the EU-7 zeolite to consist of a single phase and to form agglomerates from individual crystals having an ellipsoidal disk-like morphology with a size of around 4 × 0.5 μm (Fig. 2).

Fig. 1 Rietveld refinement of EU-7 zeolite. Location of Cs in the 8-membered ring channels is shown in the inset.

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Fig. 2 HRSEM images of calcined EU-7 zeolite.

Indexing of the powder pattern (Fig. 1) indicated a monoclinic unit cell with lattice constants of $a = 7.32 \text{ \AA}$, $b = 5.00 \text{ \AA}$, and $c = 17.49 \text{ \AA}$ with a monoclinic angle of 114.75° . As most probable spacegroups $P2_1$, Pc and $P2_1/c$ were identified. A structure determination by Monte-Carlo and parallel tempering using FOX¹⁵ in the spacegroup $P2_1/c$ was attempted. Assuming a framework density similar to MTT and ETL zeolite, initially 4 independent tetrahedra next to 2 Cs positions were optimized, which quickly led to the conclusion the structure could be well described in $P2_1/c$ using 3 crystallographic sites for tetrahedron sites plus one site for Cs. The 3D connected structure obtained was then optimized in terms of bond angles and distances by a forcefield simulations using the Gulp program and Catlow library.^{16,17} The obtained topology was analyzed with ToposPro,¹⁸ revealing the BIK topology. Rietveld refinement of the calcined sample stored at 60°C , with the GSAS software package,^{19,20} led to localization of 2 water molecule positions next to Cs and framework and to excellent reliability factors of $R_p = 2.6\%$, $R_{wp} = 3.4\%$ and $R_{F2} = 8.3\%$. Refinement of occupation factors of Cs also resulted in very good agreement with the experimental composition.

The BIK topology is named after the rarely occurring mineral bikitaite ($\text{Li}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$). Up to now, natural zeolites with BIK topology are found only in Zimbabwe and South Carolina, show a Si/Al ratio of 2 and strictly contain Li cations for charge compensation.^{14,21} A synthetic zeolite with BIK framework type and composition $\text{Cs}[\text{AlSi}_{7.6}\text{O}_{17.1}]$ has been reported by Annehed and Fälvth.²² Later, Kato *et al.* synthesized zeolites with BIK framework type in mixed cation systems with molar gel compositions of SiO_2 : 0.028–0.5 Al: 0.1–0.6 Cs: 0–0.26 M: 30 H_2O where M is Li, Na or K.²³ It was observed the final products mainly contained Cs as counter ion and only traces of Li, Na, or K, respectively. Fig. 3 shows how the BIK topology consists of 5-, 6-, and 8-membered rings, forming straight 1D-channels delimited by 8 T-atoms. The channels have small side pockets accessible through strongly squeezed 6-membered rings, alternating along the channel direction (b).

When synthesized in purely inorganic systems the Si/Al ratio was always found close to 7.5.^{22,23} Chemical analysis of the present EU-7 zeolite indicated a Si/Al ratio of 15, while direct excitation ^{27}Al MAS NMR confirmed that 99% of the Al exists in tetrahedral co-ordination as expected for framework Al (see ESI† for Experimental details). This is the highest reported Si/Al ratio for a BIK framework type zeolite, and can be related to the

Fig. 3 Schematic representation of the BIK framework.

presence of diaminobutane during synthesis. The Cs-BIK obtained by purely inorganic synthesis by Annehed and Fälvth²² was reported in spacegroup $B2_1$, which after standardization results in a unit cell of $a = 7.36 \text{ \AA}$, $b = 5.03 \text{ \AA}$, $c = 8.74 \text{ \AA}$, with $\beta = 114.12^\circ$ in spacegroup $P2_1$. EU-7 zeolite shows a doubling of the unit cell in c -direction, but otherwise is very similar, also in position of the Cs-ion. In the present EU-7 zeolite 2 positions for water molecules were localized, which complete the coordination of the cations in the 8-membered ring channels. Cesium is coordinated by 6 framework oxygens plus 1 or 2 water molecules situated before and/or after the cation along the channel direction at distances between 3 and $3.5 \text{ \AA}$. Owing to the high Si/Al ratio only half of the cesium content compared to the previously reported material was expected. Indeed, per unit cell roughly 0.75 Cs ions are found in almost perfect agreement with the Al content (idealized zeolite formula $[\text{Cs}_{0.75}][\text{Si}_{11.25}\text{Al}_{0.75}\text{O}_{24}]$). This also implies a high dispersion of the cations over the pore system so that directly neighboring Cs ions are not probable. This is in accordance with the observed doubling of the unit cell in c direction, which may be caused by ordering of cation sites across neighboring channels. A detailed structural analysis exploring the possibility EU-7 zeolite may better be described in spacegroup Pc rather than $P2_1/c$ is currently ongoing. The zeolite showed very small micropore volume according to N_2 adsorption porosimetry, close to the detection limit of *ca.* 0.01 mL g^{-1} . Such low values are to be expected for a small pore zeolite with monodimensional pore system, in which Cs cations situated in the 8-membered rings are blocking passage to N_2 molecules, especially at the temperature of -196°C of the recording of the N_2 adsorption isotherm. Mobility of cations is expected at higher temperatures during NH_3 -SCR catalysis. Thermogravimetric analysis of as-synthesized sample showed a weight loss of 4 wt% between 30 and 200°C , assigned to H_2O . Above a temperature of 200°C , a low amount of weight loss was observed (0.4 wt%), suggesting almost no incorporation of butane-1,4-diamine in the EU-7 zeolite. This is confirmed by the Cs/Al atomic ratio of nearly 1, as determined by Rietveld refinement. These extra-framework Cs cations are located in the one-dimensional 8-membered ring channels. This is confirmed

by the lack of porosity of the calcined EU-7 zeolite as determined by nitrogen adsorption analysis. The large Cs cations are blocking access to the internal pore volume of the EU-7 zeolite. The high Si/Al ratio of the small-pore EU-7 zeolite makes this material potentially interesting for catalytic applications upon removal of the extra framework Cs cations to allow access to the internal pore volume of EU-7 zeolite. To remove Cs from the as-made material, the procedure described in example 11 of patent US4581212 was followed. Initially, a suspension of calcined EU-7 zeolite was equilibrated for 4 h in a stirred 0.5 M NH_4Cl solution (100 mL for 1 g of zeolite) under reflux conditions following recovery by centrifugation, the interstitial solution was removed by rinsing the sample with deionized water. This procedure was repeated twice. Afterwards, the sample was dried at 60 °C overnight. This treatment reduced the Cs/Al ratio to 0.39 as compared to a ratio of 1 in the as made material. Following a drying step at 60 °C, the sample was equilibrated for 2 h in a stirred 1 M HCl solution (100 mL for 1 g of zeolite) under reflux conditions. Subsequently, the solid phase was recovered by centrifugation, and rinsed with deionized water. This procedure was repeated 5 times. Finally, the zeolite was converted into the NH_4 form by slurrying it in NH_4Cl solution according to the first two steps in the procedure described above. Overall, the Cs/Al ratio was reduced to 0.22, corresponding to a Cs content 2.8 wt%. X-ray diffraction showed the structure of the zeolite remained intact after both treatments. This reduction of the Cs content allowed to investigate the potential of EU-7 zeolite as small-pore NH_3 -SCR catalyst. Cs has a high affinity for the framework and is unlikely to exchange directly with the Cu. The introduced Cu cations will exchange with the ammonium ions introduced in the post synthesis treatment. When more Cs is present, then also more pores and cation sites will remain inaccessible for the copper. Cu loaded samples were obtained by adding 2 g of Cs-depleted zeolite to a 200 mL aqueous solution containing 0.0189 g copper acetate monohydrate (Chem-Lab, 99+%). This mixture was stirred for 20 h at room temperature. The zeolite was recovered by centrifugation and rinsed with deionized water. This procedure was repeated twice. Afterwards, the zeolite was dried at 60 °C overnight. This resulted in catalysts with a Cu loading of 0.18 and 0.19 wt% and idealized zeolite formula of $[\text{Cs}_{0.39}\text{Cu}_{0.03}(\text{NH}_4)_{0.55}][\text{Al}_{0.75}\text{Si}_{11.25}\text{O}_{24}]$ and $[\text{Cs}_{0.22}\text{Cu}_{0.03}(\text{NH}_4)_{0.72}][\text{Al}_{0.75}\text{Si}_{11.25}\text{O}_{24}]$, respectively for the sample with and without HCl treatment. Despite this low amount, the Cu loaded EU-7 zeolite clearly shows NH_3 -SCR activity, as displayed in Fig. 4. Details on the NH_3 -SCR test and used set-up can be found in the ESI.†

Both copper loaded EU-7 zeolite catalysts show activity at temperatures above 200 °C. Between 200 and 300 °C, the catalyst with HCl treatment has a better NO conversion, which might be ascribed to less Cs blocking the pores. Exposing the Cu loaded EU-7 zeolite to harsh hydrothermal conditions (12 vol% H_2O , 900 °C, 3 h as described in the ESI†) reveals the extraordinary hydrothermal stability of EU-7 zeolite. The XRD patterns of the fresh and hydrothermally aged material, as well as the material after an NH_3 -SCR test, show no signs of structural collapse (Fig. 5). The high hydrothermal stability is

Fig. 4 Reaction rate as a function of temperature of the copper loaded EU-7 zeolite catalysts: sample with 0.19 wt% Cu and 2.8 wt% Cs (solid line) and 0.18 wt% Cu and 5 wt% Cs (dashed line). The feed consists of 500 ppm NO, 450 ppm NH_3 , 5% O_2 , 2% CO_2 , 2.2% H_2O balanced with N_2 gas to obtain a total flow of 15 L h^{-1} , resulting in a gas hourly space velocity of 30 000 h^{-1} .

Fig. 5 X-ray diffraction pattern of (a) Cu loaded EU-7 before reaction and hydrothermal aging; (b) after NH_3 -SCR reaction and (c) after hydrothermal aging.

necessary during regeneration of an SCR-coated diesel particulate filter. In literature, only 2 small-pore zeolites, *i.e.* AEI and LTA, have been reported to be stable up to 900 °C during a hydrothermal aging lasting at least 3 hours in the presence of at least 10% steam.^{8,24} Of these materials, the aforementioned LTA has been synthesized using hydrogen fluoride, making the process difficult to implement on industrial scale. Cu-CHA, initially praised for its higher stability compared to Cu-loaded BEA and MFI (ZSM-5),^{25,26} remains stable up to 875 °C in the presence of steam.²⁷ This study reveals BIK to be yet another robust zeolite withstanding high temperature hydrothermal aging.

In conclusion, the structure of EU-7 zeolite is revealed to correspond to a zeolite with a BIK framework type. The EU-7 zeolite in this work has the highest Si/Al ratio reported up to now for any synthetic BIK. The material is exceptionally stable in hydrothermal conditions and showed no signs of structural collapse after a harsh 3 h treatment in 12 vol% steam at 900 °C. Only AEI and LTA have been known to survive a similar treatment. All currently available synthesis routes of BIK zeolites with

high Si/Al ratio require Cs, which occupies the 8-membered ring pores causing pore blocking. Though a large part of the Cs can be removed *via* ion exchange, including an intermediate acid treatment, residual Cs still effectively hinders access to the straight 8-membered ring channels. After ion exchange with copper, EU-7 zeolite proves to be an active NH₃-SCR catalyst. The high hydrothermal stability combined with the catalytic activity makes the EU-7 zeolite a potential candidate for the next generation of NH₃-SCR catalysts, provided the accessibility of the pore system can be further improved.

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Conflicts of interest

There are no conflicts to declare.

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