Seed-assisted Synthesis Of Nanosized Beta Zeolite

As a well-established family of nanoporous catalysts, zeolites are of vital importance for the chemical and petrochemical industries. Zeolite Beta, with its interesting framework architecture and 3-dimensional 12-ring pore system, displays superior performance in re nery applications, environmental catalysis and a variety of organic reactions because of its high adsorption capacity, strong acid sites and shape/size selectivity combined with high thermal stability. Because of its unique pore structure and excellent catalytic properties, zeolite Beta is widely used in the petroleum industry, especially in the alkylation process of benzene for the production of ethylbenzene and cumene. The pore size is often a drawback when transformations of molecules of larger dimensions must be performed on zeolites or the resulting products are of a large size. One way to overcome this disadvantage and to provide improved di usion of molecules is a synthesis of nanosized zeolites.

Zeolites with nanosized crystals have a larger surface area. Thus, a much larger number of T-atoms, which play a role of active centres in the reactions, are located on the outer surface and are accessible to the reactants in the reactions. This factor plays an important role in the application of zeolites as adsorbents and catalysts, since the contact surfaces between the reactants and the zeolite is greater. The surface properties of nanosized zeolites provide new possibilities to explore adsorption and reaction of bulky molecules that do not normally interact with the micropore volume of the zeolites.

Several techniques for the preparation of zeolites with nanosized crystals are known; synthesis with space limiting agents, and seed-assisted synthesis. In seed-induced synthesis, the addition of seed crystals introduces crystallites into the system which play the role of nuclei. Crystal growth takes place over them. The higher the number of crystallites in the initial gel, the smaller the size of particles obtained. The synthesis in the presence of seeds has other advantages, namely { directing the synthesis towards the desired product and increasing the speed of crystallization. The present report provides information on the physicochemical properties of nanosized zeolite Beta crystals obtained by seeding of the initial gels with two types of seeds { crystals and suspension of mother liquor from hydrothermal synthesis of the same zeolite. The in uence of various parameters in the synthesis of nanosized zeolite Beta in the presence of seeds { time, temperature, concentration and type of seed used on yield, particle size and morphology of the resulting product is investigated. The characteristics of the obtained materials are compared with those of their counterparts synthesized without seeds.

Experimental

The following chemicals were used in the present study: Ludox HS-40 colloidal silica (40 wt.% suspension in water, Grace Davison), highly dispersed extra pure silicon dioxide (Merck), tetraethylammonium hydroxide { TEAOH (20% aqueous solution, Merck), aluminium 984 B. Barbov, Y. Kalvachev powder (Acros Organics). Zeolite Beta synthesized without seeds was prepared from a suspension with molar composition: 9TEAOH: xAl2O3 : 100SiO2 : 420H2O, where x = 0{5. Suspension preparation procedure starts with dissolution of aluminium powder into 20% solution of TEAOH till obtainment of clear solution. Silica source was added and the initial suspension was stirred for 40 min at room temperature. The crystallization was performed under static conditions for a period of 72{240 h at 393 K. The obtained solid was puri ed by four consecutive steps of centrifugation, re-dispersion in distilled water and then dried at 333 K overnight.

The rst type crystals, is obtained by crystallization, puri cation and drying of the resulting solid. The second type seeds were obtained immediately after completion of the crystallization step and the solid product remains in the mother liquor. The seed amount was adjusted to be 1, 2 and 5 wt% from the total silica amount in the gel. The crystallization was performed in stainless steel Te onlined autoclaves under autogenous static conditions for a period of K. After the synthesis, the autoclaves were quenched in cold water. The solid was puri ed by four consecutive steps of centrifugation and re-dispersion in distilled water and then dried at 333 K overnight.

Characterization

The X-ray powder di raction patterns were recorded on di ractometer D2 Phaser (Bruker) with CuK radiation, working at acceleration 30 kV and current 10 mA. The 2 scanned range was 4{50 with step of 0.05 min and 1 s acquisition time. FTIR spectra were taken on a Bruker Tensor 37 spectrometer using KBr pellet technique. For each sample, 64 scans were collected at a resolution of 2 cm over the wavenumber region 4000. The scanning electron microscopy (SEM) analyses were obtained on Philips 515 apparatus, working at 20 kV accelerating voltage. The samples were covered with gold before investigation. Dynamic light scattering (DLS) particle size distribution measurements were performed on a Brookheaven Instrument 90Plus by suspension of the samples in water.

Results and Discussion

Zeolite Beta synthesis without seeds. By using molar composition of initial gel 9TEAOH: xAl2O3 : 100SiO2 : 420H2O, where x = 0{5, zeolite Beta with high crystallinity is obtained only in very narrow window of Si/Al ratio from 30 to 50. The samples prepared with a ratio Si/Al of less than 30 are with an amorphous structure, while the samples prepared with a ratio Si=Al = 100, have a crystalline structure, but the yield is much lower. All attempts pure silica sample to be synthesized were unsuccessful. X-ray di raction patterns of samples prepared from gels with Si/Al ratio of 50 and 25. It is seen that the product with higher alumina content is amorphous. The synthesis product from initial gel with a ratio Si=Al = 1 is also amorphous despite the long period of crystallization of 240 h.

The SEM inspection of Beta zeolite was performed in order to investigate the size and morphology of the crystals. The product from initial gel with ratio Si=Al = 50 is uniform in size comprising isometric 200{350 nm particles. Investigation of the sample by dynamic light scattering shows an average size of particles of 280 nm.

In order to obtain zeolite Beta with smaller size and to reduce crystallization time seed-assisted syntheses are performed by using of two types of seeds { crystal particles and mother liquor. The seed amount was adjusted to be 1, 2 and 5 wt% from the total silica amount in the gel. In the presence of 1% seed the synthesis of zeolite Beta from initial gel with Si/Al

According to the XRD study the product obtained after 72 h crystallization time exhibited higher crystallinity, while no crystalline phase was obtained for 54 h crystallization time. The average yield of this zeolite synthesized in the presence of both types of seeds varies between 65 and 75%. Zeolite Beta was synthesized from gels with Si/Al ratio of 50 in the presence of both types of seeds with high crystallinity and the average size of particles in the range 100{200 nm. With increasing the amount of used seeds from 1 to 5% from the total silica amount in the gel the crystallization time is decreased from 72 to 24 h. The yield of obtained product is 5{8% higher with using of suspension of mother liquor as seeds.

The results of synthesis of zeolite Beta from initial gel with Si/Al ratio of 100. The obtained products are with high crystallinity, just the yield without using of seeds is very low { 37.7% even after long period of crystallization time { 120 h. By adding of seeds the yield increased and the e ect is more pronounced at 5% seeds. The product yield is higher when suspension of mother liquor is used as seeds than crystal seeds.

The SEM micrograph of sample synthesized from initial gel with Si/Al ratio of 100 with 5% crystal seed. Uniform particles with average diameter of about 100{200 nm are seen. The particle size distribution obtained by DLS analysis of all samples con rms these results. The narrowest distribution is for samples synthesized with 5% seeds.

The yield of zeolite Beta from initial gel with Si/Al ratio of 1 by using of di erent amount for both types of seed is presented. It can be seen that the yield of high silica samples is relatively low. Without using of seeds the product is amorphous even after 240 h crystallization time. A product with high crystallinity is obtained after 144 h from initial gel with 1% seed. Depending on the crystallisation time, the type and the amount of the used seeds, the yield of the resultant product varied between 2 and 19%. By using of higher amount of seeds, even the crystallization time is shorter, the yield of the product is higher. In this case also, it is seen that in the synthesis of high silica zeolite Beta in the presence of suspension of mother liquor, the yield was slightly larger than that of zeolite Beta synthesized in the presence of crystal seeds. Adding seed crystals to a crystallization system has resulted in increased crystallization rates. The enhanced rate might be due to increasing the rate at which the solute is integrated into the solid phase from solution due to the increased available surface area. Most probably the process of integration of the solute into the solid phase is faster when mother liquor is used as seeds and this fact results in higher yield.

Conclusions

Zeolite Beta with high crystallinity is obtained from the system with the following molar ratio: 9TEAOH : xAl2O3 : 100SiO2 : 420H2O, where x = 1:66, 1.0 and 0.5, when the Si/Al ratio is between 30 and 100. Samples synthesized with a ratio Si=Al