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Supporting Information

Crystallization of Aluminum polycation sulfates: Transformation of tetrahedral crystals in aqueous solution

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Section-S1

1. Experimental Procedures

1.1 Materials and preparations

All the chemicals in experiments were obtained from commercial suppliers (AR) and used without further purification. Primary polyaluminum chloride mother solutions were prepared by gradually addition of pre-weighed carbonates powder into Al(III) aqueous solutions, with basicity (OH-/Al³⁺) of 2.2 under intense agitation at 50°C following the method in the literature.¹ The resulting solutions were standing still for overnight. The white crystalline solid of Al₁₃ sulfates were obtained by addition of sulfate salts into the mother solutions, the ratio of Al_T/SO₄=1:1.² The tetrahedral crystals (type I) were produced in the presence of Na⁺ ions, the single crystals of type I suitable for analysis were obtained by adding 0.1 mol/L Na₂SO₄ solution into 0.1 mol/L above-mentioned mother solution for standing still over 24 hours. Immersion tests were conducted by soaking type I crystals into solutions directly. After soaked in water for 3 months, the type I crystals transformed into type II crystals, then the single crystals of type II suitable for analysis were obtained into type II crystals, then the single crystals of type II suitable for analysis were obtained into type II crystals, then the

To investigate the influence of Na⁺ ions to crystalline transformation, the immersion tests were conducted by soaking the type I crystals into different solutions, NaCl, Na₂SO₄, KCl, NH₄Cl and (NH₄)₂SO₄ were selected as solutes, the concentrations of cations were 0.2 mol/L, pure water was taken as a comparison. The solid samples used for XRD characterization were obtained by soaking type I crystals in solutions for one month.

1.4 Molecular dynamics (MD) calculation

The single crystal data were used to construct the model, the primitive cell of type I crystal (348 atoms: S 16; Al 52; O 264; Na 16) and $1 \times 2 \times 1$ supercell of type II crystal (336 atoms: S 12; Al 52; O 272) were built. Then first-principles MD simulations were performed with PBE-D3 at 300 K by VASP (total time 30 ps, time step 1 fs), respectively.

1.3 DFT computation

DFT computation for simulating reaction (1) was performed on Gaussian09 program.³ The computation considered Na-Al₁₃/H₂O as reactants and Al₁₃/[Na(H₂O)₄]⁺ as products. The molecular structures were optimized at B3LYP/6-31G* level, Single point calculation and frequency analysis were carried out at B3LYP/6-311G** level, and all quantum calculations have considered the bulk solvent effects of water by polarizable continuum model (PCM).⁴

1.4 VASP calculation

The single crystal data were used to build the models, and PBE-D3 (Perdew-Burke-Ernzerhof including dispersion) exchange correlation functional was adopted to optimize the structure of type I and II crystals (parameters set as k-mesh: $2\times2\times2$, cutoff energy: 400 eV, the energy converged criteria: 10^{-5} eV, the force converged criteria: 0.001 eV/Å for type I and 0.005 eV/Å for type II).⁵

1.5 Characterizations

1.5.1 XRD characterization

The XRD characterizations were performed on an X'pert PRO MPD diffractometer (PAMalytical), the characterized parameters were set as: Cu K_{α} , 40 kV, 40 mA, the data were collected from 5° to 90° (2 θ degree) and scanning rate was 1°/min.

1.5.2 Single crystal X-ray diffraction

The single crystal X-ray diffraction data were collected on a Rigaku AFC-10/Saturn 724+CCD diffractometer with graphite-monochromated Mo K_{α} radiation (λ =0.71073 Å) using the multi-scan technique. The structures were determined by direct methods using SHELXS-971 and refined by full-matrix least-squares procedures on F_2 with SHELXL-97.⁶ All non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F_2 .

1.5.3 TGA and DSC

The TGA and DSC characterization for samples were performed on a simultaneous thermal analyzer (Mettler Toledo) under air atmosphere, the thermal treatment was from 30°C to 1200°C, the temperature elevating rate was set as 10 K/min.⁷

1.5.4 SEM and EDS

The SEM microscope images were obtained on an electric microscope (HITACHI SU8020), and EDS was carried out on a equipment of IXRF model 550i.

1.5.5 ICP-OES

The aluminum concentration in solutions were determined by ICP-OES Opetima 8300.

1.5.6 Solid state ²⁷Al-NMR

The solid state ²⁷Al-NMR characterization was carried out on an instrument JNM-ECZ600R with rotation frequency of 15 kHz and relaxation time of 10 s.

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Section-S2

Crystal type	Al (wt%)	Na (wt%)	S (wt%)	Al:Na:S
Ι	19.98	1.251	7.726	13:1:4
Π	23.88	0.0569	6.914	13:0:3

Table S1. The elemental analysis results for type I and II crystals

Item	Type I	Type II
CCDC	1834654	1834653
Formula	$Al_{13}H_{76}NaO_{70}S_4$	$Al_{13}H_{79}O_{68}S_3$
Formula mass	1698.57	1614.55
Temperature/K	153	153
Crystal system	Cubic	Monoclinic
Space group	<i>F</i> -4 3 m	P n
<i>a</i> (Å)	17.779(2)	14.030(3)
<i>b</i> (Å)	17.779(2)	11.502(2)
<i>c</i> (Å)	17.779(2)	17.598(4)
α (°)	90	90
eta (°)	90	102.18(3)
γ (°)	90	90
$V(\text{cm}^{-3})$	5620(2)	2775.8(10)
Ζ	4	2
$D_{\rm c}({\rm g~cm-3})$	2.008	1.932
Reflections[$I \ge 2\sigma(I)$]	662	6959
Goodness-of-fit on F2	1.321	1.133
R1 [<i>I</i> >2 <i>σ</i> (<i>I</i>)]	0.1096	0.1273

Table S2. Crystallographic data for type I and II crystals

Selected bond & angle	Type I	Type II
$Al_{T}^{[a]}-O(1)^{[c]}$	1.811	1.78(2)-1.86(2)
Al_0 -O(1)	2.029(6)	1.95(2)-2.15(2)
Al ₀ -O(2) ^[d]	1.864(6)	1.81(2)-1.91(2)
Al ₀ -O(3) ^[e]	1.850(6)	1.80(2)-1.90(2)
Al ₀ -O(4) ^[f]	1.958(7)	1.78(2)-2.15(2)
Na-O(2)	2.55(2)	NA
Al _T -O(1)-AlO	123.9	121.9(8)-125.8(9)
Al _o -O(2)-Al _o ' ^[b]	103.0(3)	100.7(8)-108.5(8)
Al ₀ -O(3)-Al ₀ '	101.2(3)	99.3(8)-102.8(8)

Table S3. Selected geometrical data for type I and II crystals

^[a]Al_T= tetrahedral Al. ^[b]Alo/Alo'= octahedral Al. ^[c]O(1)= μ_4 -O. ^[d]O(2)= a- μ_2 -O. ^[e]O(3)= b- μ_2 -O. ^[f]O(4)= η -O.





Figure S1. The solid ²⁷Al-NMR patterns of two crystals. Blue line: type I, red line: type II.



Figure S2. The EDS analysis results for type I crystal (a) and type II crystal(b).



Figure S3. The Aluminum concentrations in NH_4Cl (a) and $(NH_4)_2SO_4$ (b) solutions during immersion tests.



Figure S4. Molecular structures of Na-Al₁₃ and Al₁₃ in type I and II crystals. For type I, Na⁺ ion and binding waters are disordered, Na⁺ ion is 1:1 to Al₁₃ molecule as shown in a simplified way.



Figure S5. Hydrogen bonds between $Na-Al_{13}$ molecules in type I crystals.



Figure S6. Hydrogen bonds between $Na-Al_{13}$ molecules and sulfates in type I crystals.



Figure S7. The packing structure of type II crystal from the view of profile (a) and top (b). To clarify the layers, the water molecules are omitted.



Figure S8. TGA curves for type I (blue line) and type II (red line) crystals.



Figure S9. XRD patterns for samples obtained after thermal treatment at 950°C for 3 hours.