

## Direct Observation of Various Al Sites in SAPO-34 by $^{27}\text{Al}$ Multiquantum (MQ) Magic Angle Spinning (MAS) NMR

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**Abstract:** The elegant 2D multiquantum (MQ) MAS NMR has been applied to investigate the coordination of Al atoms in SAPO-34. The results show that the effects of the template and/or water on the coordination of Al atoms are significant, which lead to the formation of various Al species. Up to four kinds of Al species are distinctly resolved.

**Keywords:** SAPO-34,  $^{27}\text{Al}$  MQ MAS NMR,  $^{27}\text{Al}$  MAS NMR, structure.

SAPO-34, an isotype of the chabazite structure, is known as a promising catalyst for methanol conversion to light alkenes<sup>1</sup>. It has been shown that its structure is very sensitive to water at room temperature after template removal<sup>2</sup>. Thus the presence of template and/or water has great effects on its structure modifications, particularly on the coordination states of Al sites. Although 1D  $^{27}\text{Al}$  magic angle spinning (MAS) NMR spectroscopy has been widely used to investigate the coordination state of Al in SAPOs, it is difficult to distinctly resolve the different Al species because of its complex coordination states and quadrupolar nuclear nature ( $I=5/2$ ). On the contrary, the recently developed 2D multiquantum (MQ) MAS NMR method<sup>3</sup> has been verified to be a powerful technique to elucidate the structure of aluminosilicates, silicoaluminophosphates, and aluminophosphates. In this paper, we present 2D  $^{27}\text{Al}$  3Q MAS NMR results of SAPO-34 to reveal the effects of the template and/or water on the coordination states of Al species.

SAPO-34 was synthesized hydrothermally according to published method using triethylamine as a template<sup>4</sup>. The product was calcined in air at 823K for 5 h to remove the template. The samples were equilibrated with the saturated water vapor of a  $\text{NH}_4\text{Cl}$  aqueous solution overnight before being packed into NMR-MAS rotors. The dehydrated sample was obtained by heating it at 673K for 20h with outgassing below  $10^{-2}$  Pa using a home-made *in situ* apparatus<sup>5</sup>.

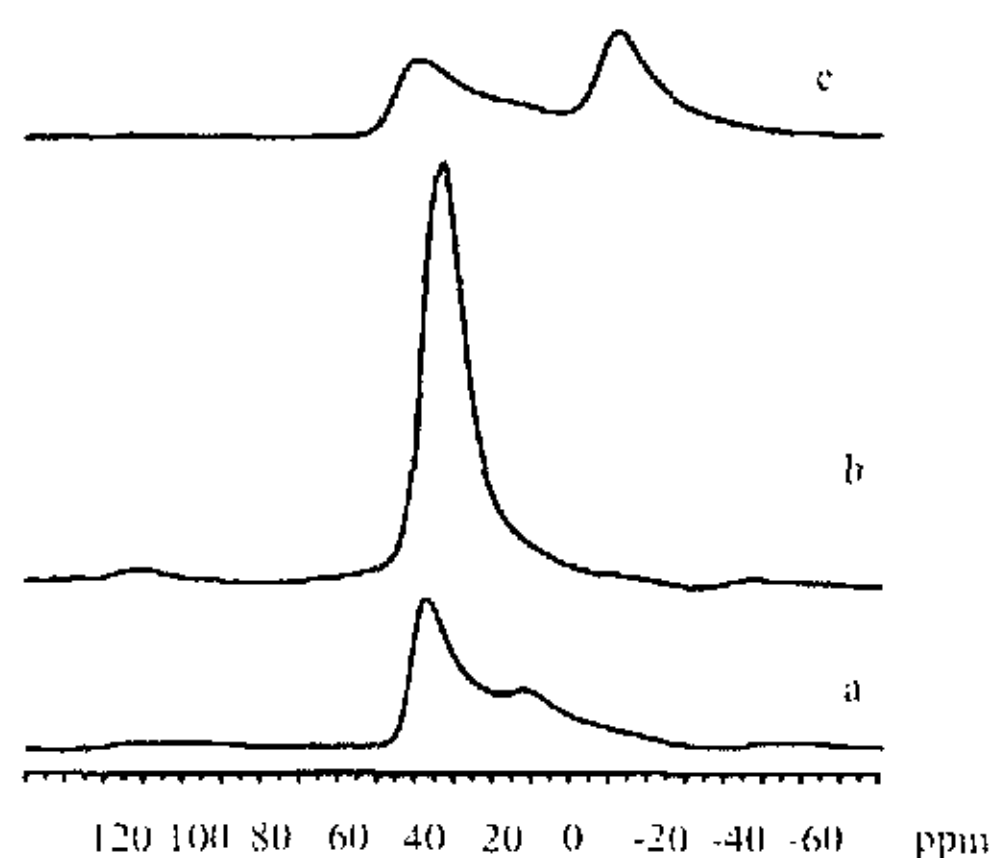
The NMR measurements were carried out at room temperature on a Bruker DRX-400 NMR spectrometer.  $^{27}\text{Al}$  MAS NMR spectra were recorded at 104.3 MHz

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(9.4 T) using a  $0.75 \mu\text{s}$  ( $\pi/12$ ) pulse with a 3 s recycle delay and 200 scans. For  $^{27}\text{Al}$  3Q MAS NMR, a three-pulse multiquantum MAS sequence was employed. In concert with the TPPI technique<sup>6</sup>, pure-phase MQMAS spectra were obtained using a z-filter method<sup>7</sup>, where the phase cycling was designed to select the coherence pathway of  $0 \rightarrow \pm 3 \rightarrow 0 \rightarrow -1$ . The spectra were recorded with  $512 \times 256$  data points and zero-filled to  $512 \times 512$  before 2D Fourier transform. For each  $t_1$  increment, 48 scans were used to accumulate the signals with a recycle delay of 2 s. A shearing transformation was performed after the 2D transform. The chemical shift was referenced to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ .

**Figure 1**  $^{27}\text{Al}$  MAS NMR spectra of SAPO-34 (a) as-synthesized, (b) calcined and dehydrated, (c) calcined and rehydrated

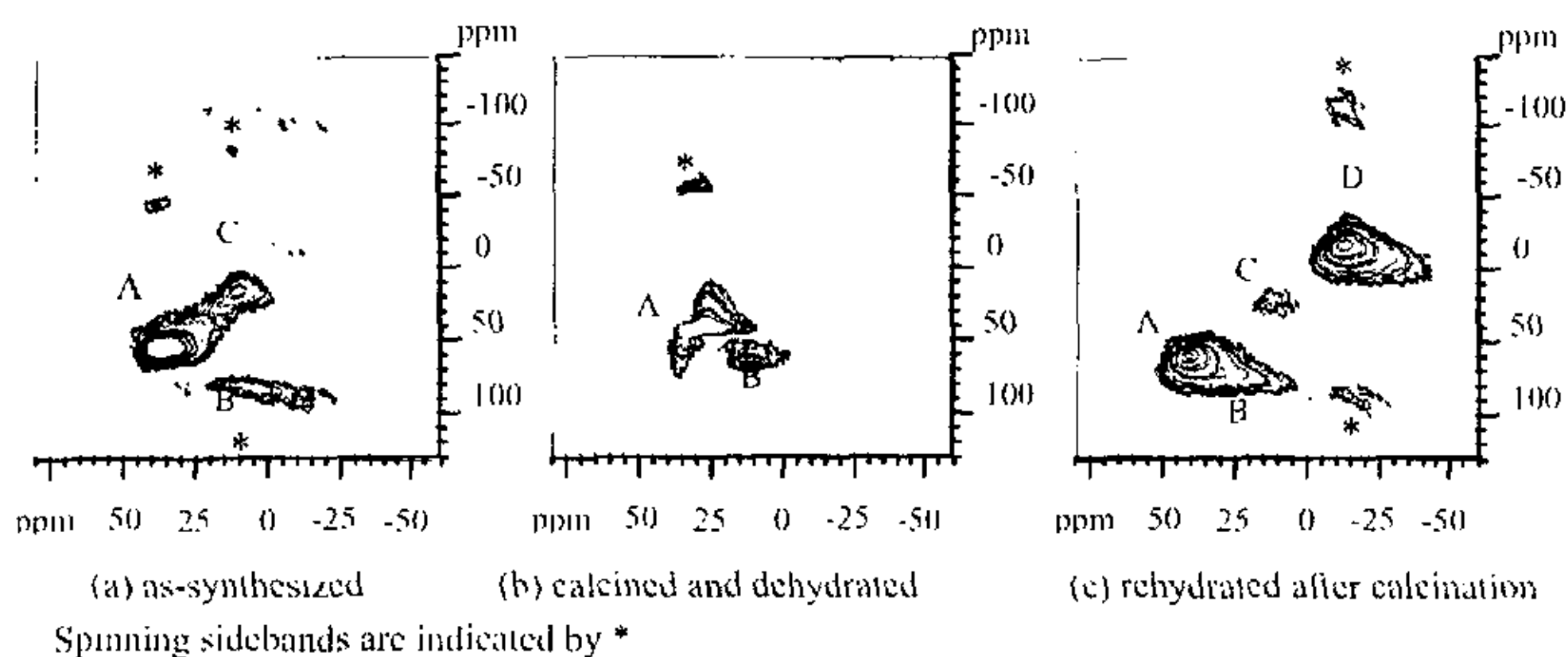


The  $^{27}\text{Al}$  MAS NMR spectra of as-synthesized, calcined dehydrated, and calcined rehydrated SAPO-34 are shown in **Figure 1**. For the  $^{27}\text{Al}$  MAS NMR spectrum of as-synthesized sample (**Figure 1a**), two components are clearly detected centered at *ca.* 37 and 11 ppm typically corresponding to tetrahedral and five-coordinate Al species, respectively. At the same time, a broad and tailing band centered *ca.* -7 ppm is observed. Its nature will be discussed later. **Figure 1b** shows the  $^{27}\text{Al}$  spectrum for the calcined and dehydrated SAPO-34 sample. It should be noted that only one asymmetric peak at *ca.* 33 ppm occurs after calcination, which can be assigned to tetrahedral coordination Al sites. Upon rehydration of calcined SAPO-34, the spectrum changes remarkably as shown in **Figure 1c**. A broad peak with a maximum at *ca.* -12 ppm, which is attributed to six-coordinated Al species, is seen with other two peaks at *ca.* 39 and 13 ppm due to tetrahedral and five-coordinate Al species respectively. It was concluded that the  $^{27}\text{Al}$  chemical shift indicative of higher coordination (five- and six-coordinated) arose from an additional secondary interaction of Al with extra-framework water, OH, and/or template in the sieve cavities<sup>8</sup>.

**Figure 2** shows the 2D 3Q MAS NMR spectra of the same samples. The isotropic chemical shift  $\delta_{\text{iso}}$  as well as the second order quadrupolar effect (SOQE) can be deduced from the position of the signals in the 2D spectrum<sup>9</sup>. Obviously, the 2D

spectra exhibit a more resolved pattern than the 1D experiments. Three Al species, marked as A, B, and C, are distinctly separated in the as-synthesized sample (**Figure 2 a**). Signal A with relatively strong intensity and SOQE value (3.9 MHz) can be unambiguously assigned to tetrahedral framework Al according to its position, and signal C, which is a relatively faint peak in the 1D  $^{27}\text{Al}$  MAS NMR spectrum, is reasonable to be assigned to five-coordinated Al species by its position. Signal B lies along the anisotropic axis and displays the strongest quadrupolar interaction (SOQE = 8.2 MHz) in this sample. From the isotropic chemical shift (52 ppm) of signal B and its SOQE value, this signal has to be attributed to tetrahedrally coordinated Al species with a quadrupolar effect stronger than that of signal A. This signal B could correspond to Al sites with Si as the nearest neighbor, *i.e.*, SAPO phase, while signal A could result from AIPO phase. Compared the results of the 1D spectrum, signal B corresponds to the broad and tailing band centered *ca.* -7 ppm, which has been proved to be caused by strong quadrupolar coupled Al species. In the 2D 3Q MAS spectrum of calcined and dehydrated sample, only two signals are left corresponding to the tetrahedral Al sites causing signal A and B, both showing reduced SOQE value after the removal of template and water. Upon rehydration an additional signal D, due to six-coordinated Al species, is observed as shown in **Figure 2c**. At the same time, signal B appears as a tail to signal A, indicating a highly distorted electronic environment and a distribution of chemical shifts. Moreover, the observed signal C is resulted from five-coordinated Al due to the adsorption of  $\text{H}_2\text{O}$  molecules near the framework Al atoms. This fact indicates that water molecules modifies the structure during hydration, and thus some of the tetrahedral Al atoms are changed to five- and six-coordinated Al species in the presence of water.

**Figure 2**  $^{27}\text{Al}$  3Q MAS NMR spectra of SAPO-34



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