Electronic Supplementary Information (ESI) for Chemical Communications

Supporting information for :

Differentiating fundamental structural units during the dissolution of zeolite A

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1. Synthesis of zeolite crystals

A gel with molar composition $1 \text{ SiO}_2 : 2.23 \text{ Na}_2\text{O} : 5.18 \text{ TEA} : 0.89 \text{ Al}_2\text{O}_3 : 246 \text{ H}_2\text{O}$ was prepared by mixing two solutions: solution 1, was formed by dissolving aluminium wire in an alkali solution which comprised the NaOH part with half of the water. The mixture was then filtered to remove impurities. Solution 2, was prepared by adding the tetraethyl orthosilicate to a solution made of triethanolamine and the second half of the total deionised water needed for the gel composition. Finally, both solutions were mixed under vigorous stirring and subsequently, the solution was aged for 30 min in polypropylene bottles. The crystallisation was carried out at 90 °C for 10 days.

After the crystallisation time finished, two thirds of the product were centrifuged and the solid product was then dried over night at 60 °C, whilst the mother liquor was kept at room temperature and protected from sunlight. The remaining product was kept in the mother liquor.

1. Crystal characterisation

The crystals obtained from the synthesis described above were characterised by X-ray powder diffraction (XRD) and scanning electron microscopy. XRD patterns were collected using a Philips X'Pert X-ray generator, with CuK α radiation, $\lambda = 1.54$ Å. The powder samples were packed carefully into an aluminium holder in order to ensure a flat, smooth surface to be scanned. The sample stage revolves at 2 Hz. All scans were run at a continuous scan rate of 0.015 ° min⁻¹. Figure 1 shows the powder diffraction pattern obtained. The X-ray fingerprint exhibits all the diffraction peaks that correspond to the LTA structure.

Scanning electron micrographs were taken using a FEI Quanta 200 with a field emission gun (FEG). The samples were prepared by spreading the zeolite powder onto double-sided carbon tape, mounted onto an aluminium microscope holder and coated with a thin film of gold to reduce charging effects and increase conductivity. Figure 2 shows an SEM micrograph of the zeolite A

crystals studied in the present work. The cubic crystals exhibit clear square {100} faces and small {110} facets, as depicted by the bevelled edges of the crystal.

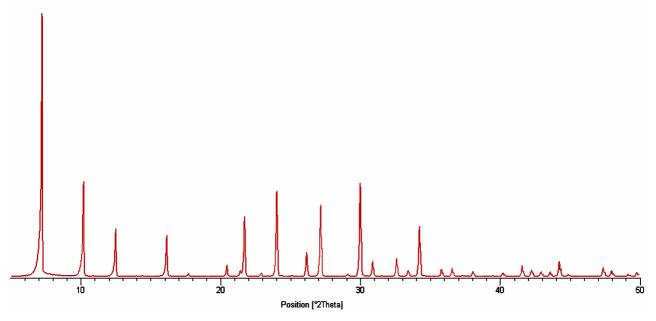


Figure 1. X-ray diffraction pattern obtained from the zeolite A sample.

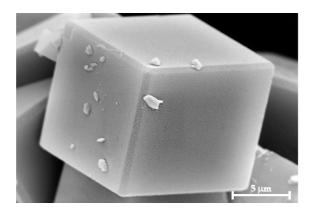


Figure 2. SEM micrograph of the zeolite A crystal.

2. Atomic force microscopy experiment

In situ AFM experiments were conducted in contact mode using silicon nitride tips with 0.58 N m⁻¹ force constants and scan rates of 3 Hz. Some experiments were conducted using continuous flow through the fluid cell, and for this purpose, a syringe pump (RazelTM model A-99 from SEMAT) was used. All the experiments were carried out at room temperature of about 25 °C.

To prepare the samples, the crystals were fixed onto a metal stub using Crystal-bond thermoplastic, warmed as necessary to soften it enough to be flattened. Then after allowing it to cool down, the sample was sprinkled onto the thermoplastic. The metal stub was reheated allowing the crystals to

embed, and finally it was cooled down to fix the crystals in the thermoplastic prior to imaging by AFM. In the case of crystals smaller than 15 μ m, a suspension with ethanol was prepared in order to obtain a good crystal distribution on the thermoplastic.

3. Image analysis

The areas dissolved, observed on the AFM micrographs, were measured using Image Tool v.3 software. This image analyzer program was developed at the University of Texas in the Health Science Centre in San Antonio and is in the public domain.