

INFLUENCE OF ALCALINITY ON SYNTHESIS OF ZEOLITE A

Josip Bronić, Boris Subotić, Durđica Brlek
Ruder Bošković Institute, Bijenička 54, 10000 Zagreb
E-mail: bronic@irb.hr

INTRODUCTION

The mechanism of hydrogel hydrothermal transformation into zeolite is well known¹ and documented in literature. Regardless of system mode (homogeneous, heterogeneous, with or without template), chemical composition, and specification of given physico-chemical parameters (kinetics of gel dissolution, crystal growth, temperature) it is solution-mediated² transformation. OH⁻ ions catalyze transformation of gel into zeolite. Increase of alkalinity of the system can have influence on preference which zeolite type^{3,4} will be obtained. So, beside the rate of crystallization and type of zeolite, pOH also affects particulate properties of the final product (particle size distribution, particle shape).

EXPERIMENTAL

Two different systems were examined: (1) homogeneous (optically clear solution saturated with Na⁺, aluminate, silicate and aluminosilicate species) and (2) heterogeneous (hydrogel – saturated solution with precipitated gel). Hydrothermal transformation of samples in both systems was made by heating of HDPE reactors (flasks) with samples at 80°C. All systems were prepared adding of the basic sodium silicate solution into the basic sodium aluminate solution. Both solutions were prepared by dissolving of appropriate amounts of sodium silicate (Fluka, > 97% Na₂O SiO₂ × 5H₂O) or sodium aluminate (Riedel de Haën, 54% Al₂O₃; 41% Na₂O) with NaOH (Kemika, >98% NaOH) in deionized water. In order to remove impurities from the sodium aluminate solutions, they were centrifuged and only clear supernatant was used for preparation of starting system. After preparation and ageing for 24 h, starting solution of systems 1 (1a, 1b, 1c) and hydrogel of systems 2 (2a, 2b, 2c) were divided among needed number of HDPE reactors, and heated in the air convection oven. Oven was preheated to desired temperature (80°C) and reactors were put in. Prior to putting to HDPE reactors, hydrogels were homogenised with a mechanical disperser. Homogeneous systems were clear during ageing (24 h).

After predefined crystallisation times a certain reactors were taken out the oven, cooled to the room temperature and centrifuged to stop the crystallisation process and separate the solid from the liquid phase. Clear liquid phase was used for determination the concentrations of aluminium (C_{Al}) and silicon (C_{Si}) in solution by AAS. The solid phase of samples was washed, dried at 105°C overnight, and used for phase analysis and measuring of particle size distribution and particles shape.

The powder X-ray diffraction (XRD) patterns of samples were collected on Phillips PW 1820 powder diffractometer using CuK_α radiation in range $2\theta = 5-50^\circ$. Particle size distribution curves of solid samples were determined with Malvern Mastersizer 2000 laser light-scattering particle size analyzer. Concentrations of aluminium and silicon in the solutions were measured by PerkinElmer AAnalyst 200 atomic absorption spectrometer, samples micrographs were made on Philips 515 scanning electron microscope.

RESULTS AND DISCUSSION

The chemical compositions of clear (homogeneous) and heterogeneous (hydrogels) systems are shown in Table 1. In system 1 (1a, 1b, 1c), concentration of Al represents maximal value which gives clear solution at given concentration of NaOH. Mixing of silicate and aluminate solutions of higher Al and Si concentrations (2a, 2b, 2c) precipitation of hydrogels was inevitable.

Table 1. Characteristical chemical composition of starting clear solutions (systems 1a, 1b, 1c) and hydrogels (systems 2a, 2b, 2c) and their phase composition at the end of crystallization made at 80°C.

System	Na ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O	Phase
1a	6.00	0.10	1.00	120.00	ZA + ZX
1b	10.00	0.30	1.00	120.00	ZA
1c	15.00	0.35	1.00	120.00	SOD
2a	5.00	0.90	1.00	83.33	ZA
2b	7.00	0.90	1.00	83.33	ZA+SOD
2c	9.00	0.90	1.00	83.33	SOD

Increasing alkalinity of the system causes that the final product of the crystallization changes from mixture of ZA+ZX via pure ZA to hydroxy sodalite (SOS) in system 1, and from pure ZA via ZA-SOD mixture to the pure sodalite (Fig. 1, Table 1). Increasing the amount of Na₂O in the system 1 over 18, does not give any solid (zeolitic) product, even at prolonged time of crystallization. Explanation for this finding is that solubility in the system is high enough to dissolve much larger amount of zeolite than the system (1c) can produce (even if we suppose that all aluminate and silicate transforms into zeolite). At the same time, increase of the amount of Na₂O in system 2 (up to 15 Na₂O), produce only sodalite at the end of crystallization.

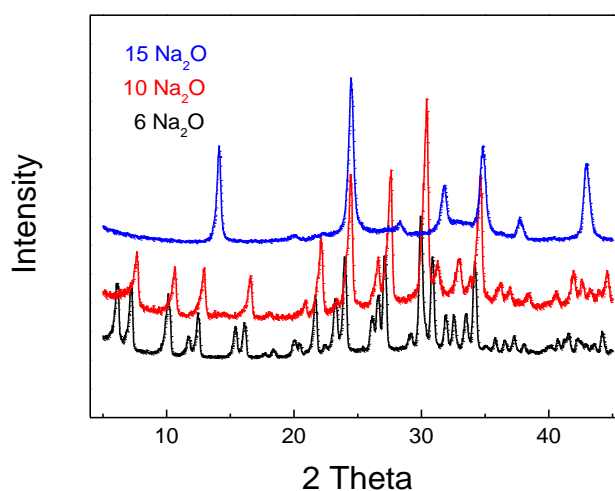


Figure 1. XRD patterns of samples obtained at end of crystallization of homogeneous system. Starting compositions of samples 1a, 1b and 1c, containing 6, 10, and 15 Na₂O, respectively.

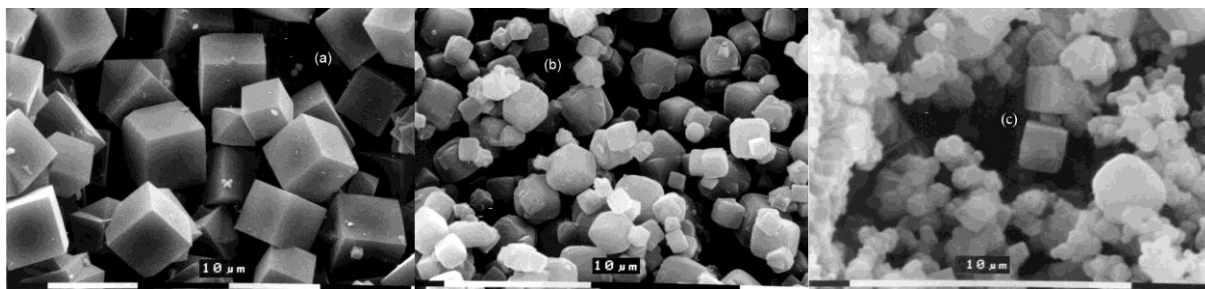


Figure 2. Scanning electron micrographs of the product at the end of crystallization: (a) sample 1a - zeolite A with some crystals of ZX (bipyramide), (b) sample 2a – pure zeolite A with rounded edges, and (c) sample 2b - mixture of zeolite A and sodalite.

Micrographs of typical zeolitic products from series 1 and 2 are shown at Fig. 2. Well formed cubes of zeolite A and bipyramides of ZX are shown at Fig. 2a, pure ZA with "rounded" edges (Fig. 2b) and mixture of ZA and SOD (Fig. 2c). Change in shape of the crystals is caused by changes in NaOH concentration as well as in concentration of Al and Si species in the system. On the contrary, Mintova⁵ at al., found that nanocrystals of ZA can be crystallized at room temperature, using the homogeneous system with organic template.

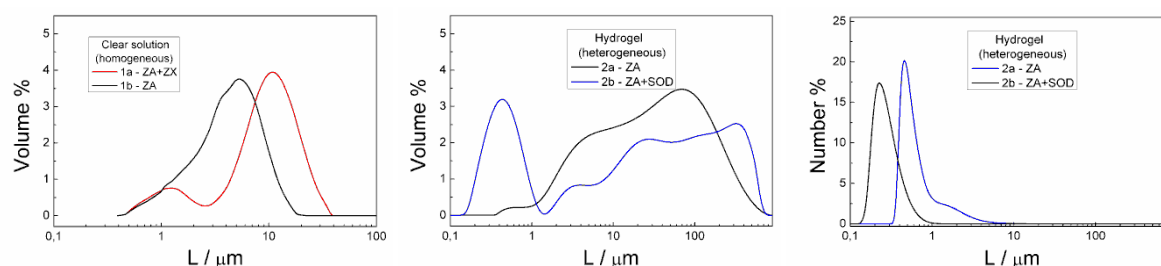


Figure 3. Particle size distribution by volume % of samples 1a and 1b (left), 2a and 2b (middle) and by number % for samples 2a and 2b (right).

Crystals size distributions of the final product by volume (Fig. 3, left side) show that increase of Na₂O content in series 1, produces more nuclei - average crystal volume size drops from 11 to 5.5 μm at the end of crystallization. Bimodal distribution of sample 1a can be assigned to the presence of ZX crystals.

Similar behaviour was observed in heterogeneous system. But it is evident, from the particle size distribution by volume (Fig. 3, middle), that large amount of gel is still present in system (particles over 20 μm). D_(0.50) value drops from 34.3 to 26.9 in distribution by vol.% for samples 2a and 2b, respectively. In spite of large amount of gel, the particle size distribution by number % show much narrow distribution and decrease of the D_(0.50) value from 0.593 (2a – ZA) to the 0.278 (2b – ZA+SOD, see Fig. 3, right side).

CONCLUSIONS

Increase of Na₂O content in homogeneous (initially clear) system causes crystallization of sodalite instead of ZA.

The same effect was observed in heterogeneous (with hydrogel) system, but at lower content of Na₂O.

Increase of Na₂O content in both systems also causes change in shape (crystals are more rounded) and increase in number of crystals (average size by volume and by number is lower).

ACKNOWLEDGEMENT

This work was done with financial support of the Croatian Ministry of Science, Education and Sports, within the Project 0982904-2953.

REFERENCES

- [1] B. Subotić, J. Bronić, Chapter 5 "*Theoretical and Practical Aspects of Zeolite Crystal Growth*" in: "*Handbook of Zeolite Science and Technology*", S.M. Auerbach, K.A. Carrado, and P.K. Dutta (Eds.), Marcel Dekker Inc., New York – Basel, 2003, 129-203.
- [2] B. Subotić, J. Bronić, T. Antičić, Chapter 8 "*Theoretical and Practical Aspects of Zeolite Nucleation*" in "*Ordered Porous Solids: Recent Advances and Prospects*", V. Valtchev, S. Mintova (Eds.) Elsevier, Amsterdam, 2008, in press.
- [3] J. Bronić and B. Subotić, M. Škreblin, *Microporous Mesoporous Mater.*, 1999, **28**, 73-82.
- [4] I. Krznarić, T. Antičić, J. Bronić, B. Subotić, R.W. Thompson, *Croatica Chemica Acta*, 2003, **76** 7-17.
- [5] S.Mintova, N.H.Olson, V.Valtchev, T.Bein, *Science*, 1999, **283**, 958-960

SINTEZA KRISTALA ZEOLITA A IZ HIDROGELOVA STARENJIH NA SOBNOJ TEMPERATURI

Josip Bronić, Boris Subotić, Durđica Brlek
Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb
E-mail: bronic@irb.hr

SAŽETAK

Mnogi fizičko-kemijski parametri utječu na procese kristalizacije zeolita kao i na njihova čestična svojstva. U ovom radu je studiran utjecaj količine Na₂O u homogenom (bistra otopina) i heterogenom (hidrogel) sustavu. Povećanjem količine Na₂O praćena su fazna i čestična svojstva produkta na kraju hidrotermalne transformacije. Analize dobivenih kristala vršene su pomoću difrakcije rendgenskih zraka na prašku, elektronske pretražne mikroskopije i dinamičkog raspršenja laserskog svjetla. Zaključeno je da se povećanjem količine Na₂O u homogenom sustavu mijenja tip nastalog zeolita od smjese ZA+ZX, preko čistog ZA do sodalita. Slično se ponaša u sustav s gelom samo su količine Na₂O kod koji dolazi do promjene - niže. Povećanjem količine Na₂O mijenja se oblik čestica, koje postaju zaobljenijih rubova, dok se njihova prosječna veličina smanjuje, što znači da u sustavu nastaje više nukleusa (kristala).

Ključne riječi: bistra (homogena) otopina, hidrogel, hidrotermalna sinteza, čestična svojstva