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Effect of reaction mixture composition and silica source on size distribution of zeolite X crystals

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ABSTRACT

Zeolite X crystals were synthesized by hydrothermal crystallization from gels with different compositions. The syntheses were performed at 95 °C using different silica sources such as sodium metasilicate anhydrous, sodium metasilicate pentahydrate, silicate solution and Cab-O-Sil. Triethanolamine was used in some syntheses in order to grow large crystals. Zeolite X crystals with diameters in the range of 1–220 μm were obtained, and Cab-O-Sil in concert with triethanolamine yielded the largest crystals.

1. Introduction

Zeolites have been of great interest in a large number of industrial applications and are used widely as catalysts, ion-exchangers, molecular sieves and adsorbents. Zeolites are aluminosilicates with well-defined porous structures, containing channels and cavities [1–3]. Different pore sizes and shapes, and the hydrophilic or hydrophobic properties of zeolites make these materials effective sorbents and hosts for organic or inorganic guest molecules [4]. Faujasite (FAU)-type zeolite X has a considerable potential in adsorption applications due to its large pore size with a diameter 7.4 Å [5–7]. Some applications of zeolite X, include use as water softening additives in detergents, and *p*-xylene separation in petrochemicals by selective adsorption. Faujasites consist of sodalite cages that are linked together by double six-membered rings (D6R) and form the supercages [8].

Zeolites are typically synthesized under hydrothermal conditions from the precursor the silicate and aluminate solutions [9]. Depending on the molar composition, starting materials, reaction temperature, and procedure for preparation of the precursor solutions, different types of zeolites and/or different crystal sizes can be crystallized.

Zeolite crystals with desired crystal-chemical properties may be grown by various means including (i) optimization of the reaction mixture ("gel") composition and gel formation, (ii) decreasing the number of heterogeneous nuclei, (iii) the addition of some organics [10,11]. Charnell [12] first reported that the addition of triethanolamine (TEA) to synthesis gels produces large zeolite A and X crystals. TEA makes a complex with aluminum and chelates it in the reaction medium. This affects the formation of the aluminosilicate gels and nucleation of crystals [13–16].

In this study, we investigate the effects of gel molar composition, silica source and the TEA content in the gel on size distribution of zeolite X crystals. X-ray diffractometer was used for product purity determination. Crystal morphology and size distribution were ascertained by scanning electron microscopy and particle size analysis. Thermal gravimetric analysis was carried out in order to determine the water content of hydrated zeolite X.

2. Materials and methods

2.1. Preparation of zeolite X

The silica precursor solutions were prepared using different silica sources: Cab-O-Sil (Cabot), sodium silicate solution (Sigma-Aldrich), sodium metasilicate, anhydrous (Alfa Aesar), and sodium metasilicate pentahydrate (Alfa Aesar). The sodium aluminate precursor solutions were prepared by dissolving sodium aluminate powder (technical, EM Science) in aqueous solutions of sodium hydroxide (Fisher Scientific) or potassium hydroxide (85%, Acros Organics). Both silica and aluminate

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precursor solutions were filtered through 0.45 μm membrane filter (Pall Corporation). In some cases triethanolamine (TEA ≥ 99%, Sigma) was added to aluminate solution. The silica solutions and TEA-containing sodium aluminate solutions were left at room temperature for a day before mixing the aluminate solutions with the silica solutions in polyethylene (HDPE) bottles. The bottles were then sealed, hand-shaken for a minute, and placed in an oven at 95 °C. After the crystallization was complete, as judged by microscopic examination, the products were repeatedly washed with reversed osmosis water, filtered and dried for 24 h at 60–70 °C.

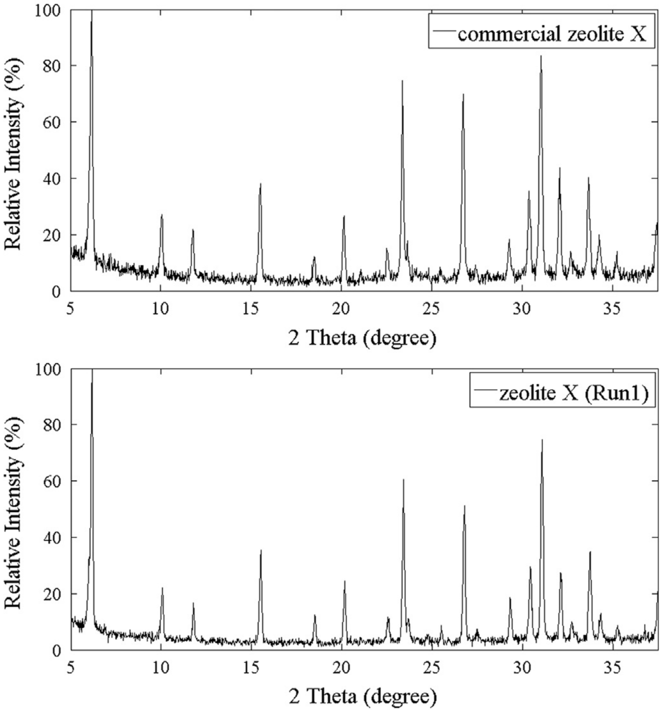

Fig. 1. XRD patterns of commercial zeolite X and typical zeolite X product synthesized with sodium metasilicate anhydrous as the silica source. Molar composition $4.76Na_2O$: $1Al_2O_3$: $3.5SiO_2$: $454H_2O$.

2.2. Characterization

The X-ray powder diffraction (XRD) patterns were collected over the °2θ range using a Bruker D5005 X-ray diffractometer (Cu*K*α radiation, 40 kV, 30 mA). Morphology and size of zeolite crystals were observed by a Hitachi S-4700 scanning electron microscope (SEM). Thermal gravimetric analysis (TGA) was carried out to determine the water content of hydrated zeolite X samples (relative humidity=0.75, room temperature, ≥ 72 h) using a Mettler Toledo TGA/SDTA 851e module. The zeolite X samples were heated up to 600 °C at a rate of 10 K min^{-1} under the nitrogen purge. Particle size distributions were measured using Aerosizer LD.

3. Results and discussion

3.1. XRD results

A typical XRD pattern of zeolite X synthesized and the XRD patterns of commercial zeolite X are given in Fig. 1. The XRD results

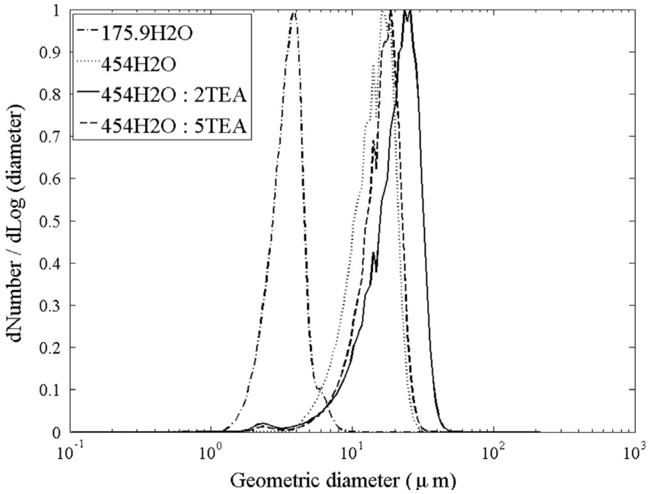

Fig. 3. Particle size distribution of zeolite X samples synthesized using sodium metasilicate anhydrous as the silica source.

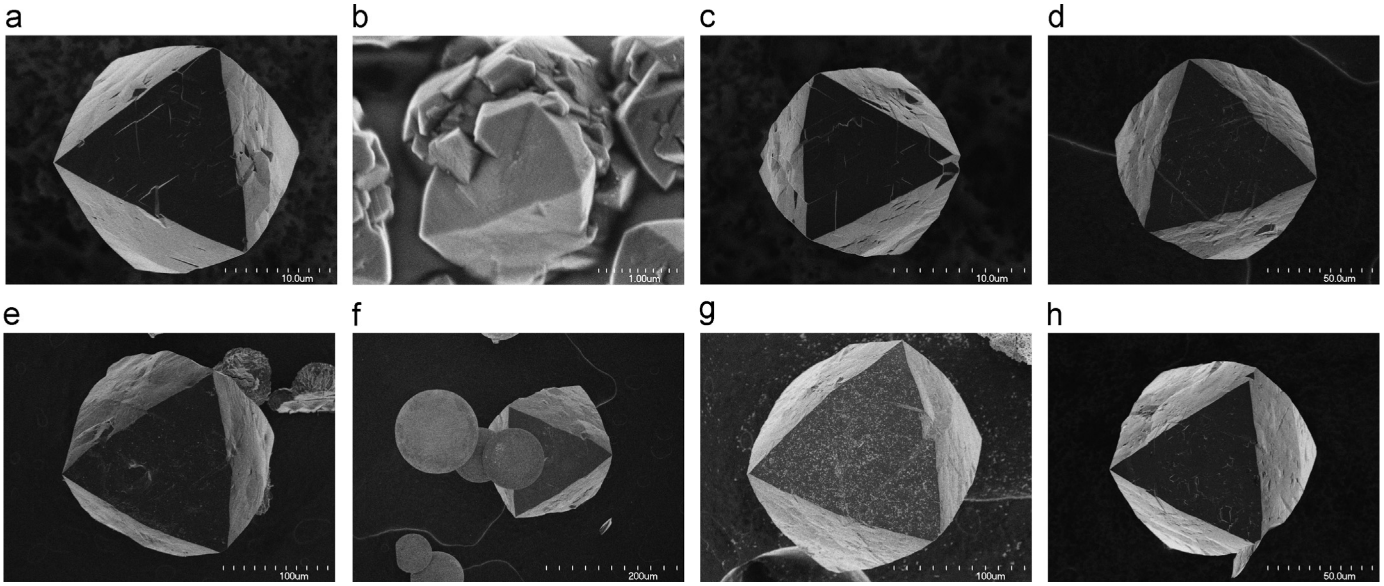

Fig. 2. SEM images of zeolite X: Corresponding runs in Table 2. (a) (Run1); (b) (Run4); (c) (Run8); (d) (Run9); (e) (Run10); (f) (Run11); (h) (Run12); (g) (Run13).