Electronic Supplementary Material (ESI) for Chemical Communications

Controlled step-wise isomerization of the Keggin-type Al_{13} and determination of the γ-Al13 structure

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SUPPORTING INFORMATION

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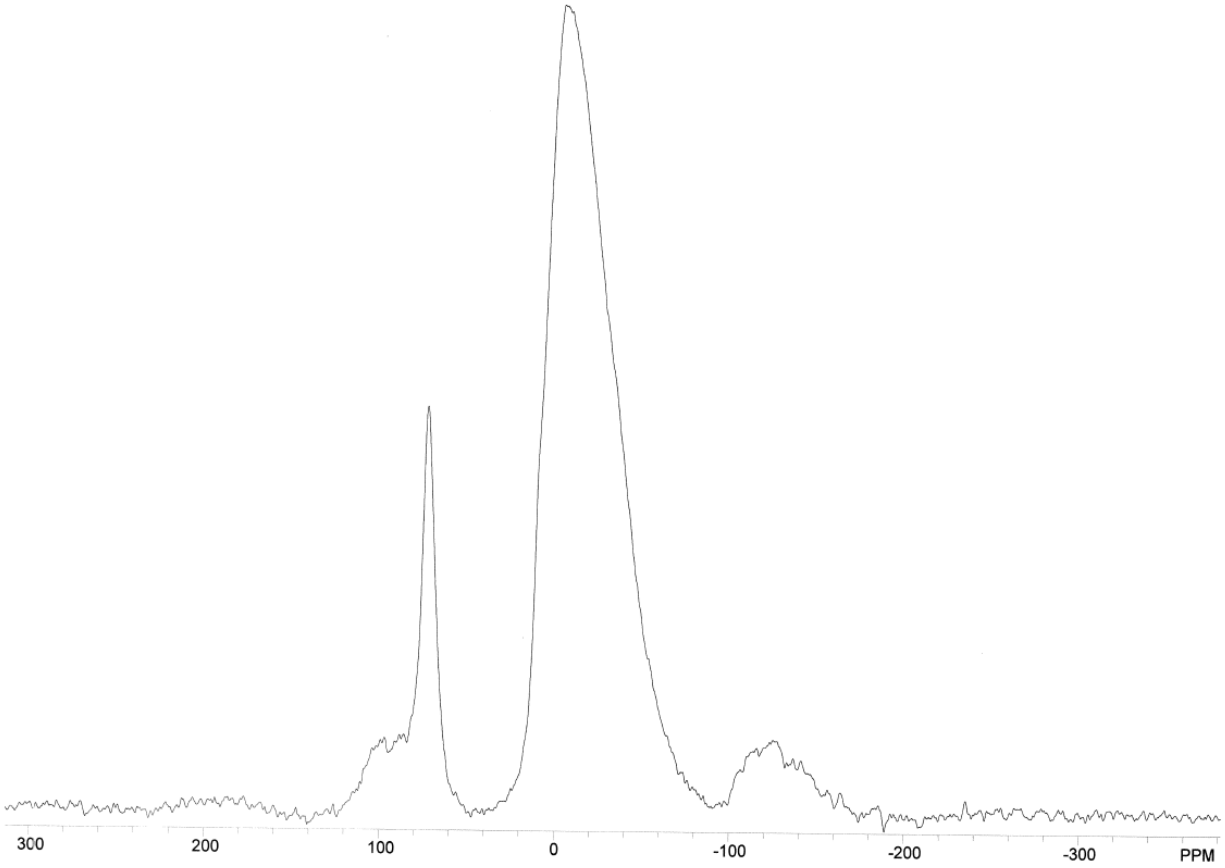
1. ^{27}Al NMR MAS spectra – γ-Al_{13} crystals

^{27}Al NMR solid-state MAS experiments were conducted on a 360MHz instrument equipped with w/ Tecmag console with a spectrometer frequency of 94.669MHz. An Al-free probe was also used, and the sample were offset similarly to 0 ppm with an Al(NO3)3·9H2O reference standard. Pulse width was 1 μs, number of scans was 8000, and the recycle delay was 300ms. The flip angle used was 15°.



2. Example laboratory scale Al_{30} synthesis

A 1000mL 3-neck round bottom flask was charged with 200mL of DI water, 60.3325g (250mmol) of $AlCl_3 \cdot 6(H_2O)$ (Reagent grade, Alfa Aeser) and 22.518g (300 mmol) glycine (Reagent grade, Sigma-Aldrich). The solution was heated to 90°C and stirred rapidly using a magnetic stir bar. A $Ca(OH)_2$ slurry was prepared as follows: 28.0724g (360 mmol) of $Ca(OH)_2$ powder (95%, Alfa Aeser) was weighed into a 50mL beaker and covered with parafilm. To this, 30.000g of H_2O was added and the resulting paste mixed well with a magnetic stir-bar while being stirred (for smaller amounts, the paste can be mixed with a stir bar or spatula). Shortly after mixing, 48.3937g (5/6 of total) of this $Ca(OH)_2/H_2O$ slurry was added via a cut-tip disposable pipette into a syringe and the syringe fit roughly into a neck on the flask. The slurry was added drop wise in 12x1 minute aliquots over a period of 1.0 hrs. The resulting solution was left to stir at 90˚C for 48 hours to obtain a solution similar to solution A. The Al:Gly ratio here was 1:1.2 and the hydrolysis ratio ([OH]/[Al]) was 2.40. Similar experiments were conducted (Pappas, I.; Vaughn, J.; Pan, L., WO 2012061280. 2012), resulting in varying degrees of Al_{30}, including the sample of Al_{30} utilized during the synthesis of γ-Al_{13}. The amount of Al_{30} present was determined by ^{27}Al liquid NMR utilizing the Td intensity of Al_{30}. Samples were run with a coaxial insert containing $NaAlO_4$ as a secondary standard while multiple $Al(NO_3)_3$ standards were used to establish a signal response-to-Al concentration calibration curve. The Td region of the Al peaks was then integrated and the %Al as Al_{30} calculated against the total signal intensity.

3. Synthesis of γ-Al_{13} from Al_{30}

Upon successful synthesis of solution A, $CaCl_2 \cdot 2H_2O$ (Reagent grade, J.T. Baker), glycine, and DI H_2O were added in larger amounts to a beaker while being stirred, resulting in a variety of different wt % solutions. The % Al in these experiments was commonly ± 0.15% of 2.6% Al, with 9.72% Ca and 16.17% glycine (±1%). In one case, a sample with 1.0% Al was utilized with 9.73% and 16.18% Gly to produce a single peak at 76 ppm. In each of these experiments, ^{27}Al NMR was used to confirm that these species contained only one peak in the Td region at δ=76 ppm.

An example synthesis is as follows:
To 71.95g of solution A (100. mmol Al, 117 mmol Ca, 84.3 mmol Gly), 18.56g of $CaCl_2 \cdot 2H_2O$ (126.2 mmol) and 13.7671g of glycine (132.0 mmol) were added, and stirred until clear. The resulting solution had a density of 1.41 g/mL, and 15.0mL of this solution was added into an isochoric vessel and heated at 140-145°C for 6 days.

4. Details for crystal growth experiments

The first γ-Al_{13} crystals were obtained via addition of acidified sulfate solutions to purified Al solution in a U-tube with a 50% (v/v) ethylene glycol in water matrix acting as a gel-like barrier, and an [Al]:[SO4] ratio between 3.0-4.0. However, these crystals were not of sufficient quality for publication, particularly because of the inability to assign solvent molecules. Further crystallization experiments were run by directly adding acidified sulfate to purified fractions. Optimal samples were seen when >5mg of γ-Al_{13} was present in solution. Single crystals were optimized in smaller test tubes or Pasteur pipettes, and large batches of crystals were grown in beakers or flasks up to 125mL.