

THE STUDY OF FORMATION OF CHABAZITE ZEOLITE USING FAU-TYPE CRYSTALS AS STARTING MATERIAL

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ABSTRACT

CHA-type zeolite is one of the most important zeolites that found application in important industrial processes and exhaust gas treatment. The simplest way to obtain aluminosilicate CHA is to transform zeolite Y under hydrothermal conditions. However, the mechanism of hydrothermal transformation of one zeolite framework type into another is not yet well understood. Herein, we report on the conversion of commercial zeolite Y (FAU) into chabazite, in KOH solution at 100 °C. The reaction course was followed using powder X-ray diffraction, Raman and NMR spectroscopy, scanning and transmission electron microscopy as well as dynamic light scattering technique. The set of experimental data pointed out that the zeolite transformation is a solution mediated process and an amorphous phase is the intermediate between FAU-type and CHA-type zeolite. The results obtained in this study shed a new light in the mechanism of the CHA formation and contribute in the understanding of the processes taking place during zeolite-zeolite conversion.

Keywords: FAU, CHA, intrazeolite conversion, mechanism

INTRODUCTION

Zeolites are crystalline microporous materials used in different areas of industry as well as in everyday life. The most common way of zeolite preparation, especially in industrial scales, is from hydrogel systems treated under hydrothermal conditions [1]. The total yield from hydrogels is pretty high. On the other hand, the "clear solutions" have the concentrations of Si and Al species usually just above the value of zeolite solubility at given conditions so the final yield is generally significantly lower than from the hydrogels [2].

The zeolites are thermodynamically metastable phases and could, under certain conditions, be transformed into another thermodynamically more stable phase. For this reason, the same reaction mixture can yield two or more different products, depending on the reaction conditions, or two or more crystalline phases can be formed at the same time. Also, the transformation of one zeolite to another under hydrothermal conditions is possible. Although in most cases the zeolite structure collapses upon or the symmetry changes, there are many examples where complete metamorphosis occurs. Since the starting chemicals (Si and Al sources) in these systems are different than in conventional hydrothermal synthesis, it is expected that the obtained crystals will have different properties than the crystals prepared in a conventional way. The mechanism of the formation of one type of zeolite from another is still not known, but many authors agree that it is liquid phase-assisted process [3-6]. For example, Subotić *et al.* concluded that the transformation of LTA-type into SOD-type zeolite was solution-mediated

process where the first step is the dissolution of the starting zeolite and the new phase is formed without any intermediates [7].

Herein we present the results of the investigation of the transformation under hydrothermal conditions of zeolite FAU-type to CHA-type at 100 °C. We have particularly focused on the characterization of the solid phase intermediates of the samples taken during the conversion.

EXPERIMENTAL

The chemicals used for chabazite synthesis were zeolite Y (UOP, LZY-64, NH₄⁺ exchanged, Na/Al = 0.17), potassium hydroxide pellets (Sigma Aldrich, 97 wt% KOH) and distilled water. NH₄-zeolite Y was calcined at 450 °C for 4 h in order to obtain the H-form (H-Y). Needed mass of H-FAU was added into the mixture of appropriate amounts of distilled water and 45 wt% KOH solution. The molar oxide composition of the studied system was 0.17 Na₂O:2 K₂O:Al₂O₃:5.18 SiO₂:224 H₂O. After agitation, prepared reaction mixture was divided into polypropylene bottles and put into convection oven preheated at 100 °C. The PP bottles were taken out at certain reaction times and immediately cooled to room temperature in order to stop the reaction. The solid phase of the samples was separated from the liquid phase by filtration over the 220 nm pore filter membrane and washed by distilled water until the pH of the filtrate was below 9. Washed solid phases were dried at 40 °C in a convention oven.

The qualitative and quantitative phase composition of the samples was determined from X-ray diffraction patterns of the solid phases measured by PANalytical X'pert PRO MPD diffractometer using Cu-K α monochromatized radiation. The samples were scanned in the range of Bragg's angles $2\theta = 5-50^\circ$, step size 0.0167° , time per step 99.68 s. Raman spectra of the samples were measured using Jobin Yvon Labram 300 spectrometer equipped with a confocal microscope, the objective with the magnification 100 \times . The measurements were done using a He-Ne laser having the wavelength of 632.8 nm. The spectra were taken for 60 s and accumulated for 5 times. Transmission electron microscope images were taken by JEOL JEM-2010 HR TEM microscope equipped with LaB₆ filament at the accelerating voltage of 200 kV. EDS measurements were performed using Princeton Gamma Tech instrument. Scanning electron microscope used was Mira-Tescan working at the accelerating voltage of 30 kV. ²⁹Si MAS NMR spectra were recorded at 79.5 MHz on a Bruker Avance III (9.4 T) spectrometer using 4 mm-OD zirconia rotors and a spinning frequency of 12 kHz. Single pulse excitation (30° flip angle) was used with a recycling delay of 30 s. Tetramethylsilane (TMS) was used as chemical shift reference.

RESULTS AND DISCUSSION

X-ray diffraction patterns of solid phases taken during the course of the reaction are shown in Figure 1 (left). The starting sample is pure FAU zeolite, while the sample taken after 24 h of hydrothermal treatment has the structure of CHA framework type. The samples taken in period between are mixtures of these two zeolites. The XRD patterns were used to calculate the amount of the formed CHA in each of the samples as represented in Figure 1 (right). According to the crystallization curve, the solid phase contains solely CHA after approximately 22 h, indicating the completion of the conversion.

Raman spectrum of the H-FAU material (Figure 2, left) exhibits one strong band at 498 cm⁻¹ assigned to the vibrations of the 4-membered rings. A shoulder at lower frequency, 483 cm⁻¹, also corresponds to the 4MRs. Two other bands that can be observed at 356 and 303 cm⁻¹ are due to the vibrations of 6MRs. The sample taken after 3 h of hydrothermal treatment of H-Y at

100 °C, shows small broadening of the band at 483 cm⁻¹. Gradually, this band shifts to 480 cm⁻¹, which is the main peak in Raman spectra of CHA. It is associated with 4MR vibrations in CHA framework. As the reaction proceeds and larger amount of CHA is formed this band becomes dominant while the main FAU band completely disappears after 13.5 h of hydrothermal treatment. Both of the applied methods, XRD (Figure 1) and Raman (Figure 2), indicate solely the presence of only FAU and CHA materials in the solid phase.

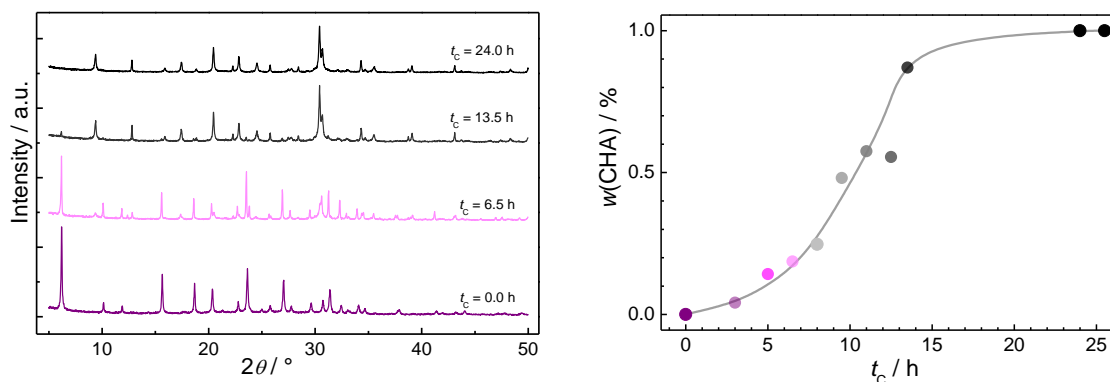


Figure 1. X-ray diffraction patterns of solid phases of the samples taken during the CHA synthesis (left) and the weight fraction of CHA present in the system as a function of reaction time (right).

There are four different resonances in the ²⁹Si MAS NMR spectrum (-106, -100, -95 and -89 ppm) of the employed H-FAU material (Figure 2, right). On the other hand, crystalline CHA obtained after 24 h of hydrothermal treatment shows five resonances centered at around -109, -104, -99, -93 and -89 ppm. Sample taken after just 2 h of reaction clearly shows the presence of Si in the environment characteristic of CHA material.

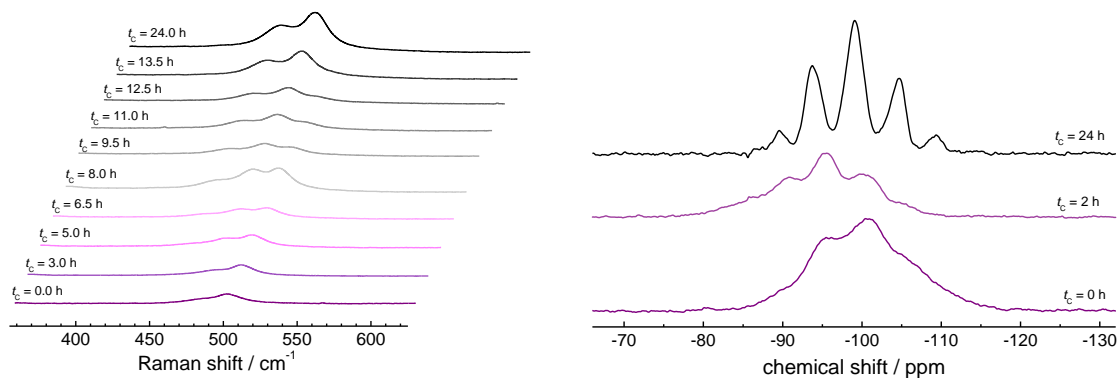


Figure 2. Raman spectra of the samples taken during the transformation (left) and ²⁹Si MAS NMR spectra of selected samples (right).

SEM images (Figure 3) of the starting zeolite show the typical of FAU-type crystals octahedral morphology. In the beginning of the reaction FAU-type crystals can still be observed, but they contain holes due to the dissolution process. First CHA crystals that are significantly smaller in size can be seen after 3 h treatment. At the end of the process only smaller particles building complex aggregates were observed. The most typical morphology of aggregates is spherical with a belt of particles passing through the "equator".

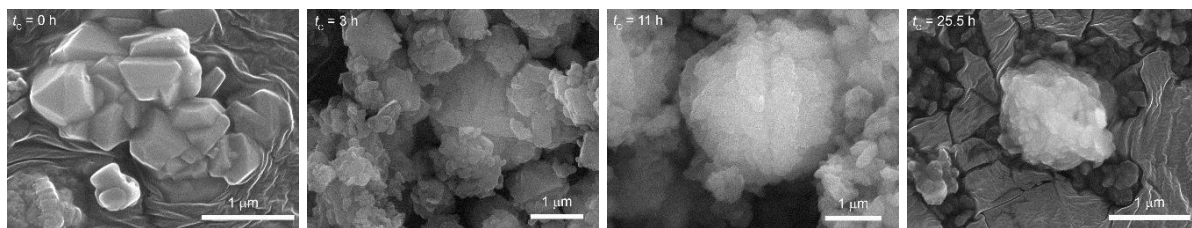


Figure 3. SEM images of the samples taken during the CHA synthesis.

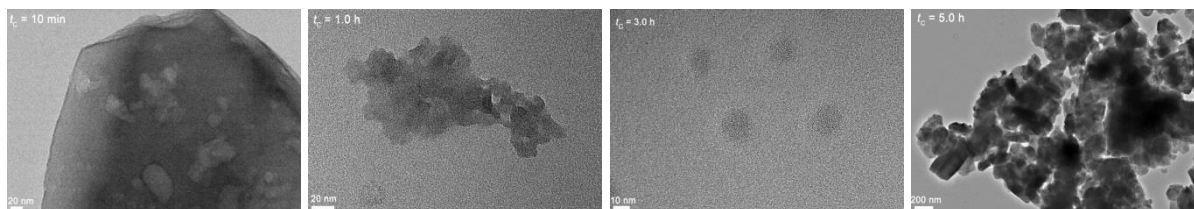


Figure 4. TEM images of the samples taken during the hydrothermal treatment of the studied system.

The presence of amorphous particles is observed after only 1 h of the crystallization. According to the TEM images, the amorphous phase is abundant in the first three hours of the hydrothermal treatment (Figure 4).

CONCLUSION

The conversion of FAU zeolite to fully crystalline CHA in studied conditions is completed after 24 h. Prepared CHA crystals are much smaller than the initial FAU ones. They build up complex aggregates of spherical morphology.

In the first three hours the amorphous phase was detected by TEM. It is worth noting that this is the first report of the presence of amorphous phase during FAU-CHA conversion. On the grounds of presented data, we propose that the mechanism of the process of FAU transformation includes three stages: i) dissolution of FAU; ii) gel formation; and iii) nucleation and growth of CHA from the gel phase.

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