A Convenient Synthesis of MAPO-36 (ATS) by Dry-gel Conversion (DGC) Technique

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MAPO-36 (ATS topology), which is one of the metalloaluminophosphate molecular sieves, was successfully synthesized by means of dry-gel conversion (DGC) technique.

Metal-substituted aluminophosphates have been the subject of a variety of studies since their synthesis was first reported by Flanigen et al.[1] The replacement of Al^{3+} by divalent, or P^{5+} by tetravalent cations can lead to Brønsted acid sites, which makes these materials useful in acid-catalyzed reactions. At the same time, molecular sieves with pores comprising of 12 T-atoms (so-called 12-ring pores as well as "large-pores") are expected to be useful because they should have ability to perform catalysis and/or adsorption on relatively bulky organic molecules. MAPO-36 (ATS topology)[2] is a magnesioaluminophosphate having one-dimensional and 12-ring channels along [001] with 6.5 × 7.4 Å of pore diameter and also annular side pockets.[3] Molecular sieves having ATS topology are interesting subjects to study in connection with the fact that SSZ-55 was very recently discovered as a silicate version of ATS.[4] In the MAPO-36, aluminium sites are partly substituted by magnesium atoms. Very often, co-crystallization of MAPO-5 (AFI topology)[2] is an obstacle to the formation of pure ATS by hydrothermal synthesis (HTS) method.[5]

In order to overcome this problem, we tried to utilize dry-gel conversion (DGC) technique.[6–8] This technique is a kind of dry-synthesis where the utilization of bulk water is avoided, which can be more specifically classified into two different but interrelated methods; vapor-phase transport (VPT, as used by Kim et al.[6]) and steam-assisted conversion (SAC, as used by Matsukata et al.[8]) methods. Various aluminosilicate,[8,9] boron-substituted,[10] and titanium-substituted[11,12] molecular sieves have been synthesized by DGC technique. Unlike the HTS method, synthesis by DGC allows nearly complete conversion of gel to high crystalline molecular sieve with high yield, and involves minimization of waste disposal and reduction in reactor volume.[6] Uniform crystals with smaller particle size are also obtained by this technique.[7,11] Moreover, there are some examples in which dry conditions are essential or desired to give particular phases and properties.[7–9,11–13]

We report here the synthetic investigation of pure ATS by DGC technique. The effect of synthetic conditions on the phase selection during the synthesis, and the characterization of the products were the main interests of the study.

Although we verified that both VPT and SAC methods work quite similarly in the ATS synthesis, we give only the results by VPT method in this report. A typical procedure with an initial gel composition $0.92Al_2O_3$–$0.17MgO$–$1.0P_2O_5$–$45H_2O$ is as follows: An aqueous solution of $Mg(OCOCH_3)_2$ (1.7 mmol) was added to an aqueous suspension of Al(OPr-*i*)$_3$ (9.2 mmol). To this mixture, 40% H_3PO_4 (10 mmol) was added and stirring was continued until the gel became homogeneous. The gel was then dried at 80 °C in an oil bath with continuous stirring. The dry-gel obtained was ground into a fine powder and poured into a small Teflon cup (20 × 20 mm I.D.), which was placed in a Teflon-lined autoclave (23 mL) with the support of a Teflon holder. Pr_3N (18 mmol) as strucuture-directing agent (SDA) and small amount (ca. 0.3 g per 1.0 g of dry gel) of water as the source of steam were taken at the bottom of the autoclave in such a manner that these vapor sources never came into the direct contact with the dry-gel. The heating protocol was 105 °C for 48 h, followed by 140 °C for 24 h. After the crystallization, the product was washed by centrifuging and dried to give 2.65 g of white powder. This as-synthesized sample was carefully calcined in a flow of air (50 $cm^3 min^{-1}$) as follows: The temperature was raised from 25 to 200 °C over a period of 1.5 h, and maintained at 200 °C for 2 h. Then the temperature was raised to 550 °C over a period of 3 h and kept at 550 °C for another 6 h, and finally cooled in ambient conditions. Characterizations were performed by various physicochemical techniques.

Table 1 shows the selected results of the synthesis by VPT, and Figures 1b and 1c show the representative XRD patterns of the resultant pure ATS. The XRD pattern of ATS contaminated by AFI (synthesized by HTS method) and the simulated pattern of ATS are also shown for comparison in Figures 1a and 1d, respectively. The conditions for pure ATS formation were optimized with the variation of gel compositions and heating protocol. As shown in Table 1, the phase selection was very sensitive to the heating protocol. When the dry-gel was isothermally heated at 140 or 150 °C for 48 h, a mixture of ATS and AFI was formed (Samples 1 and 2). Heating at lower temperature (105 °C) for 12–84 h caused no crystallization. Interestingly, stepwise heating at 105 °C for 48 h (the first step) followed by 140 °C for 24 h (the second step) gave pure ATS (Samples 3

Table 1. Synthesis of MAPO-36 by DGC technique[a,b]

Sample No.	MgO/Al_2O_3[c]	Temp./°C and Time/h[g]	Product
1	0.180	140(48)	ATS + AFI
2	0.180	150(48)	ATS + AFI
3	0.180[d]	105(48)–140(24)	ATS
4	0.180	105(48)–150(24)	ATS
5	0.180	100(48)–140(24)	ATS + AFI
6	0.180	100(72)–120(72)–140(72)	ATS + AFI
7	0.100[e]	105(48)–140(24)	ATS
8	0.050	105(48)–140(24)	ATS[h]
9	0.250[f]	105(48)–140(24)	ATS[i]
10	0.326	105(48)–140(24)	AFI + impurity

[a]Starting gel composition: $Al_2O_3/P_2O_5 = 0.92$, $Pr_3N/P_2O_5 = 1.8$, $H_2O/P_2O_5 = 40$–45. [b]VPT method was used. [c]MgO/Al_2O_3 molar ratio in the starting gel. [d]The ratio in the product determined by ICP is 0.174. [e]0.097 in the product. [f]0.240 in the product. [g]Time is shown in parenthesis. [h]Crystallinity is low. [i]With trace impurity.

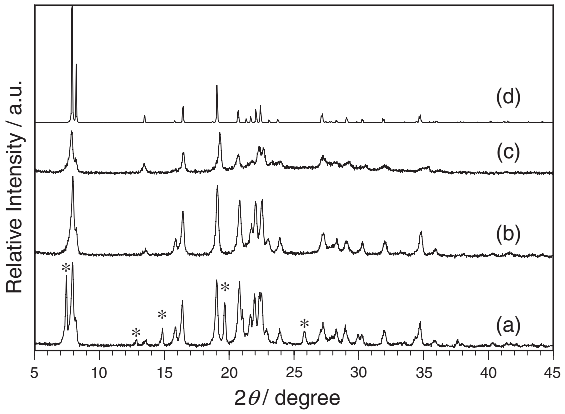

Figure 1. Powder XRD patterns of (a) as-synthesized sample obtained by HTS method (asterisks denote representative peaks from AFI impurity), (b) as-synthesized, pure ATS sample obtained by VPT method (Sample 3 in Table 1), (c) sample (b) calcined as described in the text, and (d) simulated pattern given for comparison.

and 4 in Table 1, and Figure 1b). The slight change of temperature in the second step did not hinder the formation of pure ATS, whereas very small change in the first step (from 105 to 100 °C) caused the formation of the mixture of ATS and AFI phases. The results were quite reproducible.

This observation prompted us to investigate the effect of the first step of the heating protocol. The heating time of the first step at 105 °C (denoted t_1) was varied from 12 to 72 h, fixing the second step at 140 °C for 24 h. When t_1 was 12 and 24 h, products were the ATS with considerable amount of AFI. With increasing t_1 up to 36 h, relative content of AFI decreased. Further increase in t_1 completely prevented the formation of AFI phase, leading to the crystallization of pure ATS when $t_1 = 48$–72 h. In case that the heating time of the second step at 140 °C (denoted t_2) was varied from 12 to 72 h with fixing t_1 for 24 h, the products were always the mixture of ATS and AFI with no obvious tendency of the relative content. These observations suggest that there is no phase transformation from AFI to ATS (or inverse), but there should be competitive nuclei formation of the two phases, and the first step (t_1) is critical governing factor for the nucleation.

Starting MgO/Al_2O_3 ratio influenced on the phase purity of ATS (Table 1, Samples 3, 7–10).[14] The ratios between 0.1 and 0.25 successfully gave pure ATS. The effective range was a little narrower than that previously reported ($0.14 < MgO/Al_2O_3 < 0.58$). When the ratio was below 0.1 or above 0.25, poorly crystalline ATS or AFI with other impurities were formed, respectively. Elemental analysis of the ATS product showed that the MgO/Al_2O_3 ratio in the starting gel was retained in the as-synthesized sample, suggesting that major portion of gel phase was converted to the ATS phase (Table 1, Samples 3, 7, and 9). The amount of Pr_3N was important and the pure ATS crystallized only when $0.49 < Pr_3N/Al_2O_3 < 1.96$. ATS crystallized even in the absence of external bulk water, indicating that very minute amount of water is necessary for the crystallization of ATS. In this case, water molecules adhered to the dry-gel could have contributed to the crystallization.

Thus, a convenient methodology to synthesize pure ATS was established. It should be noted that the synthesis of pure ATS by HTS[5] was still difficult even when starting from the same gel composition and carefully synthesized under exactly analogous conditions to DGC, resulting in the reproducible formation of ATS contaminated by AFI (Figure 1a).

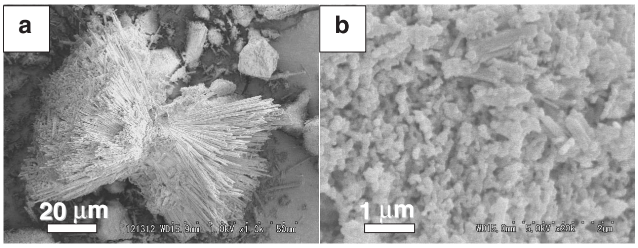

Figure 2. SEM photographs of Samples (a) and (b) in Figure 1.

Figures 2a and 2b show the SEM photographs of as-synthesized samples obtained by HTS and DGC (VPT), respectively. The sample from HTS contains particles with different morphologies (Figure 2a), being consistent with Figure 1a. In this sample, needle-like crystallites as long as 40 µm are assigned to be ATS on the basis of particle distribution and a SEM image in cited Ref. 5. Differently, very small rod-like or spherical crystallites (0.2–0.8 µm) of ATS are observed in case of DGC (Figure 2b), which is advantageous concerning catalytic use. Careful calcination steps as described in the experimental part were essential to obtain the reasonable porosity. According to the N_2 adsorption isotherm, carefully calcined ATS has a micropore volume of $0.16\,cm^3g^{-1}$ and the BET surface area of $360\,m^2g^{-1}$. NH_3-TPD profiles showed three desorption peaks between 200 and 450 °C, indicating that the sample has low to medium acidic properties. This suggests that at least some Mg atoms are incorporated in the framework. In conclusion, DGC method was successfully and conveniently applied to synthesize MAPO-36. Catalytic investigation of these materials will be forthcoming.

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