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# The role of alcohols and diols as co-solvents in fabrication of TON zeolite

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ABSTRACT

Numerous industrial catalysts and sorbents require better control of crystal size and morphology of the zeolites. Here, we report a method to selectively control the crystal size and morphology of ZSM-22 by using alcohols and diols as co-solvents in water–alcohol system. The results demonstrated the role of co-solvent in controlling the crystallization growth of ZSM-22 zeolite. Addition of co-solvent suppressed nucleation of unwanted cristobalite phase in crystallization and growth of ZSM-22 zeolite. We found that alcohols and diols as cheap co-solvent are effective in tuning and controlling crystal size, aspect ratio and co-crystalization phases of zeolite ZSM-22.

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## Introduction

Zeolites are crystalline aluminosilicate materials with numerous applications in catalytic processes, ion-exchange stages, separations, photonic and biomedical applications.

The industrial applications of zeolites are highly dependent on their framework structures, pore sizes, crystals sizes and morphologies. Therefore, changing these zeolite parameters results in endless applications of zeolites. Since the framework structure and pore size are unchanged for the same zeolite, tuning the zeolite crystal size and morphology is attracting more attention recently as an effective way of tuning properties of zeolites. Several techniques have been used to control size and morphology of zeolite crystals, for example an adjusting synthesis parameters such as aging time, the contents of zeolite synthesis mixture, crystallization temperature, crystallization time and heating mode. Alcohols and diols have been reported as a promising alternative to control zeolites crystal size and morphology.

The application of alcohols and diols in zeolite synthesis has been reported for many zeolites, such as zeolite Y (FAU), silicalite-1, ZSM-5 (MFI), sodalite (SOD) and zeolite L (LTL) [1–4].

Alcohols and diols have been incorporated in zeolite synthesis mixture for the purposes of reducing zeolite crystal size, tuning crystal morphology, using less amount of organic structure directing agent (OSDA) [5] and to inhibit or stimulate co-crystallization [4]. Table 1 shows some co-solvents that reported in the synthesis of zeolites MTT, TON, LTL and SOD.

Nanosized SOD crystals with size less than 100 nm were produced by using ethanol as a co-solvent, while using ethanol–urea mixture further reduced the SOD crystal size [4]. Addition of acetone to the synthesis of SOD zeolite results in SOD zeolite with crystal size of 200 nm and impurities of zeolite A [4]. As reported by Gaona-Gómez and Cheng [6], the aspect ratio (morphology) of zeolite LTL crystals reduced effectively by adding ethanol. Bibby et al. [7] reported that ethylene glycol and propanol were used successfully in synthesizing of aluminosilicate-sodalite and all-silica sodalite.

Recently, a comprehensive study on using alcohols and diols as co-solvents for zeolite L has been reported by Lupulescu et al. [8]. They conclude that depending on the co-solvent properties (such as hydrophobicity) and concentration, zeolite L crystal growth and morphology can be tuned and controlled selectively [8].

ZSM-22 is a medium-pore zeolite with TON framework. The pore structure of ZSM-22 is linear unidirectional (non-interconnecting) with 10-membered ring openings and effective pore size of 0.46–0.57 nm. ZSM-22 zeolite has promising applications in many shape selective reactions such as hydroisomerization [9–12], hydrocracking [13,14], dewaxing of the crude oil [15], naphtha cracking [16] and methanol-to-olefins [17,18].

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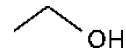
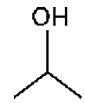
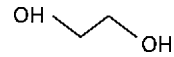
**Table 1**
Some co-solvents reported in the synthesis of one-dimensional pore zeolites (MTT, TON, and LTL) and SOD.

| Zeolite | Framework | Tested co-solvent | Reference |
|---|---|---|---|
| ZSM-22 | TON | Ethylene glycol | [6,7] |
| ZSM-23 | MTT | Ethanol, n-propanol Iso-propanol 1,2-ethanediol Mixture of (0.9 ethanol/0.1 methanol) | [6,7] |
| Sodalite | SOD | Ethanol, urea, acetone | [8,11] |
| Zeolite L | LTL | Ethylene glycol, diethylene glycol, triethylene glycol | [10] |

**Table 2**
Alcohols and diols used as co-solvents in this work.

| Co-solvent | Formula | Skeletal formula |
|---|---|---|
| Ethanol | $C_2H_6O$ |  |
| n-Propanol | $C_3H_8O$ | |
| i-Propanol | $C_3H_8O$ |  |
| Ethylene glycol | $C_2H_6O_2$ |  |

In this work, the effects of different types of alcohols and diols have been investigated in the ZSM-22 zeolite synthesis. The ZSM-22 zeolite purity, size and morphology were observed and characterized to give a brief insight into the effect of alcohols and diols as crystal growth modifiers and co-crystallization inhibitors.

## Experimental

### *Zeolites synthesis*

The ZSM-22 zeolite starting gel solution with Si/Al ratio of 46 was prepared according to procedure reported earlier by Ernst et al. [19].

The gel solution was prepared by adding silica source solution (called "solution B") to aluminum source solution (called "solution A"). Then, solution A was prepared by addition 0.88 g of aluminum sulfate octadecahydrate (99%, Fisher Scientific) before adding 4.18 g of 1,6-diaminohexane (DAH) (99.9%, Acros Organics) as organic structure directing agent (OSDA) to an alkaline solution made up of 1.95 g potassium hydroxide (99%, Sigma–Aldrich) and 44.25 g deionized water produced by ultrapure water purification system (Thermo Scientific Barnstead GenPure), the formed solution was stirred continuously at 200 rpm. Solution B was prepared by mixing 18 g silica colloidal solution (Nissan Chemical, colloidal silica, Snowtex ST-40) with 31 g deionized water. A homogeneous milky gel was formed by adding solution B to solution A.

The initial molar composition of the prepared gel was: 1 $Al_2O_3$:91.4 $SiO_2$:26.5 $K_2O$:27.4 DAH:3202·$H_2O$. The formed gel has been left under continuous stirring at 250 rpm for at least 5 min before the addition of the co-solvent as weight percentage of prepared solution (0, 2.5, 5, 7.5, 10, 20, 30 and 40 wt.%).

Samples were labeled as (T-cosolvent-wt.%), where T stands for TON, co-solvent for the related co-solvent abbreviation and wt.% for the weight percentage of the added co-solvent. Abbreviations used for co-solvent were EtOH for ethanol, PROH for 1-propanol, IPA for 2-propanol, EG for ethylene-glycol.

After the addition of co-solvent, the solution was left to age for 2 h, the gel, then was transferred to a PTFE-lined autoclave reactor. The synthesis was performed by using a rotated autoclave (50 rpm) at 180 °C for 48 h. At the end of each experiment, the sample was quenched until it reached the room temperature and washed repeatedly with deionized water by using a centrifuge (Thermo Scientific) until the pH reached ca. 7. The sample was dried for 12 h at 120 °C, then the sample was calcined at 550 °C for 12 h under a flow of air with the heating rate of 1 K/min.

### *Characterization*

The calcined zeolite was characterized using XRD and confirmed by SEM. ZSM-22 has a specific X-ray diffraction pattern which enabled us to identify the phase in all samples by using X-ray diffractometer. The crystallinity of the ZSM-22 zeolite was identified using X- ray diffraction using Rigaku X-ray diffractometer with a step size of 0.03°, with Bragg–Brentano geometry, position sensitive detector and CuK α radiation (λ = 1.5406 Å). XRD data were

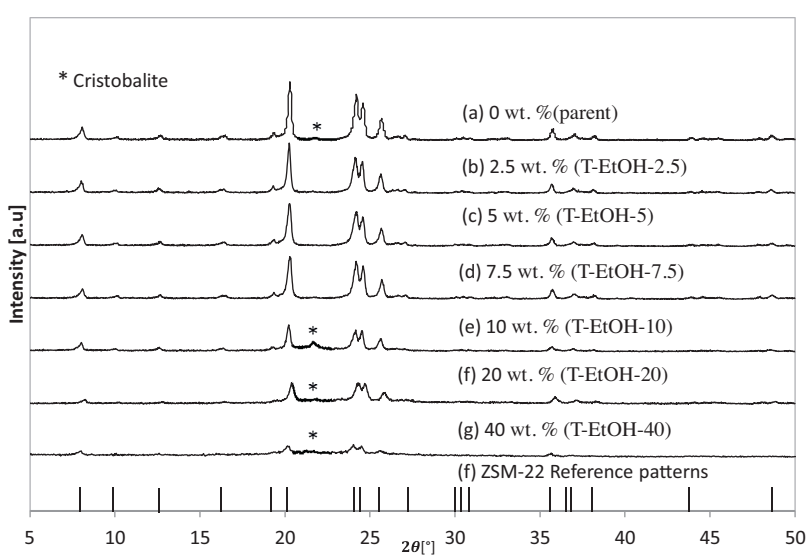



**Fig. 1.** XRD patterns of ZSM-22 synthesized with different concentration of ethanol (wt.%): (a) 0 wt.% (parent), (b) 2.5 wt.% (T-EtOH-2.5), (c) 5 wt.% (T-EtOH-5), (d) 7.5 wt.% (T-EtOH-7.5), (e) 10 wt.% (T-EtOH-10), (f) 20 wt.% (T-EtOH-20), (g) 40 wt.% (T-EtOH-40).

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