Controlled synthesis of the Al-rich zeolites of *BEA structure

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Abstract

Parameters of hydrothermal synthesis of Al-rich beta zeolites in the absence of an organic structure-directing agent and with using seeding of calcined beta crystals were systematically analysed. The parameters as a source of aluminum and silica used for the preparation of aluminosilicate synthesis gel, temperature and duration of synthesis, and the structure of the zeolite seeds were analysed using advanced equipment for hydrothermal synthesis. Particular emphasis was placed on the analysis of the effects of the synthesis conditions on phase purity, crystal morphology, and concentration of aluminium in the framework to obtain comprehensive understanding the decisive parameters controlling synthesis of Al-rich beta zeolites with structure tailored for preparation of acid and redox catalysts with desired distribution and nature of active sites.

Keywords: Al-rich beta, Zeolites, Synthesis.

1. Introduction

The discovery of new synthesis procedures yielding a high concentration of tetrahedrally coordinated Al in the framework of the beta zeolite from a dense system containing a minimum of template [1] or synthesis routes employing seeding of Si-rich beta crystals in the complete absence of an organic structure-directing agent [2-13] led to the synthesis of Al-rich beta zeolites with Si/Al $\geq$ 4. The high concentration of Al-related active sites and the highly regular structure of Al-rich beta zeolite are directly manifested in enhanced activity in acid- and redox-catalysed reactions compared with conventional Si-rich beta zeolite [9-13].

2. Experimental

Al-rich *BEA zeolites were synthesized by hydrothermal method in the absence of an organic structure-directing agent with using seeding of variety calcined beta crystals, aluminosilicate mixtures prepared from $Al(OH)_3$, colloidal silica, and NaOH at the temperatures from 120 to 140 °C and various synthesis times. The structure of the zeolites was determined by combination of standard sorption and diffraction methods. A detailed analysis of coordination of Al atoms in the framework was realised using high resolution ^{27}Al 3Q MAS NMR and ^{29}Si MAS NMR spectroscopy. A combination of ^{1}H MAS NMR spectroscopy and FTIR spectroscopy of OH groups and adsorbed molecular probes (d_3-acetonitrille, CO) were used for analysis of the concentration and nature of acid sites.

3. Results and discussion

First, the influence of sources of silica and alumina and Al/Si ratio were investigated. $Al(OH)_3$ and colloidal silica were chosen as silica and alumina source, respectively, for analysis of the effect of temperature and time on the rate of crystallization and phase purity The precursors had the Si/Al ratio approx. 12 which is a higher aluminum content compared to other reported synthesis [1-9]. By changing the preparation conditions such as temperature and time of synthesis, amount of seeds etc., the *BEA zeolites composed of different Si/Al ratios and yields. Fig. 1 (left) shows the yield depending on the amount of seeds with optimum about 10% for both syntheses with different temperatures and times. Using the amount of seeds higher than 10% results only in a small increase of the yields (max 5% higher). Using 5% of seeds for synthesis resulted in a decrease in the yield approx. about 20%. The hydrothermal treatment was quenched at different times to monitor the rate of crystallization. The crystallinity dependence on the synthesis time

for Al-rich *BEA and mordenite (MOR) at the temperatures of 140 °C and 120 °C is shown in figure 1 (right).

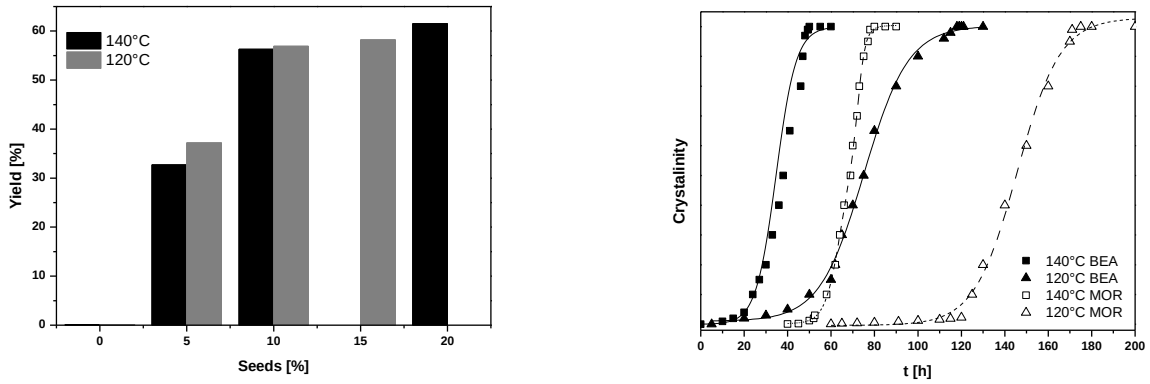

Figure 1. Yield dependence on the amount of seeds (left) and crystallinity dependence on time for Al-rich *BEA and MOR (right) at 140 and 120°C.

4. Conclusions

The influence of conditions of hydrothermal synthesis on the properties of Al-rich *BEA products such as amount of aluminium in the structure and crystal morphology was investigated. Optimization of the source of aluminum and silica used for the preparation of aluminosilicate synthesis gel, temperature and duration of synthesis, and the structure of the zeolite seeds enabled synthesis of the Al-rich *BEA zeolites with close to 100% phase purity with the yields about 80% in 48 hours.

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