

## Preparation of high silica chabazite with controllable particle size



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### ABSTRACT

In this work synthesis procedures for controlling particle size distributions of high silica chabazite (Si/Al = 100) zeolites between 0.3 and 4.5  $\mu\text{m}$  is described. The chabazite zeolite crystallization and crystal growth have been monitored using XRD, SEM and DLS. Hydrothermal treatment parameters such as time, temperature and agitation and gel composition parameters such as amounts of water and structure directing agent (SDA) have been correlated with chabazite zeolite crystal size, crystal shape, synthesis yield and crystallinity. From this data a chabazite zeolite formation and crystal growth mechanism based on experimental studies and previous studies has been proposed. It was also found that large aggregates formed in the chabazite zeolite gel before any hydrothermal treatment (1  $\mu\text{m}$  large when using zeolite gel with composition  $1\text{Al}_2\text{O}_3:100\text{SiO}_2:60\text{TMAOH}:3100\text{H}_2\text{O}$ ). The size controlling parameter and size controlling synthesis step of the chabazite zeolite (below 1  $\mu\text{m}$ ) has been identified as the primary fractal aggregation of the silicium/aluminium/SDA species.

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### 1. Introduction

The chabazite type zeolites, and their SAPO forms, have been and remain to be of high interest both for academia and industry [1–8]. The unique topology and aluminosilicate framework have made it useful as catalyst in the methanol-to-olefin (MTO) process [9–11,3]. As well as an effective reduction catalyst when ion exchanged with copper [12,13]. In Addition, several novel separation technology applications have been discovered. Chabazite-type membranes and materials have now successfully been employed for separation of light-gas mixtures i.e.,  $\text{CO}_2/\text{CH}_4$ ,  $\text{H}_2/\text{CH}_4$ ,  $\text{H}_2/n\text{-C}_4$  and dehydration of water/alcohol mixtures [14–20]. The useful properties of the chabazite zeolite can be correlated to its framework. The chabazite framework consist of CHA and D6R building blocks arranged in an AABCC sequence layer, see Fig. 1 [9]. The D6R units are linked by 4-rings [9]. The framework form a three dimensional channel system consisting of large barrel shaped cavities connected with apertures formed by 8-rings. The CHA building block have internal dimensions of  $6.7 \times 4.2 \text{ \AA}$  and the 8-ring window in a cation-free chabazite has a dehydrated aperture of  $3.8 \times 3.8 \text{ \AA}$  [9,10].

A literature search reveals a large number of methods to prepare chabazite zeolite [1–8]. However, procedures for controlling

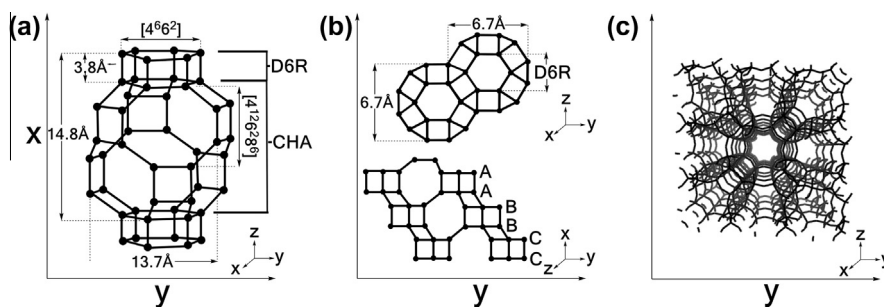
high silica chabazite particle size using N,N,N-1-adamantammonium as SDA has not been reported. In fact it has been shown difficult to control the chabazite zeolite synthesis [7,8]. In addition to this, achieving particle size control of high silica zeolites constitute a particular challenge. At high silicium/aluminium ratios impurities and competing zeolite structures (phases) are induced as well as Si-O<sup>-</sup> connectivity defects [7,8]. Yet obtaining high silica chabazite zeolites (SSZ-13) is desirable since these zeolites are less hydrophilic compared to low silica chabazite (zeolite-D) zeolites. Hydrophobic zeolites have been shown to be less hygroscopic and therefore useful in separation technologies involving adsorption of organics from aqueous matrices [21,22]. Furthermore, the zeolite Si/Al ratio is also known to affect the acidity, and high silica zeolites are therefore sometimes desirable for selectivity reasons in catalytic applications [23,24]. The objective of this study was to find a method for controlling the particle size of high silica chabazite (Si/Al = 100) as well as correlating hydrothermal and gel composition variables with zeolite growth and crystal size.

### 2. Experimental

#### 2.1. Materials and reagents

Aluminium hydrate (Aldrich, 50.0–57.5%), tetraorthosilicate (TEOS) (Aldrich, 98%), TMAOH (Sachem 1.0 M, Zeogen 2825) and distilled water was used as received for the preparation of the high silica chabazite. Millipore, MILLEX®V, Durapore®, PVDF,

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**Fig. 1.** Chabazite framework molecular structure showing ideal dimensions of: (a) T-atom (Si/Al) structure along the z, y axis; (b) T-atom structure along x, y-axis (upper) framework D6R sequence AABCC (lower); (c) 3-D line space image showing the chabazite 3D channel structure.

0.1  $\mu\text{m}$  membrane and a Sartorius stedium, 5.0  $\mu\text{m}$  Minisart<sup>®</sup> filter was used for cleaning the aqueous solutions used for dynamic light scattering (DLS) analysis.

## 2.2. Synthesis of high silica chabazite

The material was prepared from an unseeded reaction mixture, forming a gel with the following composition:  $1\text{Al}_2\text{O}_3:100\text{SiO}_2:40\text{--}110\text{TMAdaOH}:2100\text{--}5100\text{H}_2\text{O}$ , aluminium hydrate, tetraorthosilicate (TEOS), TMAdaOH and distilled water were added in that order to a beaker and the mixture aged 24 h under stirring at room temperature. Then the mixture was transferred to an autoclave and crystallized under either static, tumbling or stirred conditions for 24–168 h at various temperatures. The autoclaves were cleaned periodically in an aqueous 15% HF solution between the runs. The product was collected and calcined at 550  $^\circ\text{C}$  for 12 h with 6 h ramping. For amounts and conditions see Tables 1–6.

## 2.3. Characterisation and analysis techniques

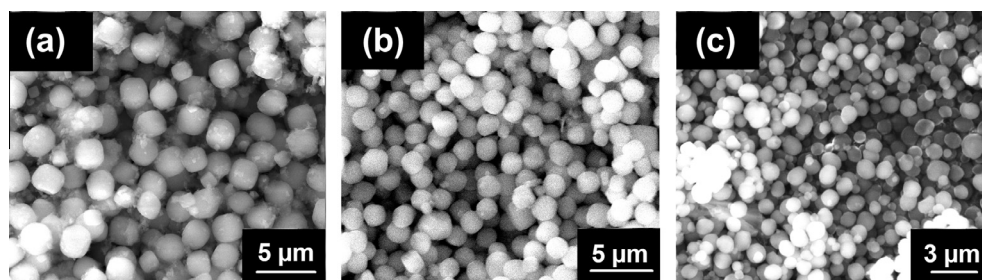
SEM was performed with a FEI Quanta 200 FEG-ESEM. Samples were prepared by dispersing a small amount of zeolite in ethanol and then grinding the mixture and placing a droplet onto the metallic sample holder containing carbon tape.

Powder X-ray diffraction (XRD) was carried out on a Bruker D8 Discover diffractometer the D8 is equipped with a focusing monochromator, giving monochromatic  $\text{CuK}_{\alpha 1}$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and a position sensitive Linxeye detector. The crystallinity of the samples were estimated by integrating the area of the high intensity peaks at  $2\theta$ : 9.6 $^\circ$ ; 14.1 $^\circ$ ; 16.3 $^\circ$ ; 17.8 $^\circ$ ; 21.0 $^\circ$ ; 25.0 $^\circ$ ; 26.4 $^\circ$  and 31.2 $^\circ$ , and weighing the total area against the different zeolite synthesis runs.

Determination of specific surface area was carried out on a Beslsorp-mini II instrument at  $-196 \text{ }^\circ\text{C}$ , using nitrogen adsorption and the BET (Brunauer Emmett Halenda) method [25]. All samples were outgassed at vacuum and dried at 80  $^\circ\text{C}$  for 1 h and then 4 h at 250  $^\circ\text{C}$  before measurement.

Dynamic light scattering (DLS) was carried out on a Zetasizer Nano ZS Malvern Instruments with an Avalanche photodiode detector, equipped with a He-Ne laser working at 633 nm ( $\leq 5 \text{ mW}$ ). For analysis a refractive index of 1.482 was used and a material absorption of 0.1. Samples were prepared by taking a small fraction of the solid material and dispersing it into a glass beaker containing 5.0 ml filtered distilled water (0.1  $\mu\text{m}$  Millipore, MILLEX<sup>®</sup>VV, Durapore<sup>®</sup>, PVDF membrane). The beaker was then immersed in a sonic bath for 1 minute. 3.0 ml of this solution was then transferred into another glass beaker containing 3.0 ml filtered distilled water (0.1  $\mu\text{m}$  Millipore, MILLEX<sup>®</sup>VV, Durapore<sup>®</sup>, PVDF membrane). This beaker was then immersed into the sonic bath for 1 minute. 2.5 ml of this solution was transferred into the quartz cuvette through a syringe fitted with a single use filter unit (5.0  $\mu\text{m}$ , Sartorius stedium, Minisart<sup>®</sup>) and analysed with light scattering. The maximum delay times were always chosen to allow for the correlation functions to decay to a well-defined zero level. The instrument has an in-built function which indicates a suitable counting rate to avoid too low or too high concentrations of the studied systems, which otherwise would give statistically poor correlation curves or influence from multiple-scattering. All experiments were carried out in Non-Invasive-Back-Scatter (NIBS) mode with a measuring angle of 175 $^\circ$  and temperature of  $25 \pm 0.1 \text{ }^\circ\text{C}$ . The sampled correlation curves, for particle size determination, were done with the SDP (Size Distribution Processor) algorithm, which is based on the CONTIN program [26]. The results that are presented in Tables 1–6, which gives the obtained SDP results for the sizes as Intensity weighted diameters. The reported standard deviations are those obtained from repeated experiments on the same sample. The particle size analysis was done directly after the preparation of the sample, this to ensure that no reduction of particle size occurs due to sedimentation.

Solid state NMR experiments on calcined zeolite samples were performed at 11.7 T on a Bruker Avance III spectrometer using a 3.2 mm triple resonance MAS probe head at room temperature. The MAS rate was 20 kHz for all experiments. The  $^{27}\text{Al}$  NMR spectra were obtained using  $\pi/12$  pulses at an rf-field of 94 kHz, 10000



**Fig. 2.** Representative SEM images of chabazite zeolites prepared from zeolite gel:  $1\text{Al}_2\text{O}_3:100\text{SiO}_2:60\text{TMAdaOH}:3100\text{H}_2\text{O}$ , hydrothermally treated for 96 h at 160  $^\circ\text{C}$  under (a) static, (b) tumbled and (c) stirred conditions.

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