Supporting Information

Transitions in Al Coordination During Gibbsite Crystallization Using High-Field ^{27}Al and ^{23}Na MAS NMR Spectroscopy

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Table S1: Hydrated ^{27}Al quadrupolar line parameters from Figure 1

Sample	pos (ppm)	lb (ppm)	Q_{CC} (MHz)	η_Q	Integration (%)
gel	7.3	3.8	5.6	0.05	11.6
	13.0	3.1	5.5	0.52	74.0
	40.6	6.7	5.6	0.35	9.6
	66.2	7.1	4.5	0.60	1.4
	72.9	7.3	5.0	0.13	3.5
G1	11.9	3.8	4.6	0.27	94.6
	40.4	10.3	6.8	0.73	3.3
	61.9	14.1	6.4	0.60	0.5
	71.8	10.1	5.9	0.13	1.5
G2	11.5	3.1	4.1	0.27	98.1
	40.8	9.8	6.4	0.73	1.5
	65.8	4.1	3.4	0.60	0.1
	71.9	4.7	4.0	0.13	0.3
G3	11.7	2.4	3.2	0.99	98.7
	40.8	13.1	7.4	0.73	1.3
	60.8	14.4	6.4	0.60	0.1
	70.9	2.6	3.0	0.13	0.1
G4	11.3	2.9	3.2	0.55	98.4
	34.6	18.1	8.1	0.73	1.6

Table S2: Dehydrated ^{27}Al quadrupolar line parameters from Figure 1

Sample	pos (ppm)	lb (ppm)	Q_{CC} (MHz)	η_Q	Integration (%)
gel	6.3	7.6	6.5	0	9.1
	12.3	5.3	5.7	0.32	48.2
	40.6	9.3	6.8	0.25	27.6
	64.2	10.6	5.5	0.60	5.6
	71.9	8.5	5.4	0.13	9.5
G1	11.9	4.0	4.5	0.05	92.9
	40.6	11.0	6.8	0.73	4.1
	61.8	14.4	6.4	0.60	1.2
	71.9	10.6	6.0	0.13	1.8
G3	11.5	2.4	3.2	0.98	99.2
	37.2	8.0	5.8	0.73	0.7
	71.9	6.2	4.6	0.13	0.1
G4	11.3	2.6	2.9	0.98	98.4
	37.4	11.4	6.9	0.73	1.5
	64.8	14.4	6.4	0.60	0.1
	71.9	6.2	4.6	0.13	0.1

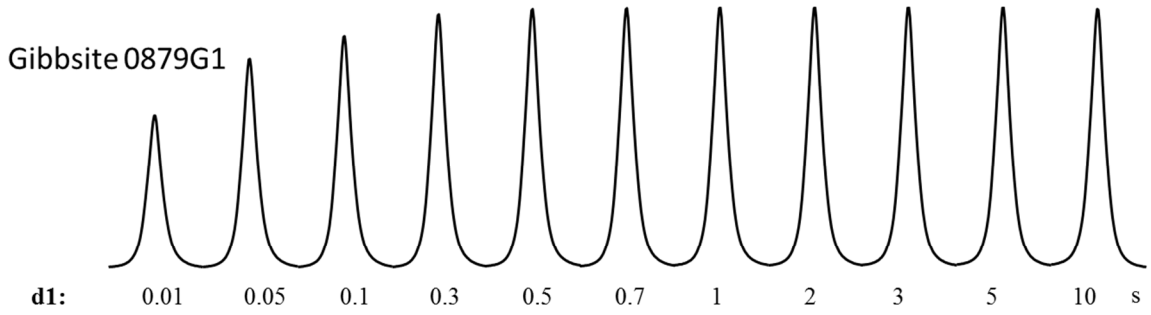

Figure S1. ^{27}Al recycle delay (d1) calibration on 0879G1 Gibbsite.

Table S3. Fitting Results of Figure 5 **^{27}Al spectra**.

Sample name	Site name	Chemical shift (ppm)	Q_{CC} (MHz)	η	Lb (ppm)	Area ratio (%)
G5 (20-40 nm) hydrated	Octa-site	11.3	2.8	1.0	2.7	99.02
	Penta-site	38.9	6.9	0.6	10.3	0.74
	Tetra-site	-	-	-	-	-
		73.5	4.7	0.5	4.2	0.24
G5 (20-40 nm) dehydrated	Octa-site	11.3	2.8	1.0	2.7	98.17
	Penta-site	40.0	6.8	0.6	8.4	1.00
	Tetra-site	63.0	4.2	0.5	7.8	0.08
		72.8	4.8	0.5	8.0	0.75
G6 (10-30 nm) hydrated	Octa-site	11.3	2.6	1.0	2.7	99.3
	Penta-site	38.8	6.9	0.6	11.5	0.57
	Tetra-site	-	-	-	-	-
		74.5	5.0	0.5	9.0	0.12

G6 (10-30 nm) dehydrated	Octa-site	11.3	2.6	1.0	2.7	98.4
	Penta-site	40.1	6.9	0.5	12.9	1.06
	Tetra-site	63.0	4.2	0.5	8.2	0.06
		73.1	5.2	0.5	11.4	0.49
G7 (6-20 nm) hydrated	Octa-site	11.3	2.6	1.0	2.6	99.26
	Penta-site	40.1	6.9	0.6	10.3	0.60
	Tetra-site	-	-	-	-	-
		73.4	4.8	0.5	8.3	0.14
G7 (6-20 nm) dehydrated	Octa-site	11.3	2.6	1.0	2.7	97.62
	Penta-site	39.9	6.8	0.6	9.4	1.33
	Tetra-site	62.8	4.2	0.5	8.4	0.14
		72.9	5.4	0.5	10.9	0.90

^{23}Na Spin Counting

To consider the role of the sodium in the solids, it is helpful to discern the number of Na atom associated with one unit of the gel model structure given in Figure 2. The spin counting experiment is briefly described below. Under the same experimental conditions as those for acquiring the ^{23}Na MAS NMR spectra of the experimental samples, including the same probe tuning and match conditions, a ^{23}Na MAS NMR spin counting reference spectrum containing a single peak was acquired on a reference sample consisting of a full rotor of dried H-ZSM-5 zeolite sample and a known amount of, e.g., 3.1 mg of 0.1 M NaCl aqueous solution that was delivered to the center of the rotor by injection using a micro syringe. The use of zeolite with no Na is to create a diamagnetic environment for the MAS rotor that is similar to our experimental samples so that the matching and tuning conditions of the probe can be made the same. To

estimate, we can consider a simplified case where R1 to R13 are Al atoms, in this case the oxygen atoms are shared between two structures with each having 50%. For the dehydrated model of gel in Figure 2b, the unit model structure would contain 7Al + 19O + (13/2) O + 12 H. The molecular weight is approximately $7\times 27 + 19 \times 16 + 6.5\times 16 + 12\times 1 = 609$ g/mole. As such, 9.888×10^{17} model structures would be present in each mg of sample. There are about 0.183886×10^{17} Na atoms per mg of dehydrated gel. Thus, in average each model structure contains only about 0.0186 Na, or about 54 structural units share one Na. Details regarding the calculation are shown in Table S4

Table S4. The number of Na in the sample =

$(N_X/N_Y)^*(Y/X) \times 1.87 \times 10^{17}$ Na = $(1600/N_Y)^*(Y/X) \times 1.87 \times 10^{17}$ Na

Sample #	Weight	Absolute intensity	Number of scans	$(Y/X) \times 1.87 \times 10^{17}$ Na	Na/mg
H-ZSM-5	17.9 mg Zeolite + 3.1 mg 0.1 M NaCl in D_2O	X=278291264	N_X=1600		(1.87×10^{17} Na contained in 3.1 mg 0.1 M NaCl in D_2O)
Hydr-Gel	19.9 mg	Y=552605752	N_Y=1564	3.798×10^{17} Na.	0.191×10^{17} Na/mg
Hydr-G1	24.6mg	Y=267230024	N_Y=1600	1.796×10^{17} Na.	0.0730×10^{17} Na/mg
Hydr-G2	5.4 mg	Y=206112896	N_Y=4342	0.5104×10^{17}	0.0945×10^{17} Na/mg
Hydr-G3	24.9mg	Y=35791612	N_Y=1600	0.2405×10^{17}	0.00966×10^{17} Na/mg

Hydr-G4	24.1 mg	0	N_Y=1602	0	0
Dehy-Gel	29.3 mg	Y=1503406272	N_Y=3000	5.388×10^{17}	0.184×10^{17} Na/mg
Dehy-G1	30.4mg	Y=860121920	N_Y=3000	3.082×10^{17}	0.101×10^{17} Na/mg
Dehy-G3	24.3mg	Y=385651220	N_Y=3000	1.296×10^{17}	0.0533×10^{17} Na/mg
Dehy-G4	20.8mg	Y=362513760	N_Y=3000	1.218×10^{17}	0.0586×10^{17} Na/mg

Surface to volume ratio calculation

Gibbsite nanoparticles were approximated with the hexagonal prisms shape as shown in Figure S1 using Equations S1-S3 where $A_{surface}$ is the surface area of the hexagonal prism, V is the volume, R is the surface area to volume ratio, a is the apothem height, b is the length of the side of the base and h is the height of the prism. Geometric parameters were estimated from scanning electron micrographs, where the apothem height and length of the base were assumed to be equivalent. The height of the prism was estimated to be 20 nm for all samples.

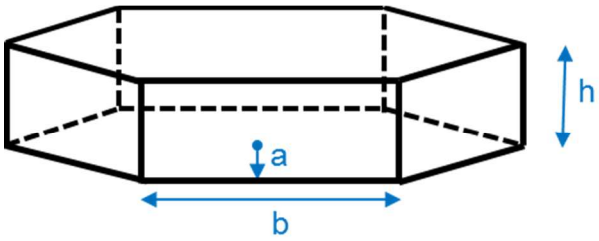

Figure S2. Hexagonal prism where a = apothem height, b = length of the base and h= height of the prism.

$$A_{surface} = 6b(a + h) \qquad \text{Equation S1.}$$

$$V = 3abh \qquad \text{Equation S2.}$$

$$R = \frac{A_{surface}}{V} \qquad \text{Equation S3.}$$

$$= \frac{2(a + h)}{ah}$$

XRD Gibbsite Fitting

The XRD pattern of Gibbsite was fit in Jade (v 9.5.1) between 2θ = (10,80). Curve fitting utilized automatic preferred orientation and XRD peak displacement. The intensity values of the d-list were refined in the end. A Pearson-VII function was used and the peaks were approximated with IPC-Curves. The results of the fit are shown in Figure S2. In Figure S2, the red curve is the residual, the green curve is the produced fit, and the black curve is the experimental data. The powder diffraction file (PDF) used was 00-007-0324 ($Al(OH)_3$)

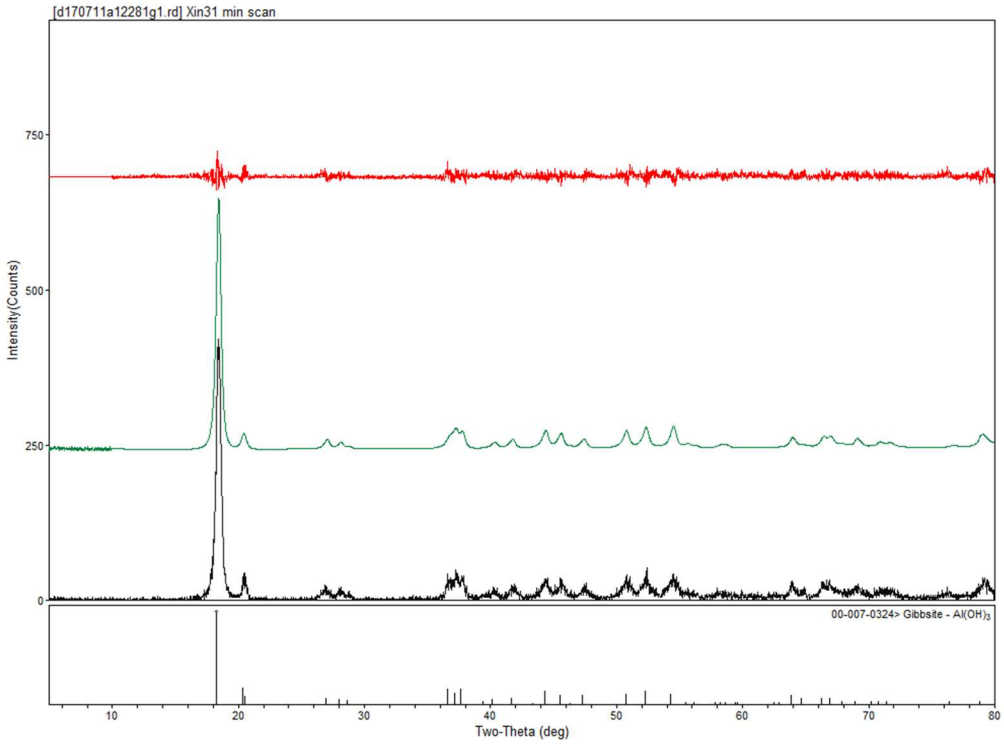

Figure S3. The results of the XRD peak fitting. The experimental data is shown in black, the simulated fit is shown in green and the residual is shown in red. The powder diffraction file is shown in the bottom window.