Synthesis and characterization of a novel small pore aluminophosphate molecular sieves from hexamethyleneimine template at atmospheric pressure

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Abstract

Novel small pore aluminophosphates molecular sieves $AlPO_4$-Atm1, $AlPO_4$-Atm2 and $AlPO_4$-Atm3 have been synthesized using hexamethyleneimine template at atmospheric pressure (373K) for the first time. Gel composition Al_2O_3: P_2O_5: 1.16HEM: $45H_2O$ was taken as the standard one which gives $AlPO_4$-Atm12. Change in water molar ratio to 67.5 gives $AlPO_4$-Atm2. On changing the aluminium source from catapal B to aluminium isopropoxide in same molar gel composition gives $AlPO_4$-Atm3. All the materials were characterized by XRD, SEM, TG/DTA, C & N analysis, FT-IR and MASNMR analysis. Elemental analysis shows that Al and P are in equal molar composition. XRD analysis shows that the synthesized samples are highly crystalline and new. SEM shows the morphology change with structure. TG/DTA analysis reveals the presence of maximum four stage elimination of templates. Carbon and nitrogen analysis gives the amount of template present in the sample. ^{27}Al MASNMR shows the presence of single type tetrahedrally co-ordinated aluminium atoms in $AlPO_4$-Atm1. ^{31}P MASNMR of the same sample shows the presence of two type of tetrahedrally co-ordinated phosphorous atoms.

Keywords: Hexamethyleneimine; atmospheric pressure; $AlPO_4$-Atm1; $AlPO_4$-Atm2; $AlPO_4$-Atm3

1. Introduction

A new generation of molecular sieves, aluminophosphates ($AlPO_4$s) were reported by Wilson *et al*. having framework compositions comprising $[AlO_2]^-$ and $[PO_2]^+$ tetrahedral [1-3]. Aluminophosphate molecular sieves are the first reported novel class of crystalline microporous oxide framework structures synthesized without silica [1,4]. These molecular sieves are similar to zeolites in some properties and it has been claimed that they may be used as adsorbents, catalysts and catalyst supports. The new $AlPO_4$ family currently includes about twenty two three dimensional framework structures of which at least sixteen are microporous and six are two dimensional layer type materials. Most of these three dimensional structures are novel, eg. $AlPO_4$-5, -31, -41 and -22. Some of the aluminophosphates are structurally similar to zeolites, eg. $AlPO_4$-17 (erionite) and SAPO-35 (levynite). The neutral aluminophosphate frameworks with no extra framework cations are moderately hydrophilic. Their

framework composition with an Al/P ratio of 1 has a wide structural diversity.

Aluminophosphates are synthesized hydrothermally in the temperature range 373-531K from a reaction mixture containing sources of aluminium, phosphorous and an organic amine or a quaternary ammonium salt [5] which gets entrapped or clathrated within the crystalline products under autogeneous pressure. Since the aluminophosphate framework is electrically neutral, the template is not needed as a charge balancing agent; therefore, its incorporation into the structure is a function of its electronic nature, size and shape relative to the channel volume to be filled. The entrapped organic species are removed by thermal decomposition. Moreover, these novel structures exhibit thermal stability. Most of these remain crystalline after calcination around 400-600°C , which is necessary for the removal of the organic template and make the intracrystalline void volume free for the adsorption and catalysis. A single template can give rise to multiple $AlPO_4$ structures and a variety of structures can be synthesized from a single template. $AlPO_4$-5 is synthesized using a large variety of organic templates. On the contrary $AlPO_4$-16 has been synthesized with only one template, namely, quinuclidine [1]. In the present work the usefulness of HEM in hydrothermal synthesis of $AlPO_4$ molecular sieves at atmospheric pressure is established. By varying the synthesis reactants many $AlPO_4$ molecular sieves, viz., $AlPO_4$-Atm1, $AlPO_4$-Atm2 and $AlPO_4$-Atm3 have been obtained. These materials have been characterized by conventional techniques like XRD, SEM, FT-IR, TG/DTA, and MAS NMR.

2. Experimental

The typical procedure for the synthesis of $AlPO_4$-Atm is as follows. 7.16 g of catapal B (74.2% Al_2O_3, Vista Chemicals, U.S.A) was mixed with 20 ml of distilled water and stirred well. 11.5 g of orthophosphoric acid (85%, s.d.fine, India) was added dropwise to the mixture and stirred well. A white thick paste was formed. Which was aged overnight. 5.82 g of hexamethyleneimine (98%, Aldrich, U.S.A) along with 20 ml of distilled water was mixed well with the paste and the resulting gel (Al_2O_3: P_2O_5: 1.16HEM: 45H_2O) was charged into a glass round bottom flask. The gel was refluxed at 100°C for 24 h. The products (named as $AlPO_4$-Atm1) were cooled, washed several times with distilled water and dried at 110°C and subjected to physicochemical characterization.

The other aluminophosphates such as $AlPO_4$-Atm2 and $AlPO_4$-Atm3 were synthesized using similar procedure by increasing water molar ratio for 67.5 and changing the aluminium source to aluminium isopropoxide.

The samples synthesized during the course of work were analyzed by X-ray powder diffraction (Rigaku, Model D/MAX III VC, Japan; Ni filtered Cu-Kα radiation, λ = 1.5404 Å; graphite crystal monochrometer; computer controlled automated diffractometer). The morphologies of all the aluminophosphates synthesized were investigated using a scanning electron microscope (JEOL, JSM 5200). Simultaneous TG/DTA analysis of the crystalline phases were performed on an automatic derivatograph (Setaram TG-DTA 92). The framework region (400-

1300 cm^{-1}) of the synthesized aluminophosphates were analyzed using a Nicolet 60SXB FT-IR instrument in the diffuse reflectance mode using a 1:300 ratio of the sample to KBr mixture. MASNMR spectra were recorded in the solid state with a Bruker DRX 500 spectrometer operating at a field of 11.7 Tesla. ^{27}Al spectra were recorded at a frequency of 130.3 MHz, with a pulse length of 2μs and a spinning speed of 3-5 KHz. ^{31}P spectra were recorded at a frequency of 202.45 MHz with a pulse length of 1.5μs and the recycle delay was 4 s. 1M $Al(NO_3)_3$ and 1M H_3PO_4 solutions (for aluminium and phosphorous) were used as standards.

3. Results and Discussion

The elemental composition of the all aluminophosphate molecular sieves are similar. Carbon and nitrogen analysis shows that the carbon (7.90, 6.25 and 5.078%) and nitrogen (1.74, 1.16 and 0.943%) contents are in decreasing order from $AlPO_4$-Atm1 to $AlPO_4$-Atm3. Results shows that the use of aluminium isopropoxide ($AlPO_4$-Atm3) did not encapsulate isopropanol in structure. Only hexamethyleneimine is incorporated. Use of excess water reduces the amount of template incorporation. Equal molar ratio of carbon and nitrogen present shows that the template is not decomposed in any of the synthesis. Hydrogen content also decreased in the above order (3.097, 2.05 and 1.88%). Use of more water did not result in increase the amount of water adsorbed. The elemental composition of all the molecular sieves are having Al_2O_3: $0.99P_2O_5$.

The X-ray diffraction patterns of $AlPO_4$-Atm1, $AlPO_4$-Atm2 and $AlPO_4$-Atm3 are given in Fig. 1. The X-ray diffraction patterns of all the molecular sieves are not matching with any of the reported aluminophosphate molecular sieves and their analogs. The appearance of first peak after 10°, 2θ for all the molecular sieves shows that they are small pore molecular sieves. Appearance of small mesoporous peak in $AlPO_4$-Atm1, is observed. This can be eliminated on calcinations.

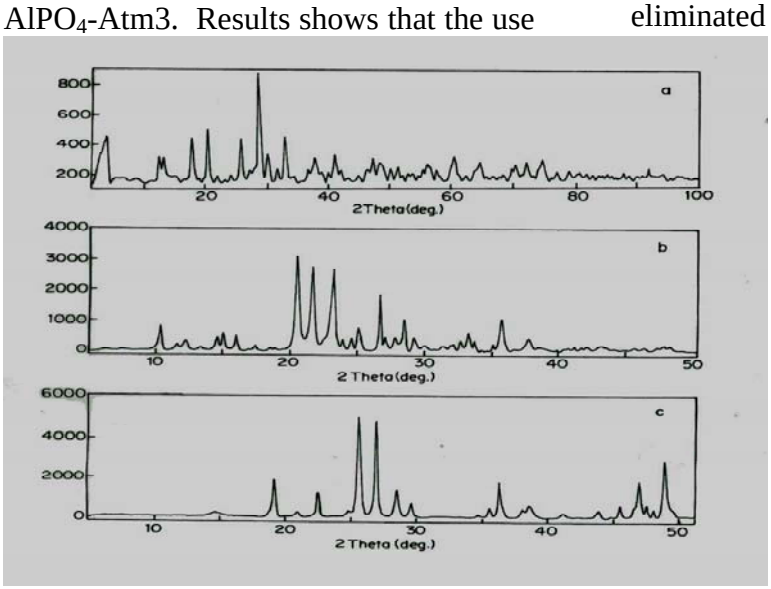

Fig. 1: X-ray diffraction patterns of a) $AlPO_4$-Atm1, b) $AlPO_4$-Atm2 and c) $AlPO_4$-Atm3.

The SEM photographs show that the morphology and particle size (Fig. 2) depend on the structure. $AlPO_4$-Atm1 was having spheroidal morphology with 1 μm particle size. $AlPO_4$-Atm2 was having flag morphology with 10 x 6 μm size. $AlPO_4$-Atm3 was having spherical morphology with 5.5 μm size. All the samples shows uniform particles confirm the percentage of crystallinity.

Fig. 2: Scanning electron microscopic photographs of a) $AlPO_4$-Atm1, b) $AlPO_4$-Atm2 and c) $AlPO_4$-Atm3.

The TG/DTA plots are presented in Fig. 3a-c. The weight loss of $AlPO_4$-Atm1, $AlPO_4$-Atm2 and $AlPO_4$-Atm3 occurs in three to four stages. The first stage endothermic loss (14, 2.25 and 0.55%) at 100°C is due to loss of physisorbed water and template. All the molecular sieves losses its physisorbed material in a single step. The oxidative decomposition of hexamethyleneimine occurs in three stages in $AlPO_4$-Atm3 (5.86% (137-406°C), 12.32%(406-603°C) and 3.29%(603-811°C)) as against two stages in $AlPO_4$-Atm2 (4.23% (299-348), and 2.89%(348-820°C) and $AlPO_4$-Atm1 (9.79% (156-353°C) and 7.46% (353-814°C). The small pores make the oxidative decomposition and elimination of products difficult and leads to an extra combustion stage. The higher temperature required for the elimination of the template in all the aluminophosphates are due to the presence of partially ionized templates.

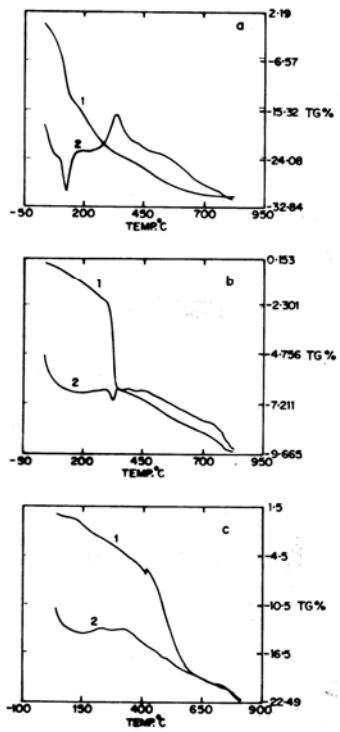

Fig. 3: TGA(1) and DTA(2) of a) $AlPO_4$-Atm1, b) $AlPO_4$-Atm2 and c) $AlPO_4$-Atm3.

FT-IR spectra recorded in the framework region of the aluminophosphates, $AlPO_4$-Atm1, $AlPO_4$-Atm2 and $AlPO_4$-Atm3 are presented in Fig. 4. The IR spectrum of all the molecular sieves shows three bands at 1160-960, 936-720 and 569-406, which are characteristic of aluminophosphate molecular sieves. They were assigned to tetrahedral (T-O-T, where T = Al or P) asymmetric, symmetric, double ring, bending and pore opening vibrations [6]. $AlPO_4$-Atm1 show an additional peak at 1150 cm^{-1}. $AlPO_4$-Atm2 gives an extra peak at 959 cm^{-1}. $AlPO_4$-Atm3 having strange peak order as all the peaks were doubled.

The ^{27}Al MAS NMR spectra of $AlPO_4$-Atm1, as shown in Fig. 5a, have single peak resonances around δ -7.62 indicate octahedral co-ordination [7]. An additional small peak appeared at 15 ppm is due to the spinning side bands. The two peaks observed in ^{31}P NMR spectra of this compound (Fig. 5b) is attributed to tetrahedrally coordinated, crystallographically distinct phosphorous atoms [8], P(1) and P(2). As noted earlier [8], the $P(1)O_4$tetrahedron is more strongly hydrogen bonded than is $P(2)O_4$. Thus P(1) with lesser electron density has a resonance at δ -13.54 while P(2) has at δ -19.74.

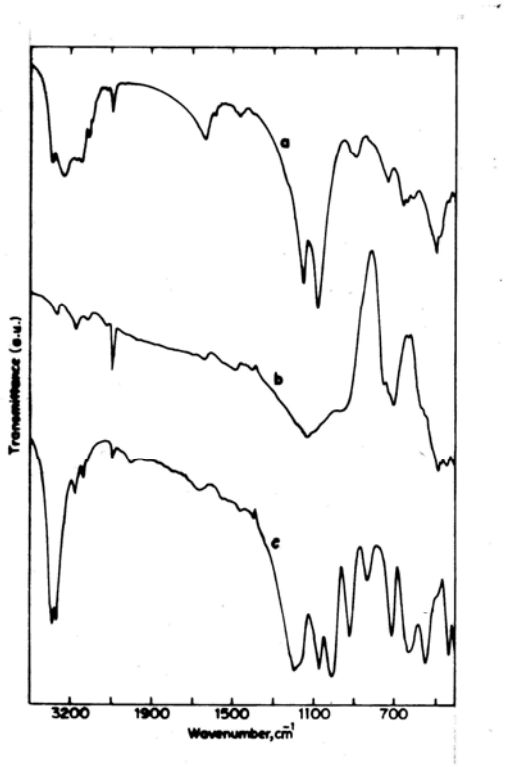

Fig. 4: FT-IR spectra of a) $AlPO_4$-Atm1, b) $AlPO_4$-Atm2 and c) $AlPO_4$-Atm3 in the framework region.

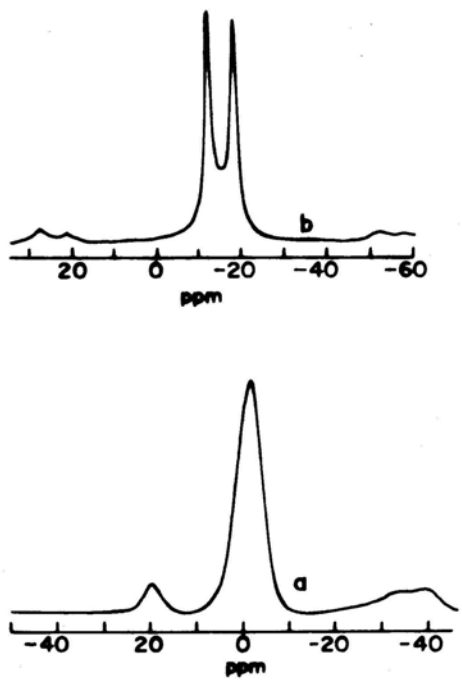

Fig. 5: a) ^{27}Al and b) ^{31}P MASNMR spectra of $AlPO_4$-Atm1.

The solvent employed in the synthesis of $AlPO_4$-n are essentially water as the non-aqueous media preparation requires higher temperature. An important aspect of the synthesis of $AlPO_4$-n is the use of hexamethyleneimine as the templating agent. Hexamethyleneimine owing to its bigger size heterocyclic ring has little chance to act as a template during the synthesis of small pore $AlPO_4$. In our system we believe that Hexamethyleneimine and the solvent interact during the reaction leading to the formation of $AlPO_4$-Atm and its successful synthesis suggests that other suitable templating agents for different $AlPO_4$-n structures in atmospheric pressure may be found. On refluxing, the concentration of template on reactant surface becomes more and it is known that the template content in small pore molecular sieves is more, so it is concluded that the atmospheric synthesis give mostly small pore molecular sieves.

4. Conclusions

In summary, the synthesis of small pore aluminophosphate ($AlPO_4$-Atm) molecular sieves will contribute substantially to our understanding of the nature and chemistry of $AlPO_4$-n and other related materials. Owing to the greater diversity of atmospheric pressure refluxing systems there is a considerable potential for the synthesis of a variety of novel molecular sieves by the use of this technique.

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