

THE PRESENCE OF CITRIC ACID IN SYNTHESIS OF SOME ZEOLITES

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ABSTRACT

Many transition metal cations (e.g., Cu, Fe, Co, Ni, etc.) are widely used as catalysts for different reactions. Often they are placed within zeolites (as inert carrier) and many preparation pathways have been tested in order to obtain stable catalyst and to prevent metal leaching from the catalyst. The fixation of the metal cations, during hydrothermal synthesis of zeolite catalyst may be a basis for solution of both problems.

Use of the transition metal and complexation agents to introduce them to the zeolite during synthesis is one of the preparation methods. Here, we have used citric acid as complexation agent for Zn²⁺ ions in preparation of some zeolite types.

Keywords: zeolite synthesis, citric acid, Zn ions, sodalite, analcime.

INTRODUCTION

A stable metal ion – organic complexes are very important in biological systems, e.g. human plasma. The citric acid, C₆H₈O₇, can form complex species in a wide range of pH values. In order to enhance its catalytic activity, it has been used as complexing/directing agent in the process of some zeolites synthesis (ZY), via changing the crystals surface acid properties [1, 2]. The citrate anion, as a mineralizer (complexation agent for zinc), in the synthesis of zincosilicate having mordenite framework, was also reported [3]. Smaller amounts of this tricarboxylic acid (as an additive) present in the reaction mixture, promotes elongated form of silicalite crystals over particles with usual (1:1) aspect ratio [4].

The transition metal cations within zeolites (e.g., Cu, Fe, Co, Ni in zeolite Y and ZSM-5), are widely used as catalysts for different reactions [5], and many preparation procedures have been tested in order to prevent metal leaching from the catalyst to the reaction system [6]. Metal ion fixation via incorporation into the zeolite framework can be the solution of this problem. Recently, M. Kato and coworkers have synthesized mordenite and analcime incorporating cobalt atoms into their framework [7].

In this paper, we describe our intention to synthesize one of high-silica zeolites in the presence of citric acid and Zn²⁺ ions.

EXPERIMENTAL

The starting hydrogel was prepared by mixing aluminate and silicate components. Zinc(II) nitrate and citric acid were dissolved separately and added to the Na-aluminate solution forming Al component. Si component is solution of NaOH and Na-metasilicate. Various compositions were used for starting solutions: $x \text{ Na}_2\text{O} \times y \text{ ZnO} \times \text{Al}_2\text{O}_3 \times z \text{ SiO}_2 \times 1900 \text{ H}_2\text{O} \times y \text{ CA}$, where CA is the citric acid, $x=60-80$, $y=0-3$, and $z=4-60$.

After homogenization (magnetic stirrer), the solutions were transferred into Teflon-lined autoclaves, sealed and heated for 100-180 hours at 120 °C in a convection oven. The solid phase was separated by centrifugation, washed in demineralized water, dried at 105 °C and characterized by: powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), optical and scanning electron microscopy (OM, SEM), and energy dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

The starting reaction mixture was mostly transparent solution, without precipitate. After at least 100 h of hydrothermal treatment, at 120 °C under static conditions, appearance of the solid phase was observed. Systematic research of various starting solution compositions showed that the most of the systems produce solid phase which consist of mixture of sodalite, analcime and unknown component (also some other zeolite types, but in small quantity). Examples which illustrate characterization of multi-phase and pure single-phase (by XRD) systems (zeolite crystals) are shown in Figs. 1-4, on two typical representatives: S1 (sodalite and analcime) and S2 (sodalite). Even small changes of the chemical composition (Al, citric acid) of the starting solution have large impact to the phase composition of the final product (Table 1).

Table 1. Chemical (as molar oxide) and phase (determined by XRD) composition of the systems, after crystallization at 120 °C.

System	Na ₂ O	Al ₂ O ₃	SiO ₂	ZnO	H ₂ O	Cit ₂ O	Phase (XRD)
S1	1.167	0.050	1	0.033	31.667	0.033	SOD + ANA
S2	1.333	0.017	1	0.050	31.667	0.050	SOD
S3	1.167	0.017	1	0.017	31.667	0.017	CAN
S4	1.167	0.017	1	0.033	31.667	0.033	SOD + GIS

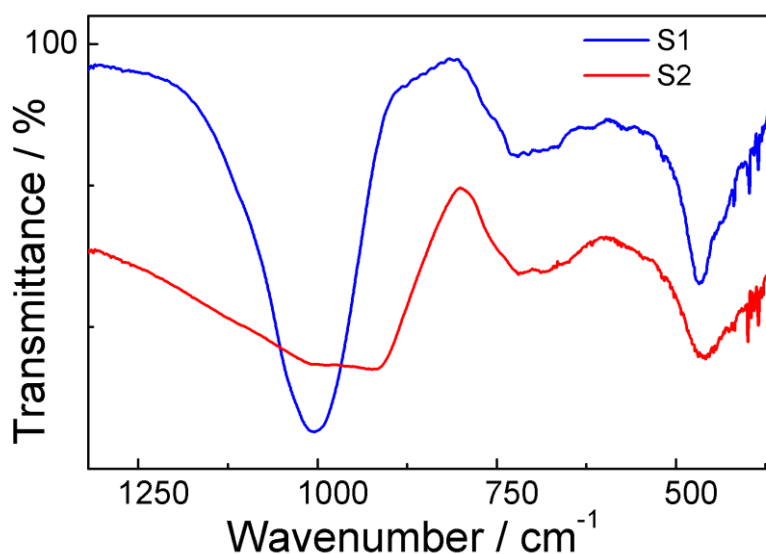


Figure 1. FTIR spectra of the final products, synthesized from System 1 and System 2.

FTIR spectra are similar and have the same peaks in both systems (Fig. 1). The only surprising difference is narrower peak around 1000 cm⁻¹ (assigned to the internal and external tetrahedra asymmetric stretching mode) [8,9] which is shifted towards higher wavenumbers in the S1 (mixture of sodalite and analcime).

XRD patterns of S1 show that analcime and sodalite are present in similar quantity, while S2 consists of sodalite crystals only (Fig. 2). Lower content of Al in the S4 than in S1, results in appearance of the new zeolite type (GIS instead of ANA) together with sodalite.

Decreasing content of the citric acid (also Zn²⁺ ions) in S3 gives only cancrinite crystals as final product (Table 1.).

The solid phase obtained from System 1, that consists of relatively large monocystals of the analcime (ca 30 µm) and relatively small sodalite clusters (ca 1 µm), is shown in SEM

photographs (Fig 3). Monocrystals of the analcime were formed by polycentric growth of the all crystal planes (rough surface of sharp edges), while sodalite clusters are made of smaller intergrown crystals (ca 100 nm) having smooth surface.

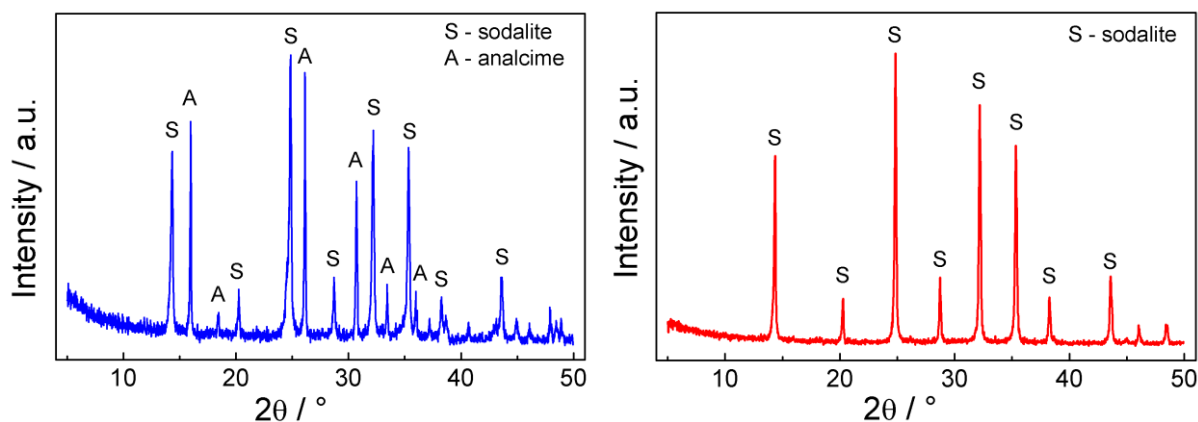


Figure 2. Powder X-ray diffraction pattern of the final products, synthesized at 120 °C, from System 1 (left) and System 2 (right).

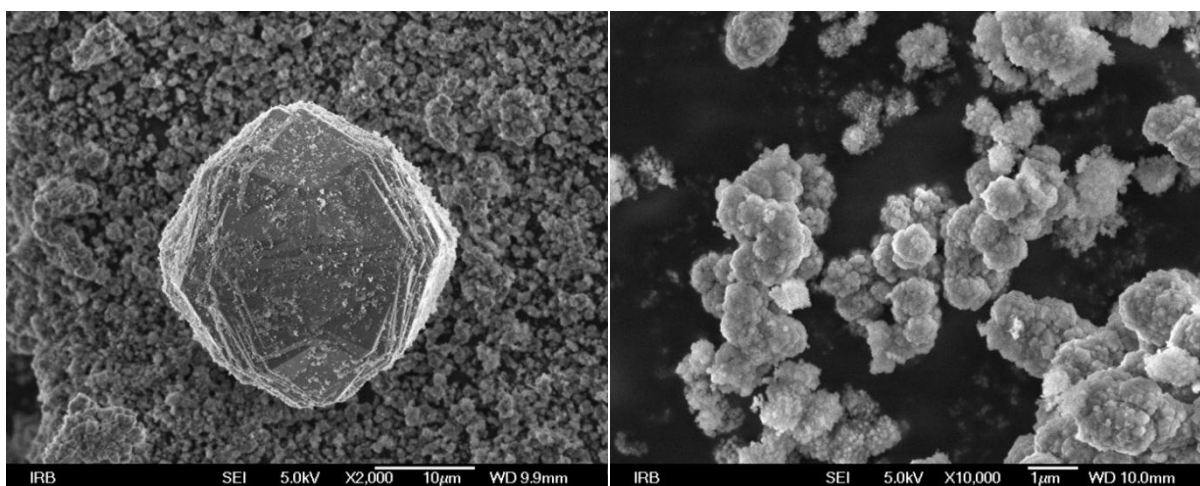


Figure 3. SEM images of the crystals, synthesized from System 1: analcime monocrystal (left) and sodalite clusters of intergrown crystals (right).

In spite of the fact that XRD pattern of S2 (Fig. 2 right) shows pure sodalite phase, presence of the analcime crystals (ca 15 μm) within bulk of sodalite clusters (3-6 μm) of many intergrown crystals (0.2-1 μm) was observed at SEM images (Fig. 4 left).

Due to the same crystallization time (ca 160 h) and fact that primary sodalite crystals in S2 are notably (~ 5 times) larger than in S1 (consecutively clusters are also larger), it is evident that crystal growth rate in the S2 is significantly higher.

Usually, Si/Al ratio is 1 in sodalite and 2 in analcime crystals. According to the EDS results, the Si/Al ratio in analcime is 2.38 and 2.42 in S1 and S2, respectively. At the same time, the Si/Al ratio in sodalite is 2.51 and 3.86 in S1 and S2, respectively. This is in accordance with Al content in the S1 and S2 starting solutions. The presence of Zn atoms (1.08 at. %) was observed in S1 analcime crystals, but it is not clear where they are positioned: incorporated into the framework structure or within voids. Therefore, this study should be continued in order to obtain pure analcime phase with Zn, and use more precise structure determination methods, such as XRD on monocrystal.

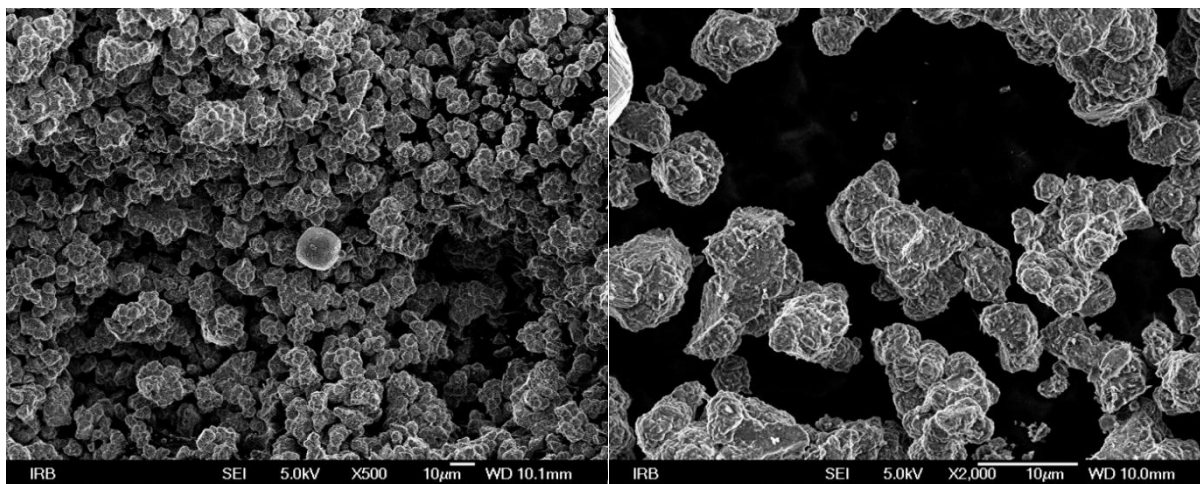


Figure 4. SEM images of the crystals, synthesized from System 2: analcime crystal in middle of photos (left) and sodalite clusters (right).

CONCLUSIONS

The hydrothermal transformation of the alkaline solution of sodium aluminate, sodium silicate, citric acid and zinc(II) nitrate results in mixture of two phases (in S1 are analcime and sodalite). Pure sodalite phase (determined by powder XRD) was obtained from System 2 (lower content of Al, and increased content of Zn and citric acid in starting hydrogel).

EDS analysis showed that the Zn is present only in small quantity (around 1 at. %) in the analcime crystals and even less in the sodalite crystals. Both phases (analcime and sodalite) have unusual Si/Al ratio: around 2.4 for analcime, 2.51 and 3.86 for sodalite in S1 and S2, respectively.

Further investigations of the systems should be towards synthesis of the pure material and its detailed characterization.

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