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The effect of gel pH on the crystallization of aluminophosphate molecular sieve $AlPO_4$-5

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The effect of initial gel pH on the crystallization kinetics of $AlPO_4$-5 when synthesized from a gel containing x Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O was studied. The pH of the starting gel was varied either by taking different amine content (*x* varied from 0.75 to 1.75) or by the addition of aqueous ammonia and sodium hydroxide solution to the starting mixture keeping amine content at $x = 1$. The increase in the gel pH was observed to enhance the rate of crystallization of $AlPO_4$-5. The role of amine in enhancing the kinetics has been discussed. © Elsevier Science Inc. 1997

Keywords: $AlPO_4$-5; crystallization kinetics; initial gel pH; NH_4^+ and OH^- ions

INTRODUCTION

Hydrothermal synthesis of molecular sieve $AlPO_4$-5, starting with a reactive aluminophosphate gel and templating organic compound at 150–200°C has been reported[1] to take several hours for complete crystallization. It has also been reported[2,3] that an increase in template concentration facilitates the crystallization of pure $AlPO_4$-5. However, the role of the template in accelerating the rate of crystallization is still not clear. In the present work, the synthesis of $AlPO_4$-5 from the gel of composition x Pr_3N : 1.0 Al_2O_3 : 1.0 P_2O_5 : 40 H_2O has been carried out by varying template concentration from $x = 0.75$ to 1.75 to study the effect of template concentration on the crystallization kinetics. The influence of NH_4^+ and OH^- ions on the crystallization kinetics has also been studied.

EXPERIMENTAL

Aluminum triisopropoxide (BDH, UK) and 85% (m/m) orthophosphoric acid (Riedel-de Haën, Germany) were used as the Al and P sources. Tri-*n*-propyl amine (Merck, Germany) was used as the templating agent. The crystallized product was characterized by X-ray diffraction (Rigaku, Dmax-III, Japan), using Ni-filtered CuKα radiation. Thermogravimetric analysis was done with a Seiko SII, 5200 (Japan) instrument under nitrogen atmosphere in which the weight loss was measured with α-alumina as the reference. C, H, and N analysis of as-synthesized $AlPO_4$-5 was carried out using a Carlo Erba 1106 elemental analyzer. Water adsorption measurements were carried out gravimetrically using a quartz spring McBain-Bakr balance with a sensitivity of 30 cm/g. Measurements of pH were done using a µ-pH system 361 from Systronics (India).

In a typical synthesis experiment, an aqueous slurry of aluminum triisopropoxide was prepared at ambient temperature (ca. 25°C) to which ortho-phosphoric acid was added. The reactive aluminophosphate gel thus formed was then stirred for 2–3 h to obtain a homogeneous gel. Tri-*n*-propyl amine was added, and the mixture was again stirred until a homogeneous gel was obtained with a stable pH, the value of which depends on the amount of amine added. The gel (100 g) was divided into equal parts and was filled in different stainless steel autoclaves (capacity = 75 cm^3), which were then kept in an air oven at 150°C (±1°C). It has earlier been established by *in situ* temperature measurement that the autoclave attains thermal equilibrium 2 h after being placed in the oven. The reaction was quenched at the desired time interval by removing the autoclave from the air oven and by cooling it in cold, running water. The product was filtered off, washed with warm distilled water, dried at 110°C, and finally was calcined at 540°C in flowing air (flow rate = 100–200 cm^3/min) for 10–12 h. The kinetics of crystallization was studied by quenching the reaction at predetermined time intervals, viz., at 30, 45, 60, 75, 120, and 180 min. The solid product obtained after decantation was washed with distilled water and dried at 110°C for 4 h. Thus dried product was characterized using X-ray diffraction and water adsorption. The pH of the solution obtained

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after decantation was also measured. The crystallinity of the samples was obtained from X-ray powder diffraction data using the equation[5]

$$\% \text{ Crystallinity} = \frac{\Sigma I}{\Sigma I_{ref}} 100$$

where I is the line intensity of the experimental sample and I_{ref} is that of the reference sample.

The reference sample of $AlPO_4$-5 was synthesized using the method reported by Wilson.[4] X-ray diffraction data for the reference sample agrees with the literature data. The intensities of X-ray lines at $2\theta = 19.92$, 21.12, and 22.55 were employed[5] for these calculations. The crystallinity of the samples was also determined by comparing water adsorption capacity at $p/p^\circ = 0.4$ against the reported[5] data for fully crystalline $AlPO_4$-5.

The variation in the concentration of amine in the gel also results in the change in its pH. To separate the effect of pH from that of amine on crystallization, the pH of the starting gel was alternatively varied by adding calculated amounts of 1.5 M aqueous ammonia (1.2 ml) or 2.5 M sodium hydroxide solution (14.5 ml) while maintaining the amine concentration corresponding to $x = 1$.

RESULTS AND DISCUSSION

The results of the kinetic studies of $AlPO_4$-5 crystallization using different gel composition are given in *Table 1*, where the crystallinity obtained at different time intervals is given. The water adsorption isotherms measured for the synthesized samples were of type V, which is characteristic of $AlPO_4$-5 structure.[6] The water adsorption isotherm along with the X-ray diffraction pattern for $AlPO_4$-5 samples synthesized with a gel composition of 1.0 Pr_3N : 1.0 Al_2O_3 : 1.0 P_2O_5 : 40 H_2O are given in *Figures 1* and *2*, respectively. Similar isotherms and X-ray diffraction patterns were obtained for other gel compositions. The present data reinforce our earlier[1] observation of the rapid synthesis of pure $AlPO_4$-5. In fact, with amine concentration corresponding to $x = 1.75$, pure phase can be obtained as early as 45 min. This is significant because the previously reported synthesis times[1] for $AlPO_4$-5 synthesis using aluminophosphate gel lie in the range of 2 to 24 h.

It can be observed from the data (*Table 1*) that the time required for the complete synthesis of pure $AlPO_4$-5 phase progressively decreases with increasing amine concentration. For example, with $x = 1$, 1.25, 1.50, and 1.75 the time taken, t_{100}, for synthesizing 100% crystalline $AlPO_4$-5 product is 180, 120, 90, and 45 min, respectively. Wilson et al.[7] have shown that the increase in amine concentration from $x = 0.6$ to 1.2 favors the formation of the pure $AlPO_4$-5 phase over other aluminophosphate phases. However, they have not studied the effect of amine concentration on the rate of crystal growth. Weyda and Lechert[3] from their study on the effect of tripropyl amine concentrations on SAPO-5 synthesis have also shown a decrease in induction as well as crystallization time with an increase in organic template concentration. The synthesis of $AlPO_4$-5 in the absence of amine results only in dense aluminum phosphate phases.[5] Thus, it is clear that the presence of an organic template is essential for getting the microporous phase formation. However, it is apparent that an organic amine, in addition to a structure-directing role, is likely to influence gel chemistry by altering the gel pH. Thus, the increase in synthesis rate of $AlPO_4$-5 with amine content (*Table 1*) may be due to either the greater number of nuclei formed in the gel having higher amine content or higher gel pH or is due to a combination of both factors. To further ascertain this aspect, synthesis of $AlPO_4$-5 was carried out starting with a gel composition of 1.0 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O whose pH was increased to 6.1 by the addition of an aqueous ammonia solution. It has been reported[6] that the presence of foreign cations other than proton, protonated amine, and quaternary ammonium ion usually caused the formation of tridymite and cristobalite-like aluminophosphate structures instead of the microporous phase. Hence, ammonium ion was used for studying the effect of enhanced pH of the starting gel.

Table 1 Synthesis of $AlPO_4$-5 from different gel compositions

Time (min)	Crystallinity (%)		pH of final solution
	XRD	Adsorption	
1.0 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O (pH = 5.8)			
60	75	88	7.4
120	93	96	7.4
180	100	98	7.9
1.25 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O (pH = 6.0)			
60[a]	89	86	7.5
90	91	94	7.5
120[a]	100	84	7.4
150[a]	97	86	7.4
180[a]	96	84	7.4
1.50 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O (pH = 6.7)			
30	30	70	7.2
60	83	81	7.5
75	98	98	7.5
90	100	99	7.6
150	67	47	7.5
1.75 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O (pH = 6.9)			
30[b]	34	59	7.4
45	100	100	7.5
60	95	91	7.5
75[a]	73	86	7.4
0.75 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O (pH = 5.3)			
60	0	—	7.3
120	IMPURE	—	7.5
180	0	—	7.2
240	0	—	7.5

[a] Samples showed 7–14% of tridymite-like aluminum phosphate structure.

[b] Sample showed 20% of cristobalite-like aluminum phosphate structure.

As can be seen from the data given in *Table 2*, t_{100} in this case is 120 min, which is the same as in the case

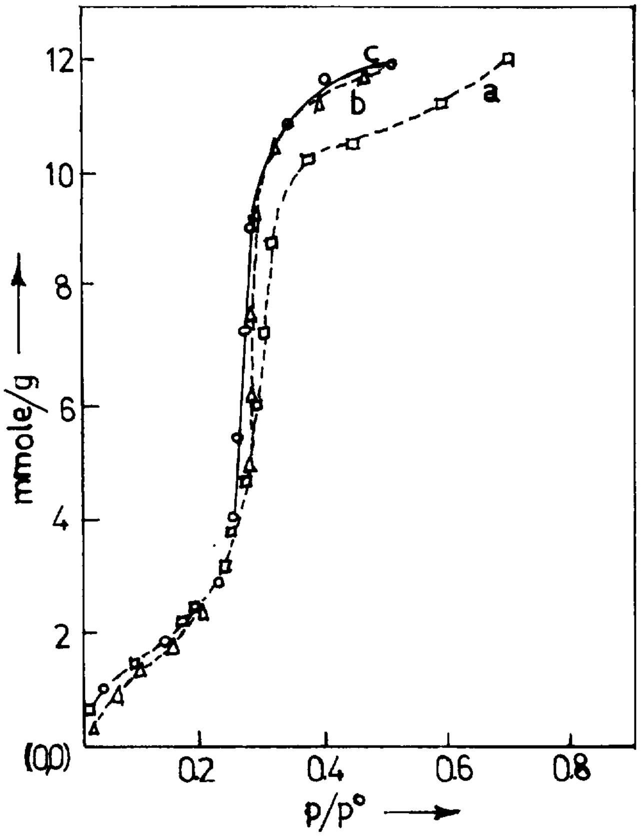

Figure 1 Water adsorption isotherms at 298 K for $AlPO_4$-5 samples obtained at various time intervals from a gel composition of 1.0 Pr_3N : 1.0 Al_2O_3 : 1.0 P_2O_5 : 40 H_2O at 150°C. (*a*) 60 min; (*b*) 120 min; and (*c*) 180 min.

with a starting gel composition of 1.25 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O (*Table 1*). This shows that the higher crystallization rate for gel with composition 1.25 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O is mainly due to the increased pH (from 5.8 to 6.1) of the starting gel caused by higher amine concentration. In other words, the role of additional amine molecules in the gel having a composition of 1.25 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O is similar to that of aqueous ammonia solution; i.e., its role is only to increase the pH of the starting gel.

To confirm this observation, syntheses were carried out with a starting gel composition of 1.0 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O and the pH of the gel was further increased to 6.7 and 7.0 by the addition of an aqueous ammonia solution. The pH values of these gels were thus brought closer to the gel having a composition of 1.5 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O and 1.75 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O, respectively. Interestingly, it can be observed from *Tables 1* and *2* that the behavior of this gel was very similar to the one containing a higher amine concentration (x = 1.5 and 1.75), showing a t_{100} of 90 and 45 min, respectively. This leads to the conclusion that an increase in the rate of crystallization is due solely to the enhanced pH of the starting gel. The reproducibility of the observations was checked by repeating the above two syntheses.

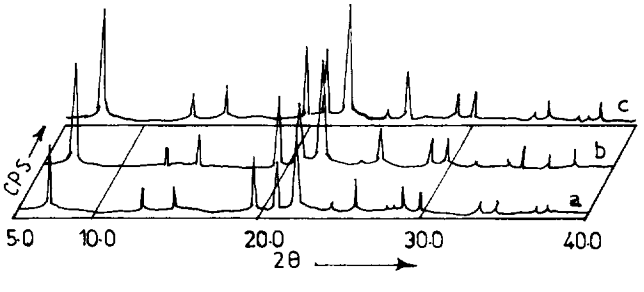

Figure 2 X-ray powder diffraction patterns for $AlPO_4$-5 samples obtained at various time intervals from a gel composition of 1.0 Pr_3N : 1.0 Al_2O_3 : 1.0 P_2O_5 : 40 H_2O at 150°C. (*a*) 60 min; (*b*) 120 min; and (*c*) 180 min.

Table 2 Synthesis of $AlPO_4$-5 from a gel having a composition of 1.0 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O whose initial gel pH increased by adding aqueous ammonia/sodium hydroxide solution

Time (min)	Crystallinity (%) XRD	Crystallinity (%) Adsorption	pH of final solution
Aqueous ammonia solution (pH = 6.1)			
45	60	81	7.5
60	80	93	7.4
90	93	99	7.4
120	100	100	7.5
Aqueous ammonia solution (pH = 6.7)			
30	69	—	7.4
60	52	90	7.4
75	61	81	7.5
90	84	98	7.4
120	68	90	7.4
Aqueous ammonia solution (pH = 7.0)			
30	67	81	7.4
45	100	100	7.5
60	94	93	7.3
75	100	93	7.4
120	72	81	7.2
180	99	86	7.7

Note: For the sodium hydroxide solution (pH = 6.9), product did not crystallize even after 2 h.

A synthesis was also carried out with an amine concentration corresponding to x = 0.75 where the pH of the starting gel was 5.3. The analysis of the crystallized products obtained at time intervals of 30, 45, 60, 75, and 90 min were found to have cristobalite- and tridymite-type aluminum phosphate dense structures. The $AlPO_4$-5-type phase formed was of low purity (<50%) as determined from X-ray powder diffraction. An initial gel composition of Al_2O_3 : P_2O_5 : 40 H_2O was also taken, and the gel pH was increased by the addition of an aqueous ammonia solution to pH 7.0. No crystallization was observed. These results show that[6] at least 1 mole of the amine is essential per mole of Al_2O_3 for an effective templating action. It can be inferred from these results that there exists a critical value of amine concentration for complete $AlPO_4$-5 synthesis and that the addition of amine beyond this value influences crystallization mainly by modifying the gel pH. Further evidence for the above conclusion comes from thermogravimetric analysis of the uncalcined $AlPO_4$-5 samples under a nitrogen atmosphere. Thermogravimetric curves of the $AlPO_4$-5 samples prepared starting with gels having different *x* values are given in *Figure 3* and *Table 3*. It can be seen that the total weight loss on heating to 600°C is around 16–17% w/w, which includes water and amine desorbed from the pores as well from the external surface of the molecular sieve. Assuming that the desorption from the external surface is complete by the first inflection point at 150°C, it can be estimated from *Table 3* that the weight loss corresponding to occluded amine is around 7.5–7.8%. This is close to the calculated value, assuming one occluded amine molecule per unit cell. Thermogravimetric data of the sample synthesized in the presence of added ammonia show around 3% higher total weight loss (*Table 3*). Meinhold and Tapp[8] have shown from the chemical analysis of the ammonium acetate-treated $AlPO_4$-5 from methanol that NH_4^+ ions are strongly sorbed on the $AlPO_4$-5. However, the weight loss in the temperature range of 150–600°C is 7.6–7.7%, which corresponds to one occluded amine molecule per unit cell. This observation reinforces the earlier finding that one amine molecule per unit cell is needed for the templating action during $AlPO_4$-5 synthesis and that the excess amine if present, influences the gel chemistry by contributing to the pH of the gel.

The increase of pH with sodium hydroxide solution addition prevents $AlPO_4$-5 crystallization. Thus, there seems to be a significant role for NH_4^+ ions, along with the pH of the gel, in facilitating $AlPO_4$-5 synthesis. To investigate this aspect, the crystallization was also carried out in the presence of several ammonium salts (*Table 4*). In all these cases, the composition of the starting gel was 1.0 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O. The amount of ammonium salt taken was such that it provided an amount of ammonium ions in the gel that would be present at pH 7.0 when made up by the addition of ammonia. As observed from *Table 4*, the crystallization of $AlPO_4$-5 was accompanied with tridymite and cristobalite-like aluminophosphate dense phases in all the cases. As observed from X-ray diffraction intensity data, the crystallinity was very low. In the case of ammonium nitrate, the material formed was X-ray amorphous. Furthermore, the initial pH of the gel in all cases was in the range 5.4 to 6.0, which is less than that obtained with the addition of ammonium hydroxide. These results establish that the pH of the initial gel is crucial for the synthesis of $AlPO_4$-5. Furthermore, the

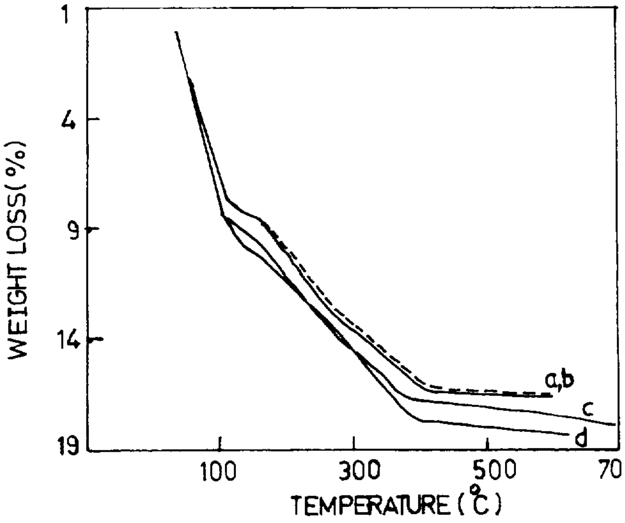

Figure 3 t.g.a. curves for $AlPO_4$-5 samples prepared from a gel composition of x Pr_3N : 1.0 Al_2O_3 : 1.0 P_2O_5 : 40 H_2O at 150°C. (*a*) *x* = 1.00, initial gel pH 5.80; (*b*) *x* = 1.75, initial gel pH 6.92; (*c*) *x* = 1.00, with modified pH 7.04; and (*d*) *x* = 1.00, with modified pH 6.08.

Table 3 Data on the thermogravimetric analysis of different $AlPO_4$-5 samples prepared using a gel composition of x Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O at 150°C

Amine concentration in gel (mole ratio, *x*)	pH of starting gel	Weight loss (%)	
		Ambient–600°C) (from t.a.)	150–600°C
1.0	5.8	16.4	7.8 (7.1)[b]
1.25	6.0	16.6	7.5
1.50	6.7	16.8	7.6
1.75	6.9	16.8	7.6 (7.0)
1.0[a]	7.0	18.0	7.7 (7.1)
1.0[a]	7.1	17.9	7.6

[a] The pH of the gel was increased by the addition of an aqueous ammonia solution.

[b] The percentages of weight loss given in parentheses are from C, H, and N analysis.

Table 4 Effect of various ammonium salt on the crystallization of $AlPO_4$-5 from a gel having a composition of 1.0 Pr_3N : Al_2O_3 : P_2O_5 : 40 H_2O

Ammonium salt	Initial gel pH	Time (min)	Final pH	Products
Acetate (1.24 g)[a]	6.0	45	6.7	5, C, T[b]
		60	5.8	5, C, T
		90	5.9	5, C, T
		120	6.4	5, C, T
		150	6.3	5, C, T
Chloride (0.86 g)	5.5	30	6.5	5, C, T
		45	8.1	5, C, T
		60	7.7	5, C, T
		90	8.3	5, C, T
		120	6.9	5, C, T
Carbonate (0.77 g)	5.9	30	8.2	5, C, T
		45	8.4	5, C, T
		60	8.2	5, C, T
		90	7.2	5, C, T
		120	7.2	5, C, T
Nitrate (1.28 g)	5.5	30	8.3	X-ray amorphous
		45	7.8	X-ray amorphous
		60	8.1	X-ray amorphous
		90	8.1	X-ray amorphous
		120	8.2	X-ray amorphous
Bicarbonate (1.27 g)	6.0	30	8.0	5, C, T
		45	8.3	5, C, T
		60	8.2	5, C, T
		90	7.5	5, C, T
		120	7.5	5, C, T
Phosphate (dibasic) (1.84 g)	6.0	45	6.7	X-ray amorphous
		90	7.1	X-ray amorphous
		120	7.0	5, C, T

[a] The amount of the salt added to 100 ml of the gel is given in parentheses.

[b] C and T denotes cristobalite- and tridymite-like $AlPO_4$ structure, respectively.

presence of external anions seems to adversely affect the crystallization of $AlPO_4$-5, possibly by binding with the aluminum species present in the gel and thus decreasing their availability for $AlPO_4$-5 synthesis.

The effect of organic amine and pH on the crystallinity of the $AlPO_4$-5 phase and crystal growth rate can be understood in terms of gel chemistry. Aluminum has the tendency to have octahedral coordination between pH 3 and 9. However, it is the tetrahedral aluminum that is the precursor for microporous $AlPO_4$-5 phase, whereas octahedral aluminum leads to a dense or undesired phase from the gel. It has been shown from n.m.r. studies[9] that depolymerization of aluminum hydroxide under the influence of phosphoric acid provokes the conversion of octahedral aluminum into tetrahedral coordination. The tetrahedral aluminum atoms, which are unstable at low pH values if stabilized in the gel, will facilitate microporous phase formation. It has been shown[9,10] that tetrahedrally coordinated aluminum originating from the depolymerization of aluminum hydroxide is stable in a gel containing amine. It is proposed that the amine molecules are bound via the phosphate tetrahedra to the initial species consisting of AlO_4 and PO_4 tetrahedra. This arrangement provides a hydrophobic environment around the active species, protecting them from the attack of water molecules and thus stabilizing the tetrahedral coordination of aluminum atoms.

Thus, increased pH may enhance the rate of depolymerization of aluminum hydroxide, which in the presence of a stoichiometric amount of phosphoric acid and templating amine molecules will stabilize the tetrahedrally coordinated Al species in the gel, thus facilitating $AlPO_4$-5 formation.[10] It is difficult to ascertain whether ammonium ions have any role similar to that of amine in stabilizing tetrahedral Al species. Because, when sodium hydroxide was used to increase the pH of the gel instead of ammonium hydroxide, no $AlPO_4$-5 was formed (*Table 2*). The presence of sodium ions in the gel may form sodium aluminate, which is reported[11] to have aluminum in octahedral coordination at low pH, thus disfavoring the formation of microporous $AlPO_4$-5.

In another set of experiments, pseudobohemite was used as the aluminum source. The 100% crystallized $AlPO_4$-5 was obtained in 30 min when synthesis was carried out with initial gel composition of 1.75 $Pr_3N : Al_2O_3 : P_2O_5 : 40\ H_2O$ having a pH of 6.5. Another synthesis, the initial gel having a composition of 1.0 $Pr_3N : Al_2O_3 : P_2O_5 : 40\ H_2O$, was taken, and the pH of this gel was increased from 4.2 to 6.5 by the addition of aqueous ammonia. The crystallization kinetics of this was followed at time intervals of 30, 60, 90, and 120 min using the X-ray diffraction method. However, the X-ray amorphous product was obtained with a gel composition of 1.0 $Pr_3N : Al_2O_3 : P_2O_5 : 40\ H_2O$ whose pH was increased by the addition of aqueous ammonia to 6.5 even after 120 min. This indicates the lack of enhancement of crystallization kinetics when pseudobohemite is used as an alumina source.

These results clearly establish the structure-directing role of amine molecules in which a minimum amount corresponding to one molecule per unit cell of the organic templates is required. It also highlights the role of hydroxyl ions in the gel chemistry influencing the crystallization kinetics.

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