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SYNTHESIS OF HIGH SILICA CHA ZEOLITES WITH CONTROLLED Si/Al RATIO

E. A. Eilertsen(a), M. H. Nilsen(b), R. Wendelbo(c), U. Olsbye(d), K. P. Lillerud(d)

a Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N - 0315 Oslo
b Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Norway
c Abalonyx AS, c/o Department of Chemistry, University of Oslo, Norway
d InGap, Department of Chemistry, University of Oslo, Norway

Abstract

Zeolites with the CHA topology have been synthesized with Si/Al ratios ranging from 15 to 133. ICP-AES analysis shows that the Si/Al ratio in the material is close to linearly related to the Si/Al ratio in the reaction mixture, while powder XRD shows that the unit cell parameters decrease with increasing Si/Al ratio. The difference between the unit cell parameters for the as-synthesized and the calcined samples show that the structure directing agent sterically hinders the contraction in the c-axis direction for the as-synthesized samples. A relationship between the Si/Al ratio in the material and the a-axis has been established. The particle size of the material also shows a dependency on the Si/Al ratio of the material.

Keywords: SSZ-13, Si/Al ratio, Chabazite, CHA, High silica.

1. Introduction

Zeolites with the CHA topology are of industrial interest, primarily as potential highly selective catalysts for application in the methanol to olefins (MTO) reaction [1]. The presence and concentration of Al in the zeolite framework determines the acidity of the material in the hydrogen form. The main challenge has been to synthesize a material with a low density of acidic sites to avoid a too rapid deactivation. In the early synthesis of CHA zeolites, the material was prepared from an inorganic gel and had typically a Si/Al ratio of less than 3 [2]. SSZ-13 was the first real high silica CHA with Si/Al ratio of about 12, synthesized with N, N, N-trimethyl-1-adamantammonium hydroxide (TMAdaOH) as structure directing agent [3]. This was reported in 1985, while a pure SiO2 CHA was reported in 1998 [4]. For the pure SiO2 CHA, the unit cell parameters were determined to be: a = 13.529 Å and c = 14.748 Å [4]. In addition, several patents on high silica CHA materials have been published [5, 6]. The application of CHA zeolites in the MTO reaction with Si/Al ratios ranging from 14 – 67 was studied by Zhu et al. in 2007 [7].

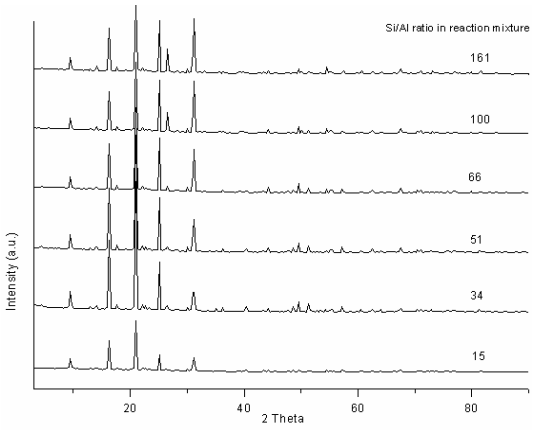
2. Experimental

The materials were prepared from an unseeded reaction mixture forming a gel with the following composition: 10 TMAda-OH : 7.5 Na_2O : 5 F- : 0.3-2.7 Al_2O_3 : 100 SiO_2 : 2200 H_2O. The gel was prepared by first mixing solutions of NaOH (1M), TMAdaOH (0.77M) and deionized water. $AlOOH•xH_2O$ and NaF was then added to the solution and stirred until the powder was dissolved. This mixture was mixed with Cab-O-Sil M5 fumed silica. The resulting viscous gel was homogenized by hand for 5 minutes and aged at room temperature for 2 hours. The gel was then heated statically for 7 days at 160 °C in a 15 mL Teflon lined steel autoclave. The materials were characterized by powder

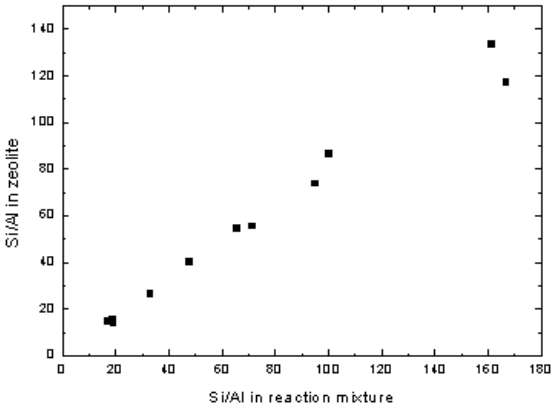
X-ray diffraction (XRD), scanning electron microscopy (SEM), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The unit cell parameters were obtained by Pawley refinement. The 2θ areas in the diffractograms with quartz peaks were excluded from the refinement.

3. Results and discussion

The synthesized materials with different Si/Al ratios exhibit the CHA topology as shown in Figure 1. In the XRD patterns for the materials with the highest Si/Al ratios, small amounts of quartz are observed as an impurity at 2θ = 26º. ICP-AES analysis as seen in Figure 2 indicates a nearly linear relationship between the Si/Al ratio in the reaction mixture and the Si/Al ratio in the material. There is, however, a slight enrichment of Al in the materials compared to the reaction mixture composition, and at very high Si/Al ratios there appears to be a deviation from linearity. The ICP-AES results show that the Si/Al ratio for the synthesized materials varies from 15 – 133, but with some uncertainty for the samples with the highest Si/Al ratios due to the presence of small amounts of quartz.



Figur 1: Diffractograms of samples with different Si/Al ratio



Figur 2: Si/Al ratio in the materials determined by ICP-AES as function of the Si/Al ratio in the reaction mixture

The synthesis of CHA type zeolites with the TMAda+ cation as structure directing agent is one of the best known examples of templating. In spite of this strong structure directing effect, it has been difficult to synthesize CHA type materials with Si/Al ratios above 12. Analysis of the variations in unit cell parameters, as seen from Figure 3, shed new light on this intriguing observation. The unit cell parameters decrease, as expected, with a decreasing amount of Al in the material. This is in accordance with the expected shorter bond length of Si-O (1.62Å) compared to the Al-O (1.73Å) bond length [8]. It can also be seen that the unit cell parameters for the calcined sample converge to the values for the reported pure SiO2 CHA when the Si/Al ratio increases [4]. However, there is a large anisotropic contraction in the as-synthesized material. The *c*-axis is nearly constant while all the relaxation of strain is seen as a large change in the *a*-axis. For the calcined material, the relaxation of strain is seen as a large change in the *c*-axis. This can be explained by the template position in the material as shown in Figure 4. Villaescusa et al. [9] showed that the template is oriented parallel or antiparallel to the *c*-axis. In the as-synthesized samples the template thus sterically hinders the decrease in the *c*-axis, while for the calcined samples there is no such hindrance. Therefore the *c*-axis is free to decrease for the calcined samples. Strong templating effect relies on a perfect match between voids in the lattice and the template, which seems to be the case at low Si/Al ratios. It appears however, that the higher the Si/Al ratio, the more strain of the CHA lattice, resulting in less favorable conditions for crystal growth.

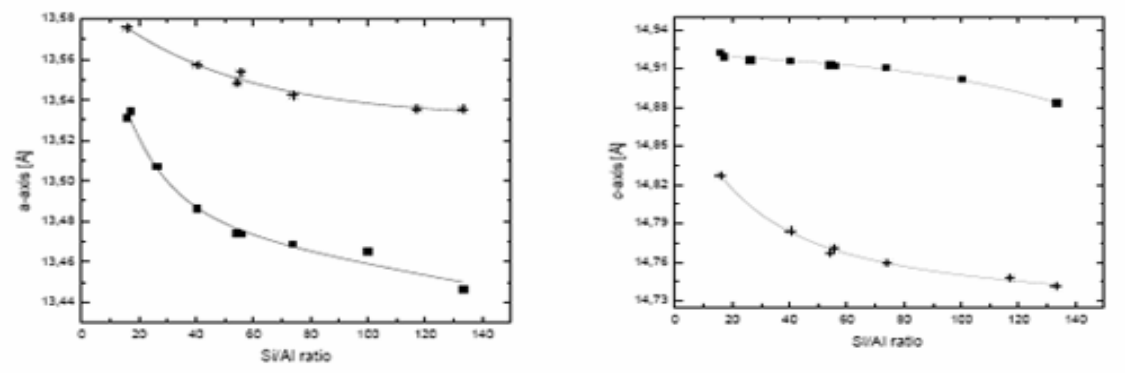


Figure 3: Unit cell parameters for as-synthesized samples (square) and for calcined samples (star) as a function of the Si/A1 ratio

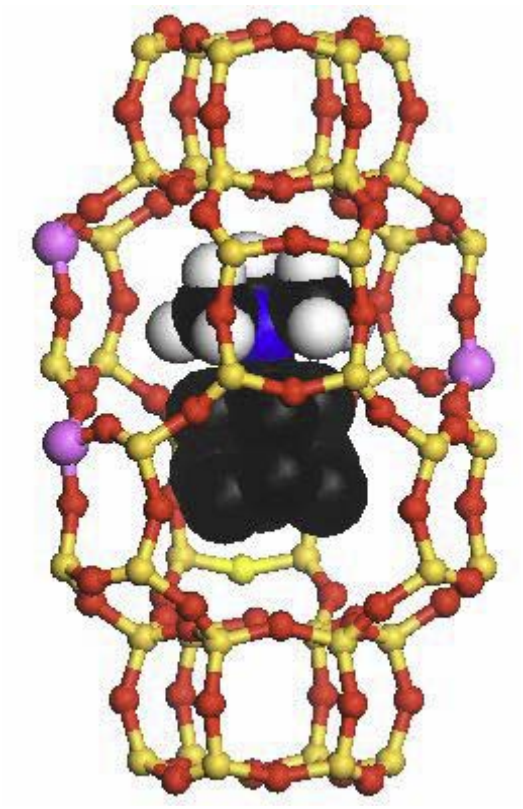


Figure 4: CHA cage with template

Another possible explanation for the difficulty of synthesizing the material over a large compositional range is that when the Si/Al ratio increases, the network takes a more neutral charge. For the structure to be electrically neutral there must be charge compensation to provide charge balance between the framework and the positively charged template. This can either be accomplished by occluded anions or lattice defects. Villaescusa et al. [9] showed that an F- anion is located in the double 6-ring in the CHA structure for the pure SiO2 CHA providing for charge balance. We note here that our attempts of making the material without F- led to a phase mixture of CHA and an unknown phase for Si/Al ratios above 60.

By plotting the crystallographic a-axis for the as-synthesized and the calcined materials against the Si/Al ratio as determined by ICP-AES, the plot fits very well to an exponential function as seen in Figure 3. This can be used to determine the Si/Al ratio of the material by measuring the unit cell parameters with XRD.

The Si/Al ratio in the material can be determined from XRD by the following relations:

$$\frac{Si}{Al} = -35.63 \cdot \ln\left(\frac{(a) - 13.45}{0.129}\right) \qquad (1)$$

$$\frac{\mathrm{Si}}{\mathrm{Al}} = -43.27 \cdot \ln\left(\frac{(a) - 13.43}{0.0621}\right) \qquad (2)$$

where a is the length of the *a*-axis in Å. Equation 1 gives a relation between the *a*-axis of the as-synthesized material and the Si/Al ratio, while equation 2 gives the same relation for the calcined material. As can be seen in Figure 5, the particle size is dependent on the Si/Al ratio in the reaction mixture. For the materials with the lowest Si/Al ratios, the particle size is about 20µm. When the Si/Al ratio in the reaction mixture exceeds 50, there appears to be a step in the particle size. For higher Si/Al ratios, the particle size is from 2 to 4 µm.

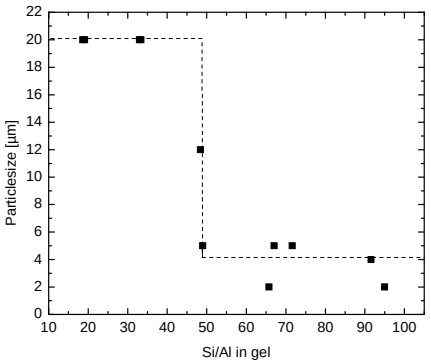


Figure 5: Particle size as function of the Si/Al ratio in the reaction mixture

4. Conclusions

The results from this work show that it is possible to synthesize zeolites with the CHA topology over a greater compositional range than previously reported, and that it can be controlled by adjusting the reaction mixture composition. The obtained Si/Al ratios have been determined by ICP-AES to be between 15 and 133. The increase in the Si/Al ratio can also be observed by an expected decrease of size the unit cell, from which it is possible to calculate the Si/Al ratio from an empirically based equation. A particle size dependency of the Si/Al ratio in the reaction mixture has also been observed.

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