Synthesis of Microporous Aluminum Methylphosphonate AlMepO-α by Steam-Induced Topotactic Transformation of AlMepO-β

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Steaming treatment of AlMepO–β at 500 °C induces transformation into AlMepO–α. This procedure easily gives pure AlMepO–α with a large adsorption capacity. A topotactic transformation mechanism through coordination of water molecules at an aluminum site is proposed from comparison of both the framework structures.

Zeolites and related microporous crystals have been of considerable interest because of various applications utilizing uniform size of channels. AlMepO–α[1] and AlMepO–β[2,3] are unprecedented "organo-zeolites" hydrothermally synthesized from boehmite and methylphosphonic acid. Both the compounds have unidimensional channels composed of 18-MR (ring composed of 18 Al and P atoms) and fringed with methyl groups. Especially, a triangular cross section of the channels of AlMepO–α showed interesting gas adsorption properties.[4] Although AlMepO–β was prepared in a pure form easily from an aqueous mixture of the starting materials, it has been difficult to obtain pure AlMepO–α. AlMepO–α samples synthesized on a bulk scale using ethylene glycol as solvent inevitably contained small amounts of AlMepO–β and non-porous phases.[5] Also the procedure giving single crystals of AlMepO–α was not practical because of a very low yield.[1] In this communication we report a new simple procedure to obtain pure AlMepO–α. Since both AlMepO–α and AlMepO–β are stable up to approximately 500 °C under inert atmospheres, their thermal stability under humid conditions has aroused interest. Several zeolites including aluminophosphates ($AlPO_4$) topotactically transform into other microporous phases upon heating under ambient conditions.[6-8] No topotactic transformation, however, has been reported for microporous crystals other

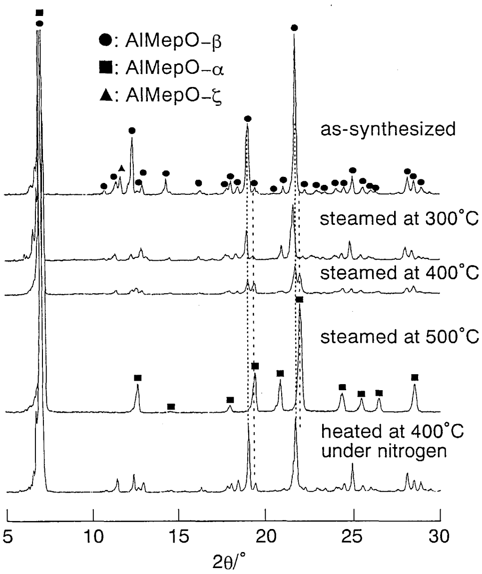

Figure 1. XRD of AlMepO–β before and after steaming at 300-500 °C, and after heating at 400 °C under nitrogen.

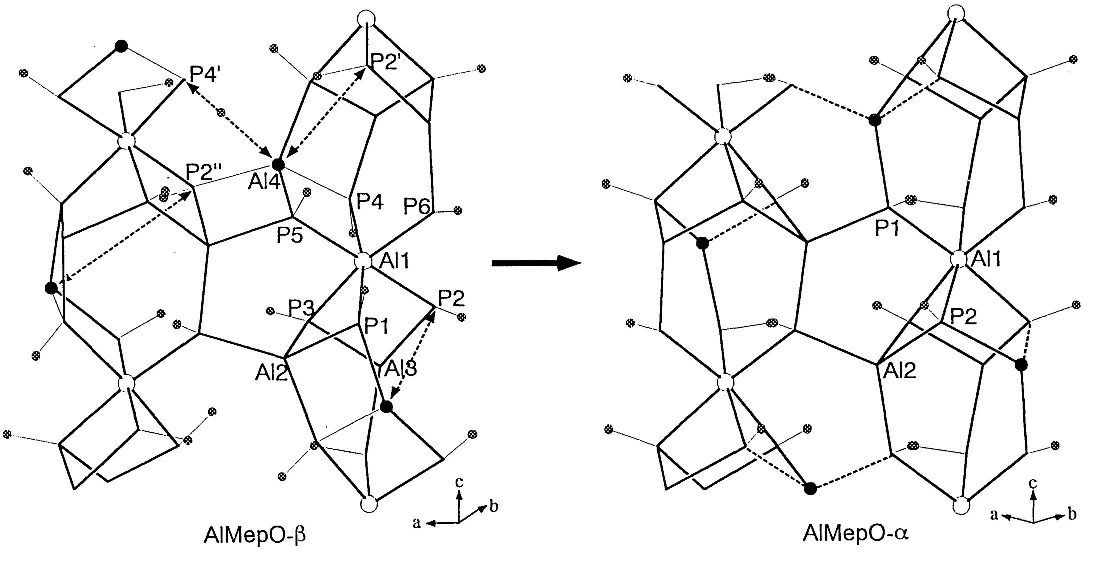

Figure 2. Comparison of framework structures of AlMepO–β (left) and AlMepO–α (right). Oxygen atoms are omitted. White, large black, and small black circles denote Al_{Oh}, Al4, and methyl groups, respectively. On the transformation, connections denoted by thin solid line are broken and reconnected [broken line with arrows (left) and broken line (right)].

than aluminosilicates and $AlPO_4$. We found out that AlMepO−β topotactically transforms into AlMepO−α upon heating only when water vapor is present.

AlMepO−β was prepared using dioxane as an additive according to the reported procedure.[5] Pulverized AlMepO−β sample (0.3 g) was steamed at 200, 300, 400, 500, and 600 °C for 3 h in a quartz tube of 40 mm diameter under a flow of water vapor (2600 ml/min)/ nitrogen (100 ml/min) mixture, respectively. According to XRD of the samples before and after the steaming treatment, AlMepO−β was fundamentally intact up to 300 °C as shown in Figure 1. AlMepO−β structure began to transform into AlMepO−α at 400 °C and completely transformed at 500 °C. Also ^{27}Al MAS-NMR supported the complete transformation. At this temperature, shortening of steaming time to 15 min did not affect crystallinity and adsorption capacity. On the other hand, no phase transformation was observed up to 500 °C under a flow of dry nitrogen. At 600 °C the sample became black and amorphous irrespective of the conditions under dry or wet nitrogen. As-synthesized AlMepO−β contains considerable amounts of dioxane probably in the unidimensional channels. Removal of the dioxane included in AlMepO−β by evacuation upon heating did non affect the transformation into AlMepO−α. AlMepO−β was obtained as needle crystals and bundles of them. According to SEM the morphology of the crystals was preserved after the transformation into AlMepO−α. The fact that no apparent morphological change was observed suggests that the phase transformation is topotactic.

Comparison of the framework topologies of both the compounds revealed the mechanism of the topotactic transformation (Figure 2). The crystallographically independent sites in AlMepO−β consist of 1 Al_{Oh} (octahedral Al), 3 Al_{Th} (tetrahedral Al), and 6 P. The positions of these sites, except Al4, look almost unchanged after the transformation. At first, two connections, Al4–P2" and Al4–P4, included in the fused 4-MR chains are broken. Accompanied by migration of the position, Al4 is reconnected with P2' and P4'. Thus, the framework of AlMepO−β can be topologically transformed into that of AlMepO−α. The single crystal X-ray analysis revealed that deviation from the ideal O-Al-O angle (109.5 °) of Al4 is the largest among the three Al_{Th} sites because Al4 locates at the node of fused three 4-MRs. The Al_{Th} site of AlMepO−α is less distorted than all the Al_{Th} sites of AlMepO−β. Actual transformation mechanism requires also consideration on oxygen atoms. It is known that hydration of $AlPO_4$ causes formation of octahedral aluminum centers by coordination of water molecules.[9,10] Under high water vapor pressure, also Al_{Th} of AlMepO−β is expected to be octahedrally coordinated by water in spite of hydrophobicity of the channels. The distortion around the Al4 sites should be advantageous to the water coordination. The coordinated water molecules can attack the neighboring phosphorus atoms. Reduction of the strain around the Al4 site will favor the formation of a new bond and to weaken the existing bond at the opposite side. The framework structure shows that Al4 and P2 (or P4) related by the broken and formed connections alternately locate almost in a linear way. The linear arrangement should facilitate the successive rearrangement of the bonds.

We have already revealed that all the synthesized samples of AlMepO−α gave peculiar nitrogen adsorption isotherms with two adsorption steps in low relative pressure region[4] (Figure 3c), while AlMepO−β gave typical isotherm of type I (Figure 3a). AlMepO−α obtained upon steaming of AlMepO−β at 500 °C for 15 min also gave an isotherm with clear two steps (Figure 3b). This result supports that the isotherm with the two steps is not caused by sample impurity but is characteristic of AlMepO−α. Larger adsorption capacity (0.140 ml g^{-1}) of AlMepO−α by the steaming procedure compared with that (0.115 ml g^{-1})[4] of AlMepO−α synthesized using ethylene glycol as solvent show that the steaming of AlMepO−β is effective route to obtain pure AlMepO−α.

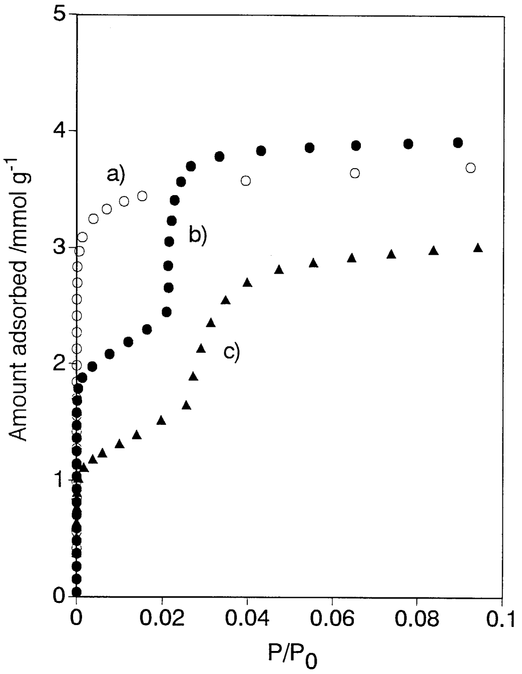

Figure 3. Nitrogen adsorption isotherms at 77 K of AlMepO−β before steaming (a), sample after steaming at 500 °C for 15 min (b), and AlMepO−α synthesized using ethylene glycol as solvent (c). All the samples were degassed at 450 °C for 10 h prior to the adsorption measurement.

References and Notes

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