

# Synthesis of the zeolite ZSM-5 by using seed crystals

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Preparation of the zeolite ZSM-5 by seeding of the starting aluminosilicate gel with the highly crystalline zeolite of the same type was studied in an aqueous—ethanolic medium. Investigated was the influence of the amount of ethanol added, of reaction temperature and time needed for crystallization of the zeolite. Suitable conditions for preparation of the zeolite ZSM-5 of high crystallinity not requiring organic templates were worked out.

A great attention is being paid to the synthesis of zeolite ZSM-5, although the first patents of Mobil Oil Corp. concerning this preparation appeared at the beginning of the seventies. Recently, this endeavour has been pointed toward a simple and cheap preparation of this zeolite by crystallization in the presence of seed crystals of the zeolite ZSM-5 thus avoiding expensive tetrapropylammonium compounds.

As known [1, 2], addition of a small amount of seed crystals of the zeolite ZSM-5 and acetone into the aluminosilicate gel resulted in formation of the zeolite ZSM-5 of a high crystallinity and a low distribution of the crystal size. Acetone added to the mixture inhibits a spontaneous formation of the ZSM-5 crystal nuclei and accelerates crystallization of the ZSM-5 around the seed crystals. Similar effect showed also ethyl methyl ketone and cyclohexanone. As found, these ketones do not act as templates for crystallization of zeolite ZSM-5. *Batista et al.* [3] reported the synthesis of high-content silicate zeolites by addition of ZSM-5 seed crystals (modules 35 and 273). In agreement with previous papers it was ascertained that addition of seed crystals lowers the crystallization time and enhances the yield of the zeolite. Structural characterization and morphology of zeolites obtained depend on the morphology of seed crystals.

In continuation of this study the influence of seed crystals of zeolite in the system water—aliphatic alcohol  $C_1$  to  $C_8$  [4], or water—mixture of by-products (linear and branched alcohols predominantly  $C_4$  to  $C_7$ ) from various refineries [5] was investigated. Also these systems are suitable for preparation of zeolite ZSM-5 of crystallinity over 90 %. Very good results were obtained with ethanol, the effect of which was examined in this work.

## Experimental

Employed were hydrosol of silicic acid (Research Institute for Crude Oil and Gaseous Hydrocarbons, Bratislava) with 31.2 mass %  $\text{SiO}_2$ , aluminium sulfate (crystalline), sodium hydroxide, and ethanol (all anal. grade; Lachema, Brno). Composition of the seeding zeolite Na-ZSM-5 (Research Institute for Crude Oil and Gaseous Hydrocarbons, Bratislava) with the ratio  $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3) = 28.1$  was as follows: w/mass % (in recount to the anhydrous state): 2.44  $\text{Na}_2\text{O}$ , 0.1  $(\text{NH}_4)_2\text{O}$ , 0.22  $\text{CaO}$ , 5.54  $\text{Al}_2\text{O}_3$ , 91.7  $\text{SiO}_2$ ; the X-ray analysis confirmed the zeolite of ZSM-5 type. Its specific surface  $S = 374\,460 \text{ m}^2 \text{ kg}^{-1}$  and specific volume of pores  $V = 1.71 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$

Zeolites were prepared so that a solution of aluminium sulfate (0.87 g in  $30 \text{ cm}^3$  of water) and sodium hydroxide (1.57 g in  $37 \text{ cm}^3$  of water) were successively added dropwise to an agitated hydrosol of silicic acid (25.2 g). Then ethanol and seeding zeolite (0.36 mass %; related to the mass of starting mixture) were added to the formed aluminosilicate gel of the mole composition: 0.15  $\text{Na}_2\text{O}$ , 0.01  $\text{Al}_2\text{O}_3$ , 1.0  $\text{SiO}_2$ , 36  $\text{H}_2\text{O}$ . This mixture was homogenized for 20 min at room temperature and transferred into the  $120 \text{ cm}^3$  steel ampoule, inside coated with teflon and inserted in an electrically heated block equipped with a transistor temperature controller. Temperature in the ampoule was measured by means of a platinum resistance thermometer. Samples were heated without stirring for a pre-set time, cooled and filtered. The crystalline portion remaining on the filter was washed with distilled water and dried under reduced pressure at  $110^\circ\text{C}$  for 4 h.

The zeolites were identified and their crystallinity was determined from the X-ray diffraction analysis. The portion of the crystalline phase of the zeolite (crystallinity  $K$ ) was deduced from the calibration curve of model mixtures containing variable amounts of the zeolite ZSM-5 of high crystallinity (zeolite identical with the seed crystals), cristobalite (internal reference) and an amorphous constituent. Compared were surfaces of three typical diffraction maxima of the zeolite ZSM-5 in the region  $2\theta = 22.5\text{--}25^\circ$  with the surface of the diffraction maximum of cristobalite fitting just into the interstice of the X-ray diffraction record of the zeolite ZSM-5 and located at the highest of the

above-mentioned three diffraction maxima. The function  $\left( \sum_{i=1}^3 S_i \right) / S_{\text{int. stand.}} = f(K)$  had a linear course. It was calculated by the least-squares method and employed for determination of crystallinity of the zeolites prepared. Such a determination afforded more reproducible results than that based upon heights of diffraction maxima.

Conditions for diffraction analysis of zeolite samples: apparatus DRON 2.0 (USSR), radiation  $\text{CuK}\alpha$ , C-monochromator, slot 0.5, angle rate  $(2\theta) 1^\circ \text{ min}^{-1} \text{ cm}^{-1}$ , sensitivity  $2 \times 10^3 \text{ imp s}^{-1}$ , filament voltage 35 kV, current 14 mA, time constant 2, reproducibility of results in terms of relative error  $\pm 5\%$ .

## Results and discussion

One possibility how to prepare a zeolite ZSM-5 in a rather simple way is seeding of the starting aluminosilicate gel by addition of the zeolite ZSM-5 of

high crystallinity. As shown [4, 5], good results were obtained when an aliphatic alcohol participated in the hydrothermal synthesis. Very convenient proved to be ethanol and therefore, we investigated the influence of ethanol, reaction time and temperature on the crystallinity of the product at a constant addition of the seed crystals. The addition of ethanol ranged within 0 and 1.16 mol per 1 mol  $\text{SiO}_2$  in the starting gel. Relation between the crystallinity of the desired products and addition of ethanol is shown in Fig. 1.

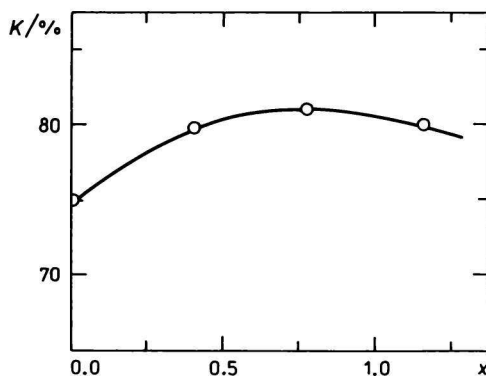


Fig. 1. The effect of addition of ethanol ( $x/\text{mol}$ ) on the crystallization of the zeolite ZSM-5 at  $190^\circ\text{C}$  and 14 h reaction time.

The highest crystallinity of the product was achieved at  $x(\text{EtOH}) = 0.778 \text{ mol}$ . However, in the examined range the amount of ethanol only little influenced the crystallinity of zeolite. At a zero addition of ethanol the X-ray diffraction record showed the presence of  $\alpha$ -quartz, but its quantitative representation was not estimated. The good quality of the product was obtained by heating at  $190^\circ\text{C}$  for 10 h; prolongation of time above 14 h resulted in appearance of  $\alpha$ -quartz whilst the portion of the crystalline phase of zeolite decreased (Fig. 2).

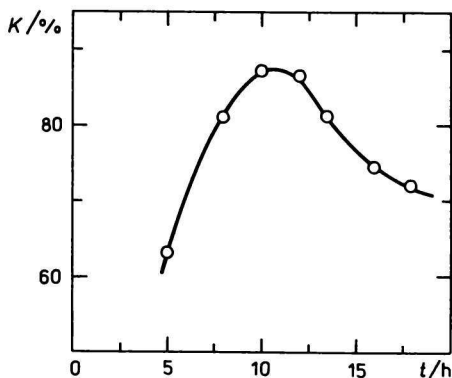


Fig. 2. The effect of reaction time on the crystallization of zeolite ZSM-5 at  $190^\circ\text{C}$  in the presence of 0.778 mol EtOH.

Results achieved at 150–210 °C and 10 h and 14 h reaction times are shown in Fig. 3. The best crystallinity of the zeolite was obtained at 180 °C and 10 h reaction time (92 %) or at 170 °C and 14 h (93 %). Above this temperature the proportion of crystalline phase of zeolite in the product decreased and above 200 °C a marked formation of  $\alpha$ -quartz was observed in line with [1, 2]. The mole ratio between  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (the module) in the zeolite prepared varied within 35 and 41, whilst that of the starting mixture was 100. Lowering the module with respect to the starting material was also reported in [1, 2] on use with acetone.

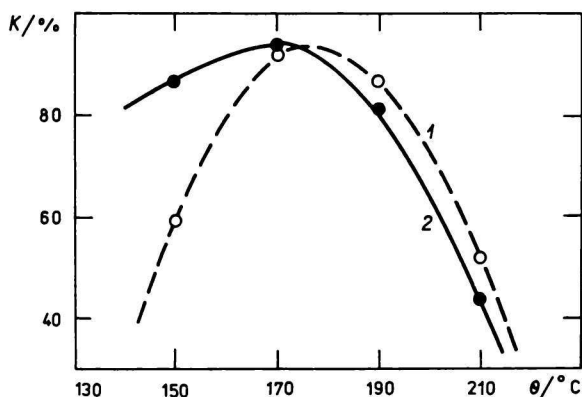


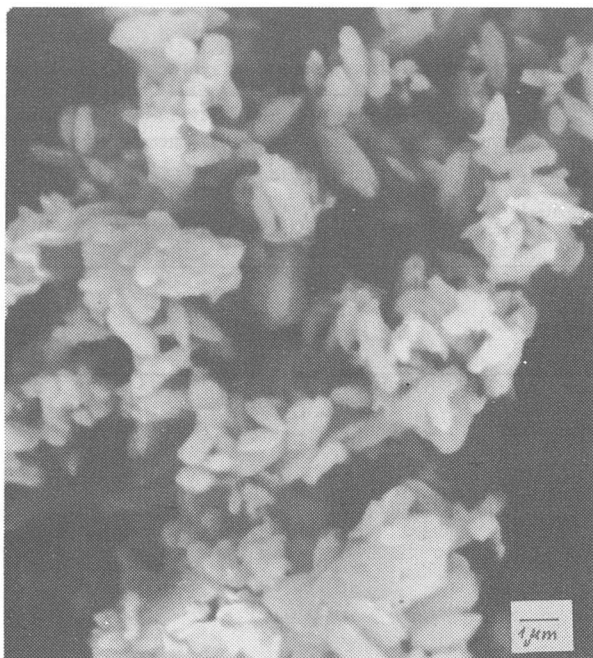
Fig. 3. The effect of temperature on the crystallization of zeolite ZSM-5 in the presence of 0.778 mol EtOH and the seed crystals (0.36 mass %) for time: 1. 10 h, 2. 14 h.

Figs. 4 and 5 show the scanning electron micrographs (SEM) of the seeding zeolite and the zeolite ZSM-5, respectively, obtained at 180 °C for 10 h; the particle sizes of the synthesized zeolite are evidently greater than those of the seeding zeolite.

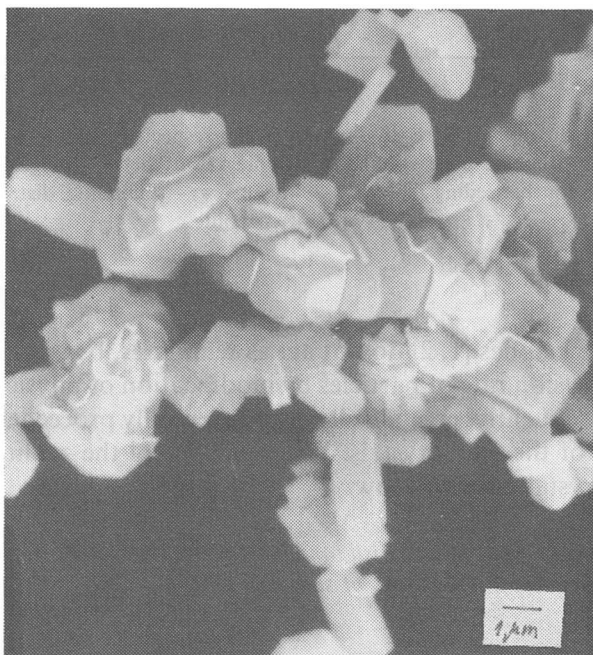
Table 1 lists the physical parameters of the seeding zeolite and the product as calculated from the measured values [6]. The zeolite module was determined by chemical analysis, the integral and differential pore distribution is illustrated in Fig. 6.

Physical parameters (specific surface, specific pore volume, middle pore radius, integral and differential pore distributions) of the ZSM-5 type zeolite prepared at 180 °C for 10 h ( $K = 92\%$ ) are very close to those of the seeding zeolite (relative error up to  $\pm 5\%$ ). Modules of all zeolites prepared by seeding were higher than that of the seeding zeolite itself.

In the absence of the seed crystals in water—ethanol an amorphous product was formed, which means that the seed crystals are prerequisite for the synthesis. Ethanol or other aliphatic alcohols applied successfully [4, 5], as well as



*Fig. 4.* Seeding zeolite ZSM-5.



*Fig. 5.* The prepared zeolite ZSM-5.

Table 1

Calculated values of physical parameters for synthetic ZSM-5 type zeolite

| Parameter                                    | Seeding zeolite      | Zeolite prepared     |
|--|----------------------|----------------------|
| $n(\text{SiO}_2) \ n(\text{Al}_2\text{O}_3)$ | 28.1                 | 37                   |
| $S \ (\text{m}^2 \text{kg}^{-1})$            | 374 460              | 386 218              |
| $V \ (\text{m}^3 \text{kg}^{-1})$            | $1.71 \times 10^{-}$ | $1.78 \times 10^{-}$ |
| $r \ \text{m}$                               | $9.13 \times 10^{-}$ | $9.22 \times 10^{-}$ |

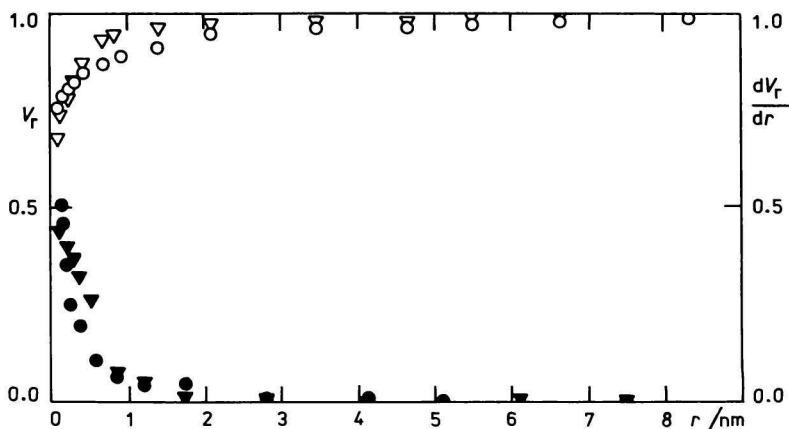


Fig. 6. Integral and differential pore distribution in the respective seeding zeolite and prepared zeolite ZSM-5 ( $V_r$  — relative pore volume,  $r$  — pore radius).  $\circ$  — Integral,  $\bullet$  — differential distribution of pores for the seeding zeolite;  $\nabla$  — integral,  $\blacktriangledown$  — differential distribution of pores for the synthesized zeolite.

acetone or other ketones [1, 2] do not act as templates, but probably positively influence the diffusion rate of particles by modification of physical properties of the system. Consequently, crystallization preferentially proceeded at the crystallization centres of the seed crystals. Without ethanol the zeolite ZSM-5 originated, but its crystallinity was low.

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