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Zeolite beta mechanisms of nucleation and growth

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ABSTRACT

Zeolite beta has been prepared in dilute ($H_2O/SiO_2 = 80$) and concentrated ($H_2O/SiO_2 = 20$) conditions. The rates of zeolite beta nucleation and growth in dilute colloidal solutions have been characterized using dynamic light scattering and small angle X-ray scattering. By blending TEA^+ and Na^+ in dilute solutions at low Al concentration (Si/Al = 50) it has been determined that the presence of Na^+ decreases the nucleation rate and increases the growth rate (i.e., decreases the colloidal stability of the precursor nanoparticles) because Na^+ competes with TEA^+ for surface adsorption sites and occlusion into the precursor particles. Using more concentrated synthesis solutions the role of ion pairs (e.g., $[[\equiv SiO]^- TEA^+]$, $[[AlO_2]^- TEA^+]$, and $[[AlO_2]^- Na^+]$) in the precursor particles and the zeolite beta product was investigated in detail. Thermal gravimetric analyses have helped determine relation between synthesis conditions and the ion pairs formed in the zeolite beta product. On the basis of the energies associated with these ion pairs a state diagram of zeolite beta including surface structure and phase selectivity has been developed. The relative rates of zeolite beta nucleation and growth have also been investigated at several ratios of TEA^+ to Na^+ in concentrated solutions. The synergy between these cations and anionic surface adsorption sites has led to synthesis of nearly monodisperse zeolite beta crystal particles having sizes from about 100 to 500 nm.

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1. Introduction

Zeolite beta [1] is a model material to study the effects of Al and B heteroatom substitutions and structure directing agents (SDA) on zeolite nucleation and growth rates because it can be synthesized with Si to heteroatom ratios from 3 to ∞ [2–4]. The broad heteroatom synthesis concentration range is due to the variety of SDAs available to crystallize zeolite beta. In addition to charge, these SDAs range from inorganic (e.g., Na^+) to organic, the latter group containing one or two quaternary ammonium groups in addition to moieties such as benzyl groups [3–7], heterocyclic amines [4,8] and ammonium groups [6–8], methylene chains, and methyl groups.

A significant number of investigations of zeolite nucleation and growth have been reported [9–11]. The proposed nucleation mechanisms vary from classical [12] to complex mechanisms wherein an amorphous phase changes to become crystalline by internal Si–O–Si rearrangements [13]. There are also disagreements regarding zeolite growth mechanisms, commonly attributed to either colloidal aggregation [14] or monomer addition [15]. To test the validity of these models we have previously investigated zeolite beta formation in dilute solutions. Three populations of particles were observed during crystallization [16,17]. Initially at room temperature supersaturated silica self-assembles into primary particles (<3 nm). Upon heating the primary particles to 120 °C, the least colloidally stable ones aggregate into secondary particles. The secondary particles have a density and composition similar to zeolite beta, change structurally over time to become zeolite beta nuclei, and aggregate into tertiary particles (zeolite beta) that subsequently ripen into well-ordered crystals exhibiting a well-defined morphology. Based on these observations a two-step model was proposed to describe zeolite beta nucleation [16,17]. In this model the density and composition of the secondary particles becomes similar to zeolite beta upon heating and afterwards, a slower evolution of the secondary particle structure occurs to complete nucleation.

Here we show that competition between TEA^+ and Na^+ for association with $[AlO_2]^-$ and $[\equiv SiO]^-$ sites (anionic sites in particles and at their surfaces) affects both the nucleation and growth of zeolite beta. From critical coagulation concentration (CCC) measurements using as-prepared zeolite beta precursor nanoparticles agreement with the prediction that steric hindrance is the repulsive force that stabilizes them in solution is found [18]. Using more concentrated synthesis solutions ($H_2O/SiO_2 = 20$), we determine how interactions between cations and $[AlO_2]^-$ substitutions in precursor particles can affect their T-atom density ($[SiO_2]$ plus $[AlO_2]^-$) and the phase selectivity of the synthesis solution. Na^+

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is important to control the T-atom density of the precursor particles in the synthesis of zeolite beta because it is necessary to nucleate zeolite beta at high Al concentrations. On the other hand, it slows down nucleation at low Al concentrations.

2. Experimental

2.1. Materials

For synthesis of zeolites and preparation of colloidal dispersions the following material components were used. Tetraethyl orthosilicate (TEOS) was supplied by Sigma–Aldrich at 98% w/w purity. Sodium hydroxide was supplied by Fisher Scientific at 99.8% w/w purity. Tetraethylammonium hydroxide (TEAOH) (35% w/w) in water was supplied by Alfa Aesar. Sodium aluminate ($NaAlO_2$) was supplied by EM Science and contained 3.5% w/w water. The aluminum triethoxide was supplied by Gelest or Strem Chemicals the later of which had a purity of 99% w/w. NaCl was supplied by Fisher Scientific having a purity of 99.9% w/w. Tetraethylammonium chloride (TEACl) was supplied by Sigma–Aldrich at ≥98% w/w purity.

2.2. Synthesis and solution preparation for CCC measurements

Synthesis solutions at two concentrations were investigated. The molar composition of the dilute set of solutions was 1 Si- $(OCH_2CH_3)_4$/80 H_2O/X NaOH/Y TEAOH/0.02 $NaAlO_2$ where $X + Y = 0.6$ and X was 0 or 0.1. The dilute solutions were prepared as described in reference [17]. The molar composition of the concentrated set of solutions was 1 $Si(OCH_2CH_3)_4$/20 H_2O/X NaOH/Y TEAOH/L $Al(OCH_2CH_3)_3$ where $X + Y = 0.5$, X was 0 or 0.1, and $0.01 < L < 0.18$. The concentrated synthesis solutions were prepared in two-steps. In the first step all components were mixed excluding $Al(OCH_2CH_3)_3$ and the solution was stirred until $Si(OCH_2CH_3)_4$ was hydrolyzed (~2 h). Afterwards, $Al(OCH_2CH_3)_3$ was added and the solution was stirred for ~24 h. Synthesis solutions were heated at 120 °C to prepare zeolite products. After separation (see below) solid products were dried at 120 °C for 2 h before they were calcined at 550 °C for 8 h using a 3 °C/min temperature ramp rate. Calcined samples were ion exchanged into the ammonium form using 0.1 M ammonium nitrate at 80 °C at zeolite loadings of <0.02 w/w. To prepare solutions for the CCC measurements either NaCl or TEACl was added directly to as-prepared dilute synthesis solutions heated for 4 days. The resulting solutions were thoroughly mixed and aged at room temperature for one week.

2.3. Dispersion preparation and separations

Solids were separated from solution using a RC 6 plus centrifuge with a HB-6 rotor (Sorvall) and 50 ml FEP centrifuge tubes (Nalgene) operating at 12,000 rpm (RCF average 23,530g-force) for between 30 min and 2 days. To separate the smallest products an Optima L-100 XP Ultracentrifuge, Type 45 Ti rotor, and thick walled polyallomer centrifuge tubes with an aluminum cap assembly operating at 20,000 rpm (RCF average 31,293g-force) was used for about 20 min. After separation, the zeolite products were redispersed in DI water using a sonicator bath (Fisher) and a vortex mixer (Fisher) and the centrifugation procedure was repeated until the supernatant (~40 ml) had a conductivity of <200 μS/cm/g-zeolite. Colloidal dispersions were prepared at about 0.001 w/w in an aqueous solution containing 0.01 M TEACl and 0.001 M TEAOH. Before dynamic light scattering (DLS) measurements the samples were redispersed in solution using a sonicator and the vortex mixer. Colloidal dispersions were clarified using a 2 μm syringe filter (Millipore Millex-AP 20) before DLS measurements were performed [16].

2.4. Analytical

Synthesis solutions were investigated using dynamic light scattering (DLS) and small angle X-ray scattering (SAXS). The experimental setup is described elsewhere [16,17]. Solids separated by centrifugation were analyzed using scanning electron microscopy (SEM, JEOL 7400F), thermal gravimetric analysis (TGA, Mettler Toledo TGA/DSC 1 STARe System), and Cu K_α powder X-ray diffraction (PXRD, Philips X'Pert X-ray diffractometer). The TGA program used was heating from 25 to 900 °C at 3 °C/min in 50 ml/min of air flow.

N_2 adsorption isotherms were measured on a Micrometrics ASAP 2010 instrument. As-prepared zeolite samples (~0.25 g) were loaded into a borosilicate sample cell with a 1.27 cm OD and a 10 cm^3 bulb containing a borosilicate filler rod. Samples were degassed at 120 °C (SDA-containing) for at least 12 h. Relative pressures between 0.01 and 0.985 were measured using a 30 s equilibration delay. The surface area of the SDA-containing samples was analyzed by the BET method using nine points in the relative pressure (P/P_o) range between 0.05 and 0.25.

3. Results and discussion

3.1. Dilute synthesis solutions: colloidal characterization and the relative rates of nucleation and growth

Competition between TEA^+ and Na^+ in the synthesis of zeolite beta affects the rate of nucleation and the colloidal stability of the secondary particles. To this end, particle size distributions (PSD) were obtained by inverting [19] DLS autocorrelation functions collected from several as-prepared solutions. The secondary and tertiary populations are present in the PSDs but the primary particles are not shown because their light scattering signal is too weak to be detected in the presence of the larger particle populations. At very low Na^+ concentrations ($X = 0$) tertiary particles form in less than 4 days of heating (Fig. 1). When some TEA^+ is replaced with Na^+ the tertiary particles form after 6 days of heating. Because the tertiary particles have the structure of zeolite beta [17] their point of detection was used to conclude that nucleation occurs more quickly in solutions containing less Na^+. Note also that the synthesis solutions contain an excess of SDA (i.e., >80%). Then adding more SDA will not have a major impact on nucleation because it will add to the solution phase and not to the amorphous precursor phase.

Using SAXS the disappearance of secondary particles was quantified and used to infer that the growth rate of the tertiary particles increases with the addition of Na^+ into the synthesis solution. The tertiary particles can not be investigated directly using SAXS because the limit of resolution of the SAXSess instrument is about 30 nm [20] and the first-detected tertiary particles are larger than 100 nm. To show that Na^+ in the synthesis solutions destabilizes the secondary particles, only three sample SAXS patterns are presented because detailed analysis of similar SAXS patterns was reported previously [16]. In the SAXS patterns primary particles and secondary particles can be observed. Some secondary particles were stable in solution for at least 30 days at 120 °C in the samples containing less Na^+ (Fig. 2). After 60 days of heating even those secondary particles were added to the tertiary particles. In contrast, in synthesis solutions containing more Na^+ the secondary particles were not observed after 30 days of heating although some all-silica primary particles still remain in solution [16]. This shows that Na^+ enhances the tertiary particle growth rate by destabilizing the secondary particles.

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