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Synthesis of nanosized HZSM-5 zeolite under microwave irradiation: effect of the Si/Al ratio on the morphology, textural and acidic properties

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Synthesis of nanosized ZSM-5 zeolites with different Si/Al ratios

To synthesize nanosized ZSM-5 zeolites directly in the proton form, a mixture containing tetraethylortosilicate $Si(O\text{-}Et)_4$, (99%, SIGMA ALDRICH), distilled water, tetra-n-propylammonium hydroxide TPA-OH (1 M, MACKLIN)) and aluminum isopropoxide $Al(O\text{-}i\text{-}Pr)_3$ (>98%, TOKYO CHEMICAL INDUSTRY) was used.

Tetra-n-propylammonium hydroxide and tetraethylortosilicate were dissolved in distilled water and intensively stirred at 75 °C for 6 h. Then aluminum isopropoxide was added to the resulting gel and stirred until the mixture was completely homogenized, but without subsequent aging. The resulting suspension was placed in a Teflon autoclave and subjected to microwave treatment in the M6 system (Preekem Instruments, China). Crystallization was carried out at 200 °C for 3 h. The obtained particles of nanosized zeolite, designated as nanoH-ZSM-5_X, (X is the Si/Al ratio equal to 46, 51, 72, 232 or 270, respectively) were isolated by centrifugation in an ultracentrifuge at 1800 rpm, washed with distilled water and dried at 170 °C for 2 h, then they were calcined at 550 °C for 6 h to remove the organic template.

Material characterization. Powder X-ray diffraction (XRD) data were collected at a scanning speed of 1.4 °/min on a Rigaku MiniFlex 600 (CuK_α radiation, λ = 1.54187 Å) diffractometer operated at 40kV and 15mA.

The shape and size of the particles, as well as the structure of the synthesized zeolite, were determined by scanning (Hitachi Regulus8230 field-emission scanning electron microscope (FE-SEM), operating voltage 5 kV) and transmission (JEOL JEM-2100, operating voltage 200 kV) electron microscopy.

Al and Si content was determined by the ICP-OES method. An aliquot of 0.05 g of sample was taken and transferred to microwave digestion vessel (Multiwave GO Plus, Anton Paar), into which a mixture of 4 ml HF, 1 ml H_2SO_4, and 6 ml HNO_3 was added. After dissolving the sample, the resulting solution was stabilized with a saturated solution of boric acid to bind free hydrofluoric acid, and diluted with deionized water 18.2 MΩ cm (Arium Comfort II, Sartorius) to a volume of 50 ml with further dilution with 2% solution of nitric acid. A blank sample was prepared in the same way. The samples were analyzed by the ICP-OES method on Agilent 5800 spectrometer.

The textural properties of the zeolite were determined by a low-temperature N_2 physisorption on an BELSORP Mini-X (MicrotracBEL, Japan) instrument. The specific surface area was calculated by the BET model. The total pore volume was calculated at $p/p_0 = 0.99$ from the adsorption branch of the isotherm. The micropore volume was calculated by the MP method. Mesopore size distribution, volume of mesopores – according to the Barrett–Joyner–Halenda (BJH) desorption curve; micropore size distribution – according to the MP adsorption curve; determination of the external surface area – according to the t-plot adsorption curve.

The acidic properties of the catalysts were evaluated by temperature programmed desorption of ammonia (NH_3-TPD) on a USGA-101 chemisorption analyzer. Each sample was pretreated at 550 °C at 4 h in dry air, then 1 h at 550°C in N_2. After that the sample was cooled to room temperature and exposed to a N_2–NH_3 flow (1 : 1 ratio) for 30 min. Subsequently, the physically adsorbed NH_3 on the sample was purged by N_2 at 100 °C. The signal of NH_3 desorption was recorded in the temperature range up to 650 °C with a heating rate of 8 °C min^{-1}.