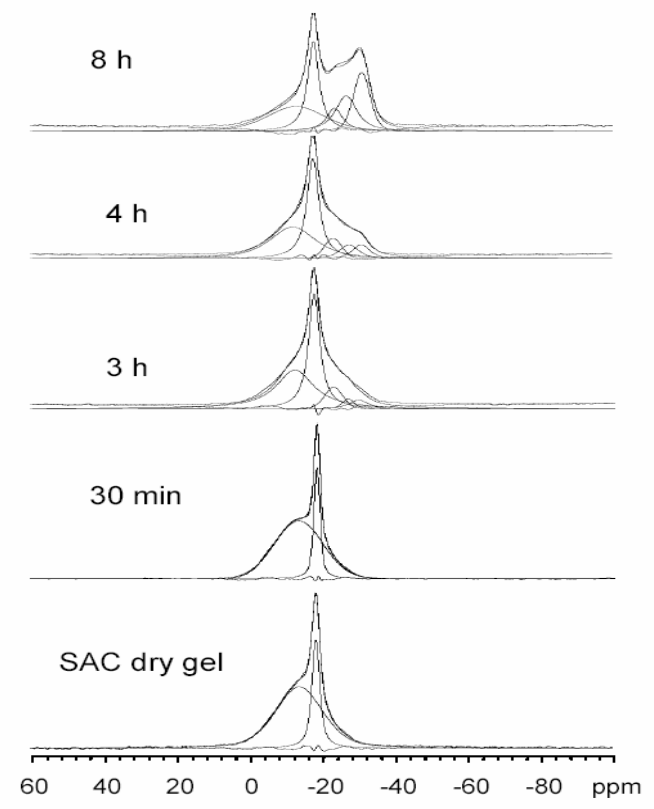
Supporting information

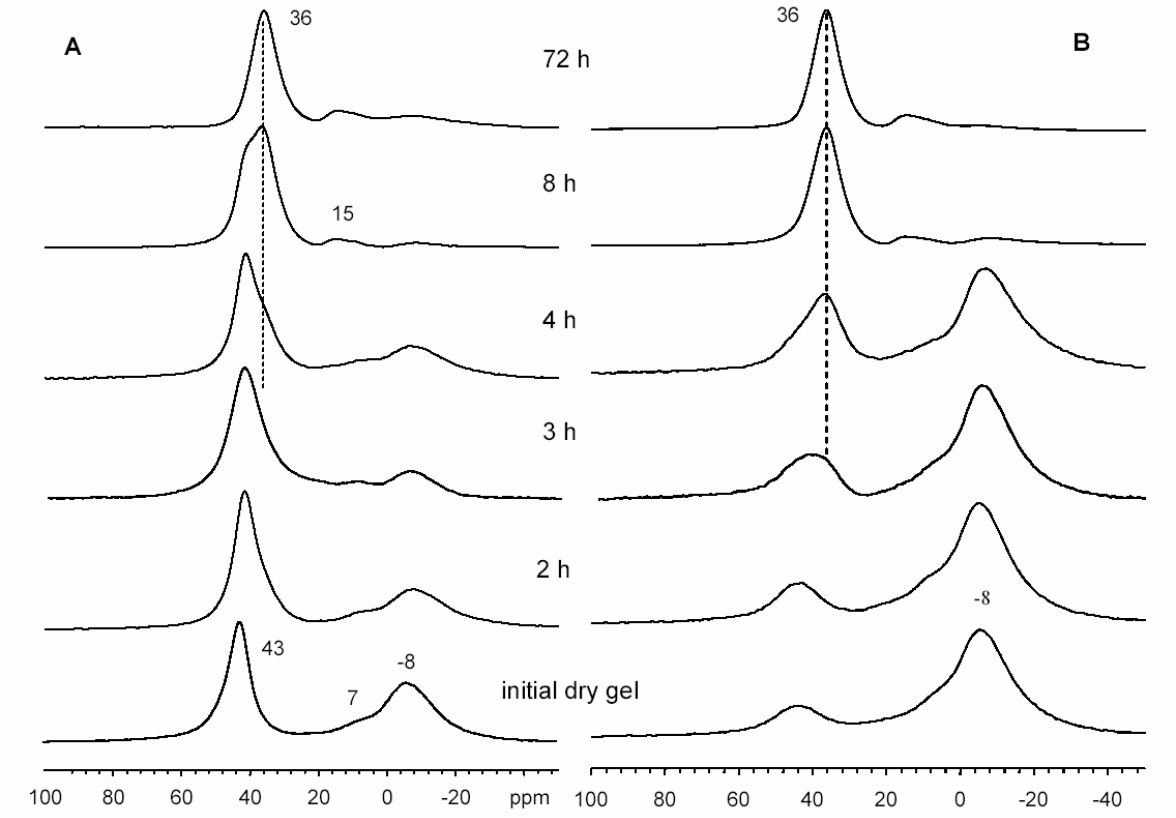


Supporting Figure S1. Deconvolution of ^{31}P MAS spectra of selected unwashed SAC gel samples.

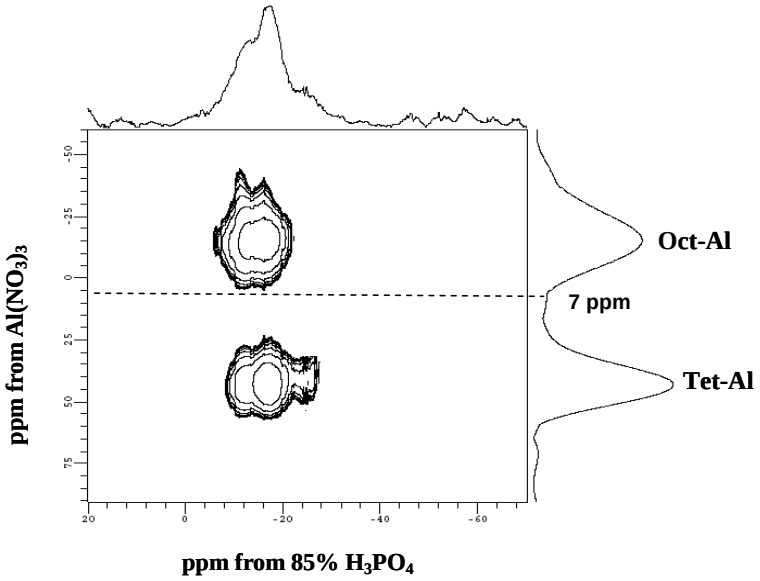
Supporting Table S1. Relative concentration of different phases based on the deconvolution of ^{31}P MAS spectra. (The three resonances in deconvoluted spectra at -24, -27 and -31 ppm are due to three crystallographi ally inequivalent P sites of $AlPO_4$-11) [1]

Sample	Amorphous phase % (-13 ppm)	Layered phase % (-18 ppm)	$AlPO_4$-11 % (-24, -27 & -31 ppm)
0 min	76	24	0
30 min	74	26	0
3 h	44	40	16
4 h	39	39	22
8 h	28	26	46

[1] Chen, B.; Huang, Y. *J. Am. Chem. Soc.* **2006**, *128*, 6437 and references therein.



Supporting Figure S2. ^{27}Al MAS spectra of (A) unwashed and (B) washed SAC gel samples

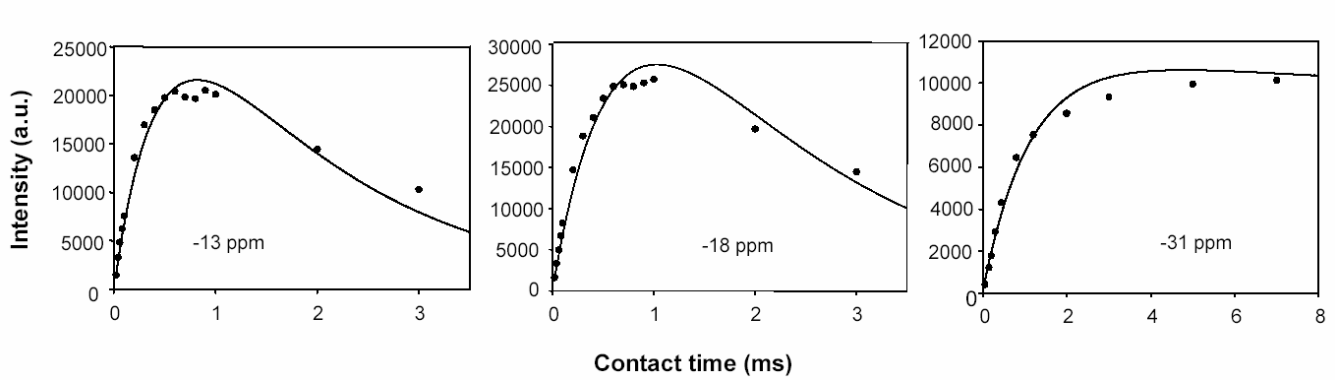


Supporting Figure S3. $^{27}Al \rightarrow {}^{31}P$ HETCOR spectrum of initial SAC dry gel with a contact time of 1 ms. For each of the 32 experiments in t_1, 4800 scans were acquired. The spinning rate was 6.5 kHz.

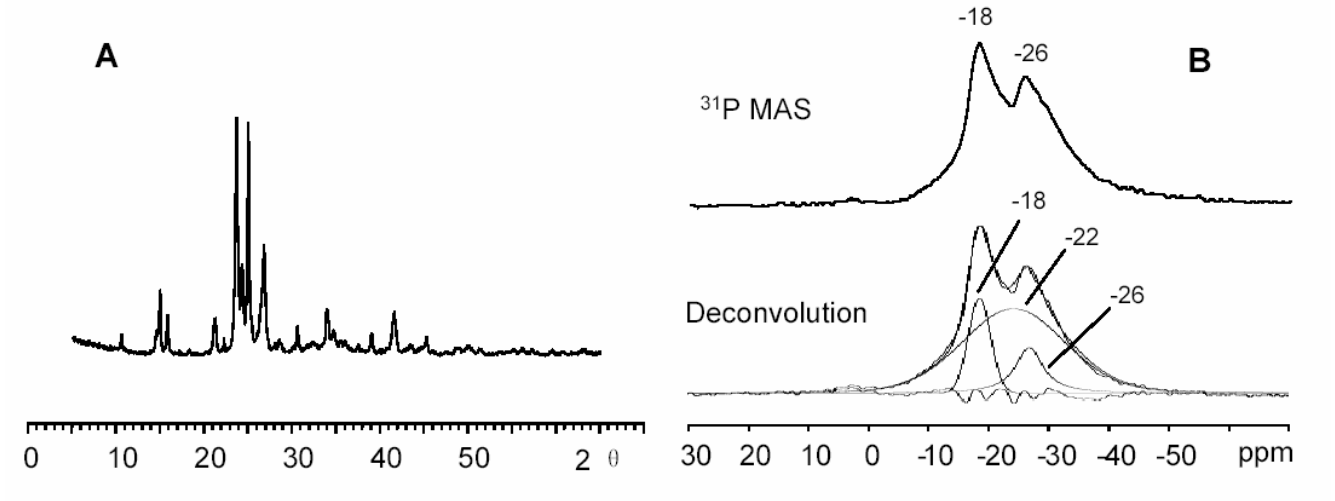
Heteronuclear correlation spectroscopy (HETCOR) is a 2D version of cross polarization (CP) experiment. Since CP is based on heteronuclear dipolar interaction that is strongly dependent on the internuclear distance, CP spectra can provide the information on connectivity between two unlike spins involved.[1,2] In the case of $^{27}Al \rightarrow {}^{31}P$ CP, only the ^{27}Al nuclei that are in the close vicinity of P atoms will appear in the HETCOR spectrum. This approach has been utilized to select P-O-Al linkage in AlPO-based materials.[2] We carried out the $^{27}Al \rightarrow {}^{31}P$ HETCOR experiment to verify the assignment that the Al signal at 7 ppm seen in the ^{27}Al MAS spectrum of unwashed initial SAC dry gel (Figure S2) is due to the unreacted alumina. The HETCOR spectrum (Figure S3) shows that both Tet-Al and Oct-Al sites are strongly correlated to the broad P resonance. However, the shoulder peak at 7 ppm in the MAS spectrum does not appear in the Al projection. This observation clearly confirms that the 7 ppm Al site is due to the unreacted aluminum oxide rather than the five-coordination Al in an AlPO species.

[1] Vega, A. J. *Solid State NMR,* **1992**, *1*, 17.

[2] Fyfe, C. A.; Mueller, K. T.; Grondey, H.; Wong-Moon, K. C. *J. Phys. Chem*. **1993**, 97, 13484.



Supporting Figure S4. $^{1}H \rightarrow {}^{31}P$ CP intensities as a function of contact time for different P sites.



Supporting Figure S5. (A) Powder XRD pattern of initial VPT dry gel heated without DPA for 72 h (only a small amount of water was placed at bottom of autoclave). (B) Deconvolution of ^{31}P MAS spectrum of 15 min VPT dry gel sample.