Template-free nanosized faujasite-type zeolites

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Materials and Synthesis

Materials
Al powder (325 mesh, 99.5 %, Alfa Aesar)
Al(OH)_3 (Sigma-Aldrich)
Sodium aluminate (Al_2O_3 ~ 50-56 wt. %, Na_2O ~ 40-45 wt. %, Aldrich)
NaOH (Sigma-Aldrich, 97 %)
SiO_2 (Ludox-HS 30, 30 wt. % SiO_2, pH=9.8, Aldrich)
Sodium silicate (SiO_2 ~ 26.5 wt. %; Na_2O, ~10 wt. %, Aldrich)

Synthesis

Y-10 sample (10 nm): The nanosized FAU zeolite was synthesized from a clear precursor suspension with a molar composition: 9 Na_2O: 0.7 Al_2O_3: 10 SiO_2: 160 H_2O. The initial reactants were mixed to prepare two initial solutions denoted A and B. Solution A was prepared by dissolving 2 g of NaOH (Sigma-Aldrich) in 4 g double distilled water (dd H_2O) followed by slow addition of 0.189 g aluminum powder (325 mesh, 99.5 %, Alfa Aesar). Solution B was prepared by mixing of 10 g colloidal silica (Ludox-HS 30, 30 wt. % SiO_2, pH=9.8, Aldrich) with 1.6 g NaOH and 3.4 g dd H_2O; as a result a turbid suspension was obtained. In order to transform the turbid into water clear suspension, the container was placed in an oven at 100 °C for 6 minutes. Solution A was added drop wise under vigorously stirring to the solution B; during the mixing, solution B was kept in ice. The resulting clear suspension was kept 24 h at room temperature; this stage we ascribed as aging. Hydrothermal crystallization was conducted at 50 °C for 45 h.

Y-70 (70 nm): The nanosized FAU crystals were prepared from turbid precursor suspension with the following chemical composition: 8 Na_2O: 0.7 Al_2O_3: 10 SiO_2: 160 H_2O. The experimental procedure described above is used for the reparation of the suspension. The hydrothermal crystallization was performed at 120 °C for 70 min.
**Y-400 (400 nm):** The FAU crystals were prepared from gel precursor with the following chemical composition: 8 Na₂O: 1 Al₂O₃: 10 SiO₂: 400 H₂O. The initial sources colloidal silica (Ludox-HS 30, 30 wt. % SiO₂, pH=9.8, Aldrich), aluminium hydroxide (Sigma-Aldrich) and NaOH (Pellet 97% Sigma-Aldrich) were mixed in polypropylene bottle and the resulted suspension was aged for 24 h at ambient conditions. The hydrothermal crystallization was performed at 100 °C for 12 h.

**X-10 (10 nm):** The ultra-small FAU-X zeolite X (X-10) was synthesized from a clear precursor suspension with a molar composition: 9 Na₂O: 1.1 Al₂O₃: 10 SiO₂: 45 H₂O. *Solution A* was prepared by dissolving 2.5 g of NaOH (Sigma-Aldrich) in 3 g dd H₂O followed by slow addition of 0.297 g aluminum powder (325 mesh, 99.5%, Alfa Aesar (this is a very exothermic reaction). *Solution B* was prepared by mixing of 10 g colloidal silica (Ludox-HS 30, 30 wt. % SiO₂, pH=9.8, Aldrich) with 1.1 g NaOH and 1 g dd H₂O; as a result a turbid suspension was obtained. In order to transform the turbid into water clear suspension, the container was placed in an oven at 100 °C for 6 minutes. Solution A was added drop wise under vigorously stirring to the solution B; during the mixing, solution B was kept in ice. The resulting clear suspension was aged 24 h at room temperature, freeze dried, and then the water content was adjusted.

The ranges of compositions yielding the FAU nanosized zeolites are given below:

**Y-10:** 10 SiO₂: 0.6-0.9 Al₂O₃: 7-9 Na₂O: 100-200 H₂O  
**Y-70:** 10 SiO₂: 0.7-0.9 Al₂O₃: 8-10 Na₂O: 160-300 H₂O  
**X-10:** 10 SiO₂: 1.1-1.4 Al₂O₃: 7-10 Na₂O: 45-200 H₂O

The solid products from all syntheses were recovered by centrifugation (25.000 rpm for 4 h), purified with dd H₂O until pH=7 and then freeze-dried prior further characterization.

A commercial zeolite Y sample, kindly provided by UOP (LZY-62), with a crystal size of 1-2 µm and Si/Al of 2.5 was used as a reference sample.
Ammonium exchange

The FAU nanosized materials were ion-exchanged with a solution of 0.2 M of NH₄Cl (1 h at 25 °C), washed with dd H₂O and calcined at 400 °C to eliminate the NH₃ and obtain the zeolite nanocrystals in acidic form. This procedure was repeated twice.
Characterization

**Powder X-ray diffraction (XRD) analysis.** Powder samples were measured using a PANalytical X’Pert Pro diffractometer with CuKα monochromatized radiation (λ = 1.5418 Å). The samples were scanned in the range 4-50 °2θ with a step size of 0.02 °. The XRD patterns analysis was performed using the MAUD program based on the Rietveld method (Chateigner, D. Combined Analysis: Structure-Texture-Microstructure-Phase-Stresses-Reflectivity Determination by X-ray and Neutron Scattering, (Wiley-ISTE, New York, 2010). The Popa formalism was used to describe anisotropic crystallite sizes and shapes (N. Popa, J. Appl. Cryst. 31 (1998) 176).

**Transmission electron microscopy (TEM).** Diluted colloidal suspensions of FAU nanomaterials were sonicated for 15 min and then 2-3 drops of fine particle suspensions were dried on carbon-film-covered 300-mesh copper electron microscope grids. The crystal size, morphology and crystallinity of solids were determined by a transmission electron microscopy (TEM) using a JEOL 2010 FEG and a FEI LaB₆ TECNAI G²30UT operated at 200 kV and 300 kV, respectively. Energy Dispersive Spectrometer (EDS) coupled with both microscopes was used to determine the chemical composition of the FAU zeolite nanocrystals.

**Dynamic light scattering (DLS) analysis.** The hydrodynamic diameters of the FAU nanoparticles in the suspensions were determined with a Malvern Zetasizer Nano. The analyses were performed on samples after purification with a solid concentration of 10 wt. % at pH=8. The back scattering geometry (scattering angle 173 °, HeNe laser with 3 mW output power at 632.8 nm wavelength) allows measurements at high sample concentration, since a complete penetration of the incident light through the sample was not required.
**Chemical analysis.** The chemical composition of the FAU samples was determined by inductively coupled plasma (ICP) optical emission spectroscopy using a Varian ICP-OES 720-ES.

**N₂ sorption analysis.** Nitrogen adsorption/desorption isotherms were measured using Micrometrics ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 250 °C under vacuum overnight prior to the measurement. The external surface area and micropore volume were estimated by alpha-plot method using Silica-1000 (22.1 m² g⁻¹ assumed) as a reference. The micropore and mesopore size distributions of solids were extracted from adsorption branch by the Nonlocal Density Functional Theory (NLDFT) and from the desorption branch using the Barret-Joyner-Halenda (BJH) algorithm, respectively.

**Thermal analysis.** Thermal analyses (TG/DTG) were performed using a Setsys SETARAM analyzer (heating rate of 5 K min⁻¹) under a 40 ml min⁻¹ flow of dry air.

**Solid State NMR.** ²⁷Al NMR spectra were recorded on a Bruker Avance 400 (9.4 T) spectrometer using 4 mm-OD zirconia rotors and a spinning frequency of 12 kHz.

**Catalytic test.** The catalytic conversion of 1,3,5-triisopropylbenzene (TiPBz) was performed in a tubular downflow reactor operating in the gas phase. For each experiment, 10 mg of the catalyst (ammonium exchanged zeolite) was loaded in the reactor and enclosed between two layers of finely ground inert (SiC, 0.25 mm). The samples were carefully dehydrated and de-ammoniated in a dry-air stream (Flow (Qₐ) = 50 mL min⁻¹), first at 100 °C for 2 h, and then the temperature was raised to 400 °C followed by a 2 h plateau at this final temperature. Dried and deoxygenated nitrogen was subsequently flowed at 400 °C, and then the reactor was cooled-down to reaction temperature (200 and 225 °C). Using this procedure, 10 mg of catalyst was loaded for each experiment. A stream of 100 mL min⁻¹ N₂ was diverted to a saturator filled with
TiPBz (Alfa Aesar, 95 % purity) maintained at 71 °C ($P_{\text{TiBz}} = 180$ Pa). The total pressure in the reactor was $1 \times 10^5$ Pa and the contact time $W/F^o$ was 82 kg s mol$^{-1}$. Stable conditions were established in the catalyst bed in less than 2 minutes so the first effluent was sampled after 2 min, thereafter at 15 min intervals and analyzed quantitatively on a CPG (VARIAN Cp 3800; HP-Pona 50 m, 0.2 mm, 0.5 μm column), fitted with a FID detector.
Figure S1 Rietveld refinement for (a) Y-10 and (b) Y-70 nanosized crystals with anisotropic particle shapes described using the Popa formalism. Vertical ticks correspond to line indexing of the FAU phase (SG: Fd-3 ICSD card 6315). The difference diagram between calculated and experimental points is shown at the bottom of each XRD pattern. Insert: crystals with octahedral shape and size of 9 nm and 38 nm for samples Y-10 and Y-70, respectively.
Figure S2. (A) DLS results of (a) Y-10 and (b) Y-70 zeolite suspensions (grey: scattering intensity expressed as a function of particles number, and black: scattering intensity expressed as a function of particles volume). (B) Pictures of Y-10 suspensions with a solid concentration of (a) 2, (b) 6, (c) 10, (d) 15, (e) 20, and (f) 25 wt. %.
**Figure S3.** Zeta potential curves of nanosized samples Y-10 and Y-70.
Figure S4. SEM pictures of sample Y-400: (a) scale bar=2 µm and (b) scale bar=1 µm, and commercial zeolite Y (LZY-62, Si/Al=2.5): (c) scale bar=2 µm and (d) scale bar=5 µm.
Figure S5. N\textsubscript{2} adsorption/desorption isotherms of a commercial zeolite Y (LZY-62).
Figure S6. Nanosized sample X-10: (a) whole pattern fitting (Le Bail method) of the experimental XRD (SG: Fd-3, a= 25.055(3) Å), (b) nitrogen adsorption/desorption isotherm, and (c) TEM image.
Figure S7. XRD patterns of (a) Y-10, (b) Y-70 and (c) Y-400 nanosized zeolites after thermal treatment at 550 °C for 6 h.
Figure S8. $^{27}$Al NMR spectra of Y-10, Y-70 and Y-400 nanosized samples and a commercial zeolite Y (LZY-62), all in H form.
**Figure S9.** TG/DTG data of samples Y-10, Y-70 and Y-400 nanosized samples (a) as-synthesized and (b) in H form.
Figure S10. Selectivity on Y-10, Y-70, Y-400 and LZY-62 catalysts during the TiPBz conversion (top of each bar, in mass. %) for 1,4-DiPBz, 1,3-DiPBz, Cumene, and Benzene, (a) at 200 °C, and (b) 225 °C.
Table S1 Chemical composition, initial reactants (silica and alumina sources) and conditions of hydrothermal treatment used for the synthesis of nanosized zeolites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na₂O</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>H₂O</th>
<th>Silica and alumina sources</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Crystalline phase</th>
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<tr>
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<tr>
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<td>01.10</td>
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<tr>
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<td>10</td>
<td>160</td>
<td>Na silicate Na aluminate</td>
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<td>45.00</td>
<td>FAU (main phase) + EMT</td>
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<tr>
<td>8</td>
<td>8.00</td>
<td>0.7</td>
<td>10</td>
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<td>Na silicate Na aluminate</td>
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<td>45.00</td>
<td>FAU (main phase) + EMT</td>
</tr>
<tr>
<td>9</td>
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<td>Ludox HS-30 Al powder</td>
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**Table S2.** N$_2$ sorption data of Y-10, Y-70, Y-400, X-10 nanosized and LZY-62 micron-sized samples.

<table>
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<tr>
<th>Sample</th>
<th>S</th>
<th>$V_{\text{micro}}$</th>
<th>$d_{\text{micro}}$</th>
<th>S$_{\text{ext}}$</th>
<th>$V_{\text{meso}}$</th>
<th>$d_{\text{meso}}$</th>
<th>V$_{\text{total}}$</th>
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<tbody>
<tr>
<td>Y-10</td>
<td>845</td>
<td>0.30</td>
<td>0.73</td>
<td>180</td>
<td>0.97</td>
<td>30</td>
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<tr>
<td>Y-70</td>
<td>850</td>
<td>0.31</td>
<td>0.73</td>
<td>60</td>
<td>0.32</td>
<td>80</td>
<td>0.63</td>
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<tr>
<td>Y-400</td>
<td>860</td>
<td>0.31</td>
<td>0.74</td>
<td>30</td>
<td>0.04</td>
<td>No</td>
<td>0.35</td>
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<tr>
<td>X-10</td>
<td>820</td>
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<tr>
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<td>0.30</td>
<td>0.73</td>
<td>26</td>
<td>0.06</td>
<td>No</td>
<td>0.36</td>
</tr>
</tbody>
</table>

S: equivalent specific surface area (m$^2$ g$^{-1}$); $V_{\text{micro}}$: micropore volume (cm$^3$ g$^{-1}$); S$_{\text{ext}}$: external surface area (m$^2$ g$^{-1}$); $V_{\text{meso}}$: mesopore volume (cm$^3$ g$^{-1}$); $d_{\text{micro}}$: micropore diameter (nm); $d_{\text{meso}}$: mesopore diameter (nm); $^a$determined by DFT method; $^b$determined by BJH method.