Roles of Amine Additives and Gel Aging on the Synthesis of $AlPO_4$ Molecular Sieves

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Received November 23, 1993⊗

^{31}P and ^{27}Al nuclear magnetic resonance (NMR) studies on $AlPO_4$ molecular sieve synthesis show the effect of aluminum source and organic amine additive on the necessity of reactive gel aging.

Phosphate-based molecular sieves,[1–3] which have been shown to overcome the 12-membered-ring (12 MR) pore-opening barrier found in most zeolites, are normally synthesized from initially acidic gels containing organic additives in an aqueous medium.[4] Few studies demonstrated that their synthesis can also be carried out in absence of additives[5] or in a nonaqueous medium.[3] It is well-known that the choice of aluminum source plays a crucial role in the synthesis and phase purity of $AlPO_4$ molecular sieves. Two Al sources, namely, boehmite form and alkoxide form, are most frequently used in $AlPO_4$ molecular sieve synthsis; they have been classified[6] as polymeric and monomeric, respectively. For the former, aging of the reactive gel has been found to be indispensable during the synthesis.[7,8] For the latter, for example, when aluminum isopropoxide is used,[6,9,10] the aging procedure seems to be unnecessary. Moreover, parameters such as temperature, duration of crystallization, and agitation will also affect the crystallization of the molecular sieves.[1–10]

Synthesis of aluminophosphate molecular sieves normally takes place by the following steps: (1) neutralization of the Al source suspended in water with nearly equimolar amount of dilute phosphoric acid to obtain the reactive $AlPO_4$ gel, (2) aging of the reactive gel, (3) addition of a particular organic additive to the reactive gel (this mixture is referred to as the precursor gel), (4) aging of the precursor gel, if necessary, and finally (5) hydrothermal treatment of the precursor gel. However, the effects of varied Al sources to the nature and formation of precursor gel and hence the detailed phenomena of the nucleation and crystal growth have been studied less extensively. We present here a preliminary report involving the use of ^{31}P and ^{27}Al NMR to investigate the gel chemistry of these systems, particularly on the necessity of aging and the role played by additives in $AlPO_4$ synthesis.

Table 1. Specification of the Gels $[1.0(Al_2O_3)\cdot 1.0(P_2O_5)\cdot n(DBA)\cdot 40(H_2O)]$ Used[a]

samples	aluminum source	amine added (n, M)	crystals obtained[b]
gel 1	pseudoboehmite		variscite, metavariscite[c]
gel 2	aluminum isopropoxide		variscite, metavariscite[c]
gel 3[d]	pseudoboehmite	0.5	tridymite[e]
gel 4[d]	pseudoboehmite	1.0	$AlPO_4$-11 or VPI-5[e]
gel 5	pseudoboehmite	1.0	$AlPO_4$-11 or VPI-5 (impure)[e,f]

[a] DBA = n-dibutylamine. [b] Upon hydrothermal treatment. [c] From ref 5. [d] Gels aged for 24 h prior to the addition of DBA. [e] From ref 10. [f] Impurities such as $AlPO_4$-11 and $AlPO_4$-H3 cocrystallized in the VPI-5 synthesis and tridymite cocrystallized in $AlPO_4$-11 synthesis, respectively.

The compositions of the reactive $AlPO_4$ gels used in this study are listed in Table 1. Gels 1 and 2 were prepared by adding dilute phosphoric acid into pseudoboehmite and aluminum isopropoxide, respectively, which were slurried in water. The effects of organic additives were studied by adding n-dibutylamine (DBA) to the gels either after (gels 3 and 4) or before (gel 5) its aging. The NMR experiments were performed on static samples of the respective gels without magic angle spinning (MAS) on a Bruker MSL-500P spectrometer. The ^{31}P NMR spectra were recorded at 202.402 MHz using a 90° pulse length ca. 8 μs; typically, 32 free-induction decays (FID) were accumulated every 15 s. For ^{27}Al NMR spectra, 300–1000 FIDs were recorded at 130.287 MHz using a pulse length of 12 μs and a recycle delay of 1 s. Aqueous $AlCl_3$ and H_3PO_4 (85%) solutions were used as chemical shift references for ^{27}Al and ^{31}P spectra, respectively.

For a solution containing H_3PO_4, the following equilibrium can be envisaged:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad (1)$$

The variation of pH (measurement accurate to ±0.1) on the aging time of the $AlPO_4$ gels is shown in Figure 1. By comparison of the $AlPO_4$ gels having different Al sources, the pH of gel 1 increased monotonically with reaction time

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⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1994.

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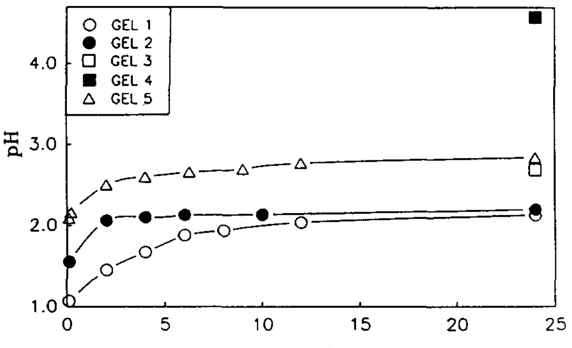

Figure 1. Variation of gel pH with aging time.

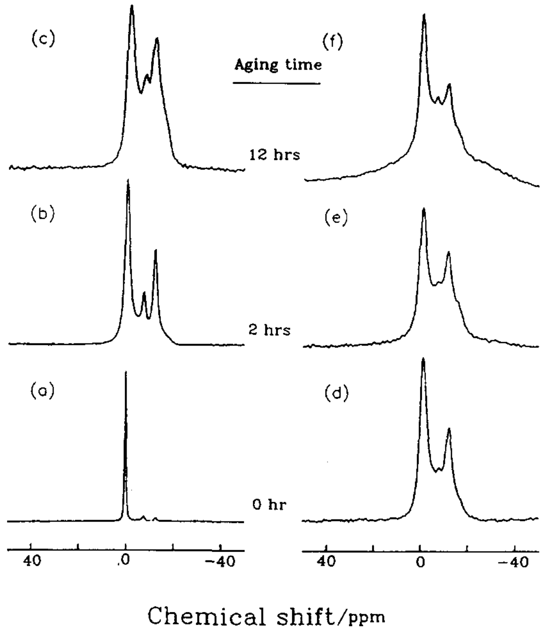

Figure 2. Variation of ^{31}P NMR spectra with aging time for gel 1 (a–c), and gel 2 (d–f); the aging time for each gel are 0, 2, and 12 h, respectively.

whereas that of gel 2 increased rapidly. Unlike pseudoboehmite, alkoxide therefore hydrolyzes rapidly to form reactive aluminum which reacts quickly with the phosphoric acid during the initial preparation of the reaction mixture. The increase of pH in these systems is due to the depletion of the acid as supported by the ^{31}P NMR results (*vide infra*).

Figure 2 displays the variation of ^{31}P NMR spectra for gels 1 and 2 upon aging. All resonance lines are shifted to high field with respect to H_3PO_4 (85%) reference whose chemical shift is taken as 0 ppm. For gel 1 immediately after mixing pseudoboehmite and phosphoric acid (time lag between mixing and measurement ca. 5 min), Figure 2a shows a sharp line at 0 ppm with two satellite peaks at −7.8 and −12.5 ppm. Upon aging gel 1 (spectra 2b and 2c), the two satellite peaks grew slowly with time and the former two peaks shifted to lower field (−1.6 and −8.6 ppm, respectively). The spectrum remains unchanged when the aging time exceeds 12 h; further aging for 1 month did not change the relative intensity of the lines. The system is said to have attained its equilibrium after an aging time of ca. 12 h. The line located near 0 ppm is assigned to free phosphoric acid units (H_3PO_4, $H_2PO_4^-$), whereas the two satellite peaks are assigned to Al complexed to $H_2PO_4^-$ ligands [e.g., $\{Al(H_2O)_5(H_2PO_4)\}^{2+}$] and to H_3PO_4 ligands [e.g. $\{Al(H_2O)_5(H_3PO_4)\}^{3+}$], respectively.[11-13] When aluminum isopropoxide is used as the Al source (gel 2), spectra 2d–f show that aging has little effect on the ^{31}P NMR spectra, indicating that the alkoxide complexes rapidly with the phosphoric acid, consistent with the conclusion drawn by the pH measurements above. The spectra remains unchanged when the aging time exceeds 12 hrs. The above results indicate that the complexes once created during the preparation of the synthetic mixture are stable and upon hydrothermal treatment can induce nucleation of unwanted phases like variscite and metavariscite (Table 1).

The effect of organic additive to the $AlPO_4$ molecular sieve synthesis has also been studied. The role of an organic additive is to provide the gel with a tetrahedral element required to build the framework in the form of "useful species" (also in tetrahedral coordination) at a reasonable rate. The concentration level of the useful species so obtained must be high enough to bring the solution out of equilibrium in order for nucleation and crystal growth to occur. Moreover, it has been reported that different amounts of amine additive promote crystallization of particular structures.[10,14,15] Since gel 2 apparently requires little aging procedure, we focus on the effects of amine additive on gel 1.

Upon addition of DBA to the reactive gel 1 after aging (pH = 2.1), the free flowing gel thickens as expected,[16] and the pH of the gel increase to 2.7 for gel 3 and 4.6 for gel 4 respectively (Figure 1); the difference being from the amount of DBA added.

The ^{31}P and ^{27}Al NMR spectra for gels 3, 4, and 5 are shown in Figure 3. For gel 3 (Figure 3, bottom), in which half a molar DBA was added to gel 1 after aging, the high-field lines in the ^{31}P NMR spectrum which represent the complexed Al species did not vanish completely, whereas for ^{27}Al NNR two lines were observed. The two ^{27}Al lines centered at 66 and −10 ppm are assigned to tetrahedral $Al(OH)_4^-$ and octahedral Al complexes, respectively.[12,13] Since only the central transition ($-^1/_2$ to $+^1/_2$) is observed for the quadrupolar ^{27}Al nuclei (spin $^5/_2$),[17] a quantitative interpretation cannnot readily be made based on the ^{27}Al spectra alone. Therefore, further quantitative analyses were made based on the ^{31}P spectra. For gel 3 (Figure 3), analysis of ^{31}P spectra using Gaussian simulation show that the integrated peak areas for the Al complexes of phosphoric acid correspond to 44% of the total spectral area. In other words, ca. 50% (within an experimental error) of tetrahedral species are generated upon adding 0.5 M amine.

When the amount of DBA is equimolar to that of phosphoric acid (gel 4), the high-field ^{31}P NMR lines which are associated with the Al complexes of phosphoric acid vanish completely (Figure 3, center), and the resonances solely arise form tetrahedral species. This is also evidenced by the appearance of a drastic increase of the tetrahedral $Al(OH)_4^-$ peak in the ^{27}Al NMR spectrum. Moreover, two

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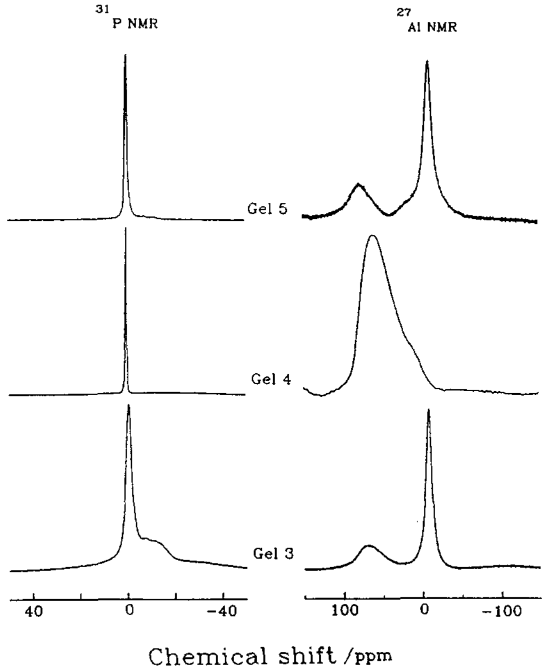

Figure 3. Variation of ^{31}P (left) and ^{27}Al (right) NMR spectra for gels 3 (bottom), 4 (center), and 5 (top). The condition of aging and the amount of amine additive added vary with each gel (see text and Table 1).

additional peaks are present in the broad bell-shaped ^{27}Al spectrum. The peak at 41 ppm can be assigned to AlO_4 tetrahedra,[18-20] whereas the peak at 24 ppm arise from pentacoordinated Al species.[21-23] The amount of amine added to the aged gel therefore controls the extent by which the useful tetrahedral species are formed. The ability of the amine to favor nucleation and crystal growth of a particular structure thus depends on its concentration in the synthesis batch (Table 1).

On the basis of the above observations we propose that the Al complexes are broken by the added amine represented by the following equations:

$$\{Al(H_2O)_5(H_3PO_4)\}^{3+} + 4R_2NH \rightleftharpoons Al(OH)_4^- + H_3PO_4 + H_2O + 4R_2NH_2^+ \quad (2)$$

$$\{Al(H_2O)_5(H_2PO_4)\}^{2+} + 4R_2NH \rightleftharpoons Al(OH)_4^- + H_2PO_4^- + H_2O + 4R_2NH_2^+ \quad (3)$$

That is, the amine abstracts protons to form protonated structure ($R_2NH_2^+$), hence resulting in an increase of pH and a surge of useful species. The validity of the above hypothesis is in accord with the results obtained from both the pH measurements and the NMR results.

However, when an equimolar amount of amine is added to gel 1 without aging (denoted by gel 5), while no apparent thickening of the gel is observed, the pH increased from 2.1 to 2.8 over a period of 24 h (Figure 1). The corresponding ^{31}P NMR spectrum (Figure 3, top) is only slightly broadened relative to that of gel 4, and the amount of tetrahedral species decreases. Since the nonaged reactive gel 1 (Figure 2a) contains very little Al complexes of phosphoric acid, we therefore conclude that the above hypothesis (eq 2 and 3) can be justified only for the gels containing substantial amount of Al complexes of phosphoric acid before the amine addition. For gel 5, the Al complexes of phosphoric acid present amount to 12.5% of ^{31}P resonances; in the ^{27}Al spectrum, the broadening of the octahedral Al peak (at ca. −10 ppm) relative to that of gel 3 indicates an increase of nontetrahedral Al species in the gel. Traces of unreacted pseudoboehmite have also been found in gel 5; they contribute to the ^{27}Al spectrum as a small shoulder (at ca. 9 ppm) of the octahedral Al peak. It is therefore desirable that, while pseudoboehmite is the Al source, the gel is aged before the amine addition. It has been found that[10] hydrothermal treatment of this nonaged gel (gel 5) resulted in the cocrystallization of impurity such as $AlPO_4$-11 and $AlPO_4$-H3 (in VPI-5 synthesis) and tridymite (in $AlPO_4$-11 synthesis). Further aging of gels 3–5 has no effect on the respective ^{31}P and ^{27}Al NMR spectra.

Upon hydrothermal treatment, the system undergoes condensation reactions through hydroxide function to form inorganic macromolecular structures. The organic amine present in the solution may in turn control the rate of the buildup and stability of the framework structure. The extend to which the tetrahedral species are generated depends not only on the concentration of the amine but also on the moment of its addition into the synthetic mixture.

In conclusion, we have shown that the use of different Al sources during the synthesis of $AlPO_4$ molecular sieves manipulate the necessity of aging and/or additives. When aluminum isopropoxide is used as the Al source, little or no aging prior to the addition of amine additive is required. On the other hand, if pseudoboehmite is used as the Al source, an aging time of 6–12 h is sufficient, and the amine additive is preferably added after the gel aging; further aging of the precursor gel is dispensable.

Acknowledgment. The support of this work by the National Science Council (NSC), Republic of China, Grant Nos. NSC82-0208-M-001-047 and NSC83-0208-M-001-092, is gratefully acknowledged. S.P. also thanks the NSC for a postdoctoral research fellowship.

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