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Microwave-assisted solvothermal synthesis of ZSM-22 zeolite with controllable crystal lengths

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ABSTRACT

ZSM-22 (TON) zeolite crystal morphology was successfully controlled using a microwave-assisted solvothermal fabrication method. Different co-solvents, including ethanol, 2-propanol, glycerol, and ethylene glycol, were also applied in the synthesis mixture. The effects of various parameters such as the aging time, the type and amount of co-solvent on the ZSM-22 crystal aspect ratio were investigated. When employing this microwave irradiation synthesis, a long aging time was crucial to obtain smaller and more uniform crystal sizes. The addition of co-solvent resulted in elongated ZSM-22 crystals, regardless of the actual co-solvent used, although ZSM-22 zeolite crystallinity was sensitive to the co-solvent type. In general, the use of a co-solvent stimulated the appearance of ZSM-5 zeolite as an impurity and the amount of this impurity was proportional to the concentration of co-solvent in the synthesis mixture.

Introduction

ZSM-22 zeolite is a medium pore size zeolite with a high silica to alumina ratio. The pore structure in the ZSM-22 zeolite crystal is linear unidirectional (non-interconnecting) with 10-membered ring openings having an effective pore size of 0.46 nm × 0.57 nm, a value that is smaller than the pore sizes of ZSM-11 and ZSM-5, (Kokotailo, Chu, Lawton, & Meier, 1978; Kokotailo, Schlenker, Dwyer, & Valyocsik, 1985; Valyocsik, 1984). Because of its high degree of shape selectivity, this material has significant potential with regard to many shape selective reactions, such as the methanol-to-olefins process (Jamil et al., 2014b).

The fabrication of zeolitic materials through the use of microwave-assisted hydrothermal synthesis (MAHyS) has been reported elsewhere (Chen, Yan, Cao, Yu, & Xu, 2009). The high rate of heat transfer rate achieved by imparting radiation to the synthesis solution is an advantage of this process and allows rapid zeolite synthesis (Tompsett, Conner, & Yngvesson, 2006). The application of alcohols and diols in zeolite synthesis has also been reported for many zeolites, such as sodalite (SOD) (Yao, Zhang, & Wang, 2008) and zeolite L (LTL) (Gomez, de Silveira, Doan, & Cheng, 2011), with the aim of reducing the zeolite crystal size and tuning the crystal morphology. As reported by Chen et al. (2007, 2009), the morphology of silicalite-1 crystals has been successfully tailored using microwave-assisted synthesis in the presence of a co-solvent. Changing the morphology of zeolites crystals by using co-solvents in conjunction with microwave irradiation is an interesting approach because it combines the advantage of employing microwaves as an effective heat source and applying a co-solvent to tune the morphology of the resulting crystals.

In the present work, ZSM-22 crystals were synthesized using different types of alcohols. The zeolitic phase, size, and morphology were observed and characterized to provide some insights into the relationship between the type and concentration of the co-solvent and the crystal size and aspect ratio.

Experimental

The ZSM-22 synthesis mixture was prepared by combining silicate and aluminate solutions, as reported in detail in our previous work (Jamil et al., 2014a). The aluminate solution was made by adding 0.9 g aluminum sulfate octadecahydrate (99%, Fisher Scientific, New Jersey, USA) and 4.2 g 1,6-diaminohexane (DAH) (99.9%, Acros Organics, New Jersey, USA), serving as a template, to a solution of 1.9 g KOH (99%, Sigma-Aldrich, St. Louis, USA) in 44.2 g deionized (DI) water. The silicate solution was prepared by adding 18 g of a colloidal silica solution (40 wt% SiO_2, Snowtex-40, ST-40, Nissan Chemicals, Houston, USA) to 31 g DI water. The gel

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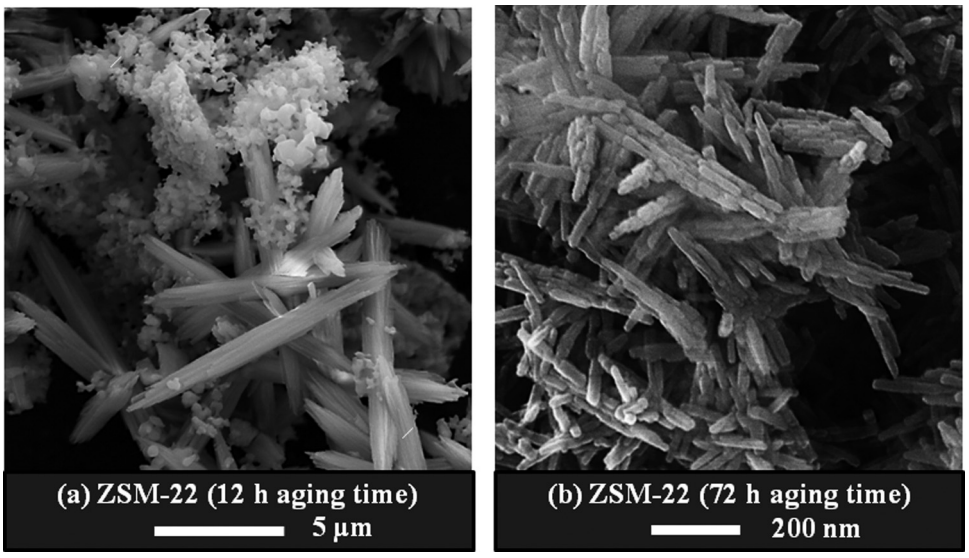

Fig. 1. SEM micrographs of ZSM-22 crystals synthesized with a Si/Al ratio of 46 and aging times of (a) 12 h and (b) 72 h.

solution was obtained by adding the silicate solution to the aluminate solution, followed by heating to 50 °C with continuous stirring at 250 rpm for 5 min before slow addition of the co-solvent with vigorous mixing. Ethanol (EtOH) (ACS reagent, 99.5%, Acros Organics), 2-propanol (IPA, ACS reagent, ≥99.5%, Sigma-Aldrich), glycerol (GLY, ACS reagent, ≥99.5%, Sigma-Aldrich), and ethylene glycol (EG, ReagentPlus®, ≥99%, Sigma-Aldrich) were used as co-solvents in this work. 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:*y* co-solvent, where *y* = 0, 0.25, 1.25, 2.5, or 5. The resulting gel was aged at 50 °C with continuous stirring at 400 rpm for 72 h for most of the experiments.

The subsequent synthesis was performed in a microwave lab station (400 W, MicroSYNTH, Milestone, Italy) at 180 °C for 12 h. The powder thus obtained was centrifuged, dried for 12 h at 120 °C and finally calcined at 550 °C for 12 h under a flow of air, applying a heating rate of 1 °C/min. The calcined zeolites (K-ZSM-22) were transformed to NH_4-ZSM-22 by ion-exchange in a 2 M aqueous ammonium nitrate (NH_4NO_3) solution under microwave irradiation (Lopes, Serralha, Costa, Lemos, & Ribeiro, 1998). In this process, a K-ZSM-22 zeolite sample (2 g) was mixed with 20 mL 2 M aqueous NH_4NO_3, such that the ratio of NH_4NO_3 solution volume to zeolite mass was 20. The temperature of this mixture was raised to 85 °C over 5 min by applying 800 W microwave irradiation and the ion-exchange was performed at this same temperature over 10 min while applying 400 W irradiation power.

The crystallinity of the obtained ZSM-22 was assessed with X-ray diffraction (XRD, MiniFlex II, Rigaku, Japan) using a Rigaku diffractometer with a step size of 0.03°, Bragg–Brentano geometry, a position sensitive detector and Cu *K*α radiation (λ = 1.5406 Å). XRD data were analyzed using the EVA 8.0 software package (Rigaku). The crystal size and morphology of each sample were investigated by scanning electron microscopy (SEM), using an SEM-FIB Tescan Lyra instrument (Czech Republic). In preparation for these observations, the ZSM-22 crystals were suspended in ethanol and a drop of the mixture was spread on a porous carbon film sample cell and allowed to dry. A low acceleration voltage of 15 kV was used during imaging.

Results and discussion

The use of microwaves as a rapid source of crystallization energy was found to be a highly efficient means of producing nano-scale ZSM-22 crystals with a narrow size distribution. During this microwave radiation synthesis, the primary features of the ZSM-22 crystal structure were evidently affected by the aging time, co-solvent type, and co-solvent concentration.

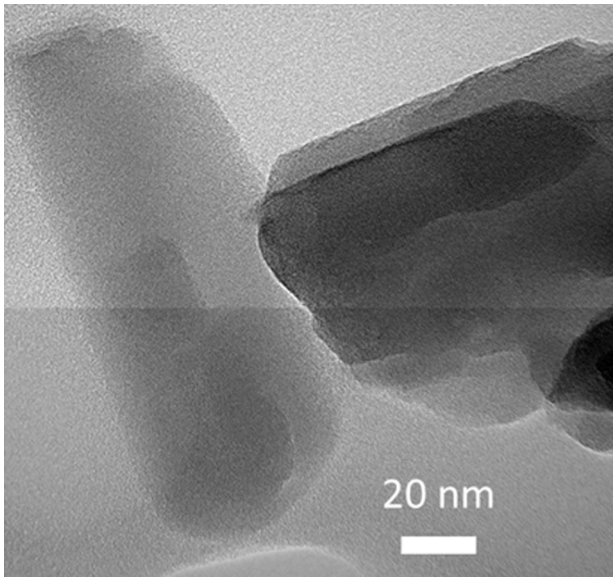

Fig. 2. TEM image of a single crystal of ZSM-22 synthesized under microwave radiation for 12 h with a prolonged aging time of 72 h.

Effect of aging time

To study the effect of aging time on the ZSM-22 crystal size and morphology, the time span was varied from 2 to 84 h. The crystal length and aspect ratio (crystal length/crystal diameter) of the ZSM-22 were found to be significantly affected by the aging time.

The crystal length reached its minimum at an aging span of 72 h. The average length of a single crystal was approximately 100 nm as determined from SEM images and confirmed by TEM (see Figs. 1 and 2). The ZSM-22 crystal length decreased with increasing aging time, similar to earlier reports concerning LTA zeolite (Alfaro, Rodriguez, Valenzuela, & Bosch, 2007), zeolite Y (Ginter, Bell, & Radke, 1992), and MFI (Valtchev, Faust, & Lézervant, 2004). In