

## COMMENTS

**Comment on “ $^{27}\text{Al}$  Multiple-Quantum Magic Angle Spinning NMR Study of the Thermal Transformation between Microporous Aluminum Methylphosphonates AlMepO- $\beta$  and AlMepO- $\alpha$ ”**

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AlMepO- $\alpha$ <sup>1</sup> and AlMepO- $\beta$ <sup>2,3</sup> are two polymorphs of microporous aluminum methylphosphonates reported by us. In 1997 a thermal transformation of AlMepO- $\beta$  into AlMepO- $\alpha$  in the presence of water vapor was reported independently by Carter et al.<sup>5</sup> (they refer the materials as AlMePO) and us.<sup>4</sup> Both proposed similar topotactic transformation mechanisms based on a resemblance between the framework structures. Recently, Brown and co-workers<sup>6</sup> tried to analyze this phenomenon using  $^{27}\text{Al}$  five-quantum (5Q) MAS NMR reported in *J. Phys. Chem. B*. They measured MAS NMR spectra of the samples supplied by Carter on an assumption that the spectrum of a sample where the thermal transformation has been interrupted before the complete transformation should be identical with that of a simple mixture of AlMepO- $\alpha$  and AlMepO- $\beta$ . As a conclusion, they suggested that the proposed topotactic transformation mechanism may not be true because the spectrum of the partly transformed sample did not match that of the mixture and that more commonplace mechanism takes place. We agree with the usefulness of this new MAS NMR technique to obtain precise information of local structures. Deep knowledge on the materials, however, is essential to understand the phenomena on the materials. They tried to interpret their result only from their NMR result without examining the reported evidences of the topotactic transformation carefully. In this Comment we attempt to show that their premise of the discussion is not correct and to give another possible explanation to their result.

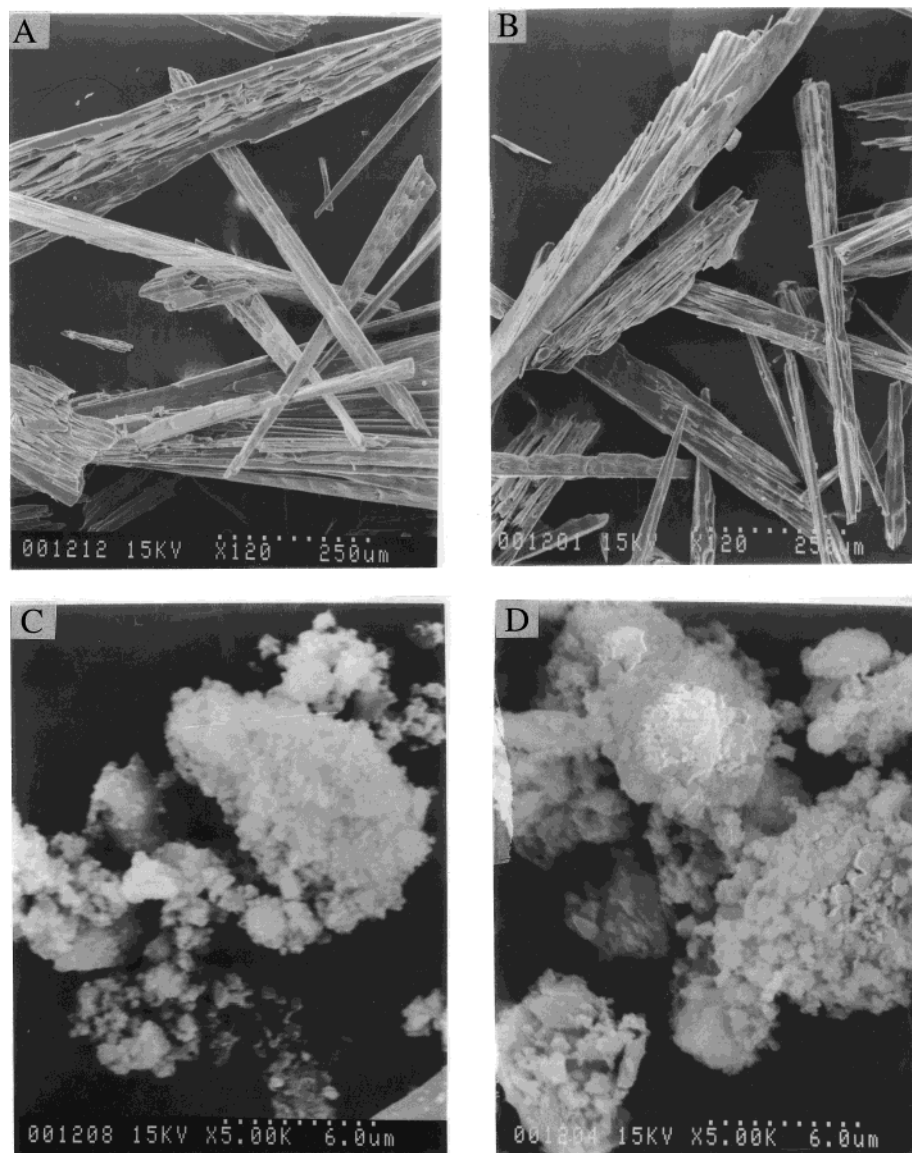
Several topotactic transformations between open framework structures were reported for zeolites and  $\text{AlPO}_4$ 's (see literatures cited in refs 4 and 5). These phenomena are generally characterized by related framework structures and no apparent morphological change of the crystals. According to a SEM image, as-synthesized AlMepO- $\beta$  has needle-shaped morphology and bundles of them as is shown in Figure 1. Each needle is fundamentally a single crystal, namely composed of a single domain, as is obvious from our single-crystal X-ray diffraction

measurement.<sup>3</sup> The topotacticity of the transformation is supported by no apparent morphological change before and after the transformation (Figure 1A,B). Brown et al. considered the nucleation growth mechanism more commonplace, and if so, such a transformation is generally followed by a morphological change of the grains. They suggested that nucleation of new AlMepO- $\alpha$  domains takes place much faster than domain growth. If this hypothesis could be correct, morphology of particles will have needle-shaped motif after transformation of the crushed AlMepO- $\beta$  crystals as AlMepO- $\alpha$  crystals prepared by hydrothermal methods.<sup>7</sup> However, Figure 1, C and D, showed that the morphology does not change throughout the transformation even when the crystals were crushed.

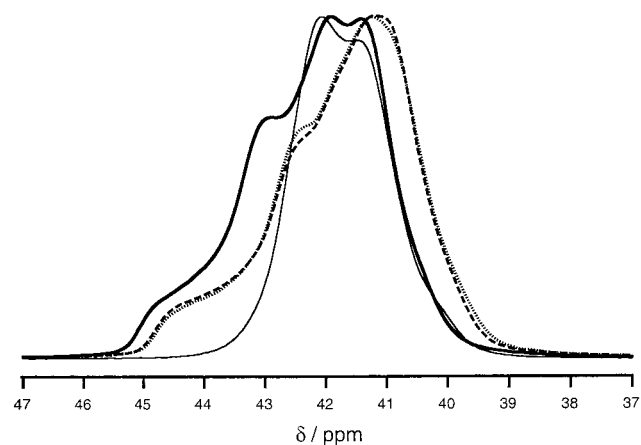
Brown et al. gave no information about the preparation and the treatment of their samples except referring to the paper of Carter et al.,<sup>5</sup> though the samples are sensitive to the way they were handled. According to ref 5, Carter's AlMepO- $\beta$  was prepared obviously using dioxane, basically following our preparation method<sup>3</sup> ( $\beta$ -DX in ref 8). Their AlMepO- $\beta$  sample, therefore, must contain a considerable amount of dioxane in the channels unless the as-synthesized AlMepO- $\beta$  was heated or degassed. The sample must have been treated between 450 and 500 °C in the presence of moisture for the transformation to take place. If this is the case, dioxane is evaporated out of the channels during heating and AlMepO- $\beta$  component of the sample during the transformation at high temperature is dioxane free. Therefore, their premise, on which the sample in the midst of the transformation should be the same as a mixture of the starting AlMepO- $\beta$  and the transformed AlMepO- $\alpha$ , is at least not correct. It is natural for us to give another explanation to their result rather than expressing doubt on the topotactic transformation mechanism.

We reported  $^{27}\text{Al}$  and  $^{31}\text{P}$  MAS NMR of AlMepO- $\alpha$  and AlMepO- $\beta$  prepared in different methods<sup>8</sup> in 1997, although Brown and co-workers<sup>6</sup> did not refer to it. We found that the spectra of AlMepO- $\beta$  were slightly different depending on the preparation procedures. Expanded spectra of tetrahedral region of  $^{27}\text{Al}$  MAS NMR (39–46 ppm) of samples prepared in different methods are shown in Figure 2. Three resolved peaks were observed by an ordinary MAS NMR for AlMepO- $\beta$  prepared in the presence of dioxane ( $\beta$ -DX). On the contrary, the sample prepared without dioxane ( $\beta$ -NA in ref 6) gave a spectrum with a relative upper magnetic field shift of ca. 0.5 ppm and less resolved peaks. Even if the relative frequency shift, as Brown et al. discussed,<sup>6</sup> can be considered, there is still a significant difference in relative peak positions and line shapes. When dioxane was removed from  $\beta$ -DX by heating at 400 °C for 2 h under nitrogen ( $\beta$ -DX-h) the peak shape became identical with that of  $\beta$ -NA. This result clearly shows that the existence of dioxane in the sample affects on the spectra of AlMepO- $\beta$ . The difference we observed between  $\beta$ -DX and  $\beta$ -NA probably arises from the difference in mean Al–O–P angles because those samples have considerably different lattice constants.<sup>8</sup> Since the 5Q MAS NMR is supposed to be more sensitive to the local structure, clearer difference between dioxane-containing and dioxane-free samples is expected in the case of Brown et al. It is, therefore, reasonable for them to

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**Figure 1.** SEM images of AlMepO- $\beta$  ( $\beta$ -DX): (A) as-synthesized sample, (B) sample A after heated at 500 °C for 2 h under a flow of water vapor (2600 mL/min)/ nitrogen (100 mL/min) mixture, (C) crushed sample, and (D) sample C treated as sample B. Samples B and D were transformed into AlMepO- $\alpha$ .



**Figure 2.**  $^{27}\text{Al}$  MAS NMR spectra of (a) as-synthesized AlMepO- $\beta$  prepared with dioxane ( $\beta$ -DX, thick solid line), (b) as-synthesized AlMepO- $\beta$  prepared without dioxane ( $\beta$ -NA, broken line), (c)  $\beta$ -DX heated at 400 °C for 2 h under nitrogen ( $\beta$ -DX-h, dotted line), and (d) as-synthesized AlMepO- $\alpha$  ( $\alpha$ -SC, thin solid line) recorded on a Bruker AMX-500 spectrometer. Other details on measurement conditions are the same as in ref 7.

observe the new peak that does not match with the peaks observed for the as-synthesized sample.

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#### References and Notes

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