Synthesis and characterization of AlPO₄-zeolites using alanine and glycine as templates

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Microporous AlPO₄-zeolites have been synthesized in the presence of glycine and alanine under mild hydrothermal conditions, maintaining temperature at 150°C under autogeneous pressure. Reaction mechanism has been proposed for the crystallization process. The use of amino acids results in tremendous effects on the pore size of AlPO₄-zeolites. The cell volume and surface area are increased while the void fraction is decreased. The products have been characterized using XRD, FTIR, Positron annihilation life time techniques and BET surface area analysis. Scanning electron micrographs show the morphological and structural changes when alanine and glycine are used as structure directing agents or templates.

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Experimental

Zeoitites are being extensively used as acid catalysts for a variety of organic reactions because they are inexpensive, non-corrosive, form more number of reactive sites and act as Lewis acid. Recently, we have used microporous aluminophosphate zeolites for the synthesis of bisphenol-A and cinnamic acid. Hydrothermal synthesis has been used to crystallize a large variety of open framework aluminophosphate zeolites with different organic amines as structure directing agents, since the initial reports on the AlPO₄-n series. This prompted us to use amino acids instead of amines and to study their relations with porous aluminophosphate structures. Studies on microporous AlPO₄-zeolites using alanine and glycine as structure directing templates are reported here.

The aluminophosphate zeolites were synthesized using commercially available Al(OH)₃ of analytical grade from Sisco Research Laboratory, 85% orthophosphoric acid of laboratory grade from Qualigens Fine Chemicals, alanine and glycine of analytical grade from Sisco Research Laboratory. For synthesizing microporous aluminophosphate zeolites with glycine and alanine as structure directing agents, firstly the aluminophosphate gels were prepared by neutralizing Al(OH)₃ (49.9 mmol) homogeneously in double distilled water (50 mL) and orthophosphoric acid (H₃PO₄) (51.76 mmol) very slowly with rigorous stirring. The obtained gel (known as reactive gel) was aged for 3 h at 60°C over a hot water bath, and the amino acid like glycine (59.3 mmol)/alanine (42.1 mmol) was added to the reactive gel, which acts as structure directing agents to yield the precursor gel. This precursor gel was aged for 3 h at 60°C over hot water bath. At every step, pH was recorded and the final precursor gel was charged around 60% into 30 mL capacity Teflon (PTFE) lined steel Morey type autoclaves made up of SS316. The employed experimental conditions are given in Table 1.

The hydrothermal runs were carried out for a period of 72 h at 150°C in a hot air oven. After the experimental runs, the autoclaves were quenched initially using an air jet and then in water. The run products were recovered carefully and washed thoroughly using double distilled water and ultrasonicated to remove adhered amino acids. Then, the run products were dried in hot air oven at about 60°C. The resultant products were subjected to the systematic characterization like powdered X-ray diffraction at room temperature (25°C) on a Rigaku Miniflex X-ray diffractometer model IGC2 [X-ray powdered diffractometer with a Cu target (λ = 1.5406 Å)]. The samples were scanned from 10° to 40° in 2θ. FTIR spectra were taken in the region 400-4000 cm⁻¹ using the JASCO-460 Plus spectrophotometer. Positron annihilation lifetime (PAL) spectroscopic studies were carried out using positron annihilation lifetime spectrometer with the 10 μCi ²²Na source sandwiched between two identical pellets of the Zeolite sample. The measured spectra were analyzed using PATFIT-88 program with necessary source corrections following the variance of fit. The BET surface area measurements were carried out for the AlPO₄ zeolite. Average specific surface area was calculated using the Micromeritics software.
Table 1 — Experimental conditions to prepare the microporous AlPO₄-zeolites

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Al source</th>
<th>P source</th>
<th>Solvent</th>
<th>Initial pH</th>
<th>pH after 3 h</th>
<th>Amino acids</th>
<th>pH</th>
<th>Gel pretreating</th>
<th>Hydrothermal reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al(OH)₃</td>
<td>H₃PO₄</td>
<td>H₂O</td>
<td>3.17</td>
<td>4.17</td>
<td>-</td>
<td>3.17</td>
<td>60 h 4.17</td>
<td>150 h 72 6.5</td>
</tr>
<tr>
<td>1</td>
<td>Al(OH)₃</td>
<td>H₃PO₄</td>
<td>H₂O</td>
<td>3.17</td>
<td>4.17</td>
<td>Glycine</td>
<td>1.44</td>
<td>60 h 3.14</td>
<td>150 h 72 5.2</td>
</tr>
<tr>
<td>2</td>
<td>Al(OH)₃</td>
<td>H₃PO₄</td>
<td>H₂O</td>
<td>3.17</td>
<td>4.17</td>
<td>Alanine</td>
<td>1.46</td>
<td>60 h 3.69</td>
<td>150 h 72 5.8</td>
</tr>
</tbody>
</table>

Results and discussion

It is well known that the reaction of 85% orthophosphoric acid with aluminum hydroxide forms aluminophosphate at 60°C. During the preparation of aluminophosphate gel, we observed that upon addition of amino acid to the mixture (aluminum hydroxide and 85% orthophosphoric acid), pH of the solution drops suddenly from 4.17 to 1.3 in case of alanine, and 1.6 for glycine, as shown in Fig 1. This may be due to the intermediate reaction (2), which carries ammonium ion. This ammonium ion carries replaceable proton, so that pH will drop to 1.4. Later, upon aging at 60°C, the intermediate reaction (2) undergoes breakage of Al-O bond at the amino acid end and loses CO₂ to form the zwitterionic salt [Eq. (3)], that later rearranges to methyl amine, which is basic in nature. It was confirmed by the chemical analysis. As a result of this, pH of the resultant solution changes from 1.44 to 3.14 as shown in the Scheme 1 (AlPO₄ with glycine). Similar reaction scheme can be proposed (Scheme 2) for the reaction of AlPO₄ with alanine.

Powder X-ray diffraction

The powder X-ray diffraction patterns were obtained from Rigaku table top diffractometer-IGC2 and cell parameters of AlPO₄-glycine and AlPO₄-alanine are shown in Table 2. The volume of the unit cell is more in AlPO₄-alanine than in AlPO₄-glycine. Hydrogen bond formations (both inter and intra interaction) increase the network.

The increase in the cell volume is also proposed from the FTIR spectra where we observe a change in the intensity of the peak 1645 to 1659 cm⁻¹. This is also proportional to the number of hydrogen bonds per unit cell.

FTIR spectroscopy

The FTIR spectra of AlPO₄ zeolites in the 400 cm⁻¹ to 1300 cm⁻¹ region consist of two classes of vibrations: (i) those caused by internal vibration of the
Table 2 — Cell parameters of AlPO₄ - blank, -glycine and -alanine

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO₄-blank</td>
<td>20.9163</td>
<td>20.9163</td>
<td>21.0513</td>
<td>90°</td>
<td>90°</td>
<td>120°</td>
<td>7975.895</td>
</tr>
<tr>
<td>AlPO₄-glycine</td>
<td>20.4641</td>
<td>20.4641</td>
<td>23.5261</td>
<td>90°</td>
<td>90°</td>
<td>120°</td>
<td>8532.295</td>
</tr>
<tr>
<td>AlPO₄-alanine</td>
<td>22.0095</td>
<td>22.0095</td>
<td>26.0017</td>
<td>90°</td>
<td>90°</td>
<td>120°</td>
<td>10908.175</td>
</tr>
</tbody>
</table>

framework TO₄ (where T = Al) tetrahedron, the primary building units (PBU) in all zeolite frameworks, which tend to be sensitive to variation in framework structure, (ii) vibration related to external linkage between tetrahedral units which are sensitive to the framework structure and to the presence of secondary building units (SBU).

The sharp peak around 1070 cm⁻¹ is due to the asymmetric stretching in AlPO₄ zeolite. Such an absorption peak may be an exclusive feature of AlPO₄ zeolite that contains the hydrated triple crankshaft chains. The strongest vibration in this region is assigned to a T-O stretch involving motions primarily associated with oxygen atoms or alternatively described as an asymmetric stretching mode ←O T→←O (Ref. 4). The exact position of the P=O varies with the sum of electronegative groups tending to pull electrons from the phosphorus, thus competing with the bond weakening tendency for the double oxygen to attract electrons (P-O), resulting in stiffer P=O bond and a higher frequency. The P=O frequency is sensitive to substitution. The presence of an OH group in the vicinity of a P=O group generally lowers the stretching frequency by 50 to 80 cm⁻¹ due to the hydrogen bonding. The broad band around 1070 cm⁻¹ has been assigned to the asymmetric stretching of PO₄ tetrahedra. The shift to higher wave number is due to the presence of large amounts of phosphorus, since the P-O bond distance is shorter than Al-O. The presence of a weaker shoulder at ca. 1137 cm⁻¹ is assigned to vibration involving ≡Al-OH nests created by the phosphorus vacancies. In the region 730-740 cm⁻¹ and below, there are many differences in the number and frequency of the absorption reflecting the variation in the framework composition. The absorption peaks at 730 to 740 cm⁻¹ correspond to the symmetric stretching vibration of PO₄ groups. The bands around 633, 582 and 481 cm⁻¹ are related to the bending vibration of PO₄ groups or in the vibration modes of the 4-membered rings of AlPO₄ chains. The stretching vibrations of PO₄ are shifted towards lower frequency indicating that the presence of the internal P=O…HO-P bonds.

Stretching modes involving motions primarily associated with the T atoms, or alternatively described as symmetric modes ←O T→O are assigned in the region of 650 cm⁻¹ to 834 cm⁻¹ (ref. 6). The weak absorption at about ~633 cm⁻¹ is due to the interaction between alumina tetrahedra of the zeolite structure and Al³⁺. There is a splitting of the peak at this region and it is due to higher O-P-O angles in the structure. The concentration of small nuclei formed during the induction period can be followed using the intensity of lattice vibration around 582 cm⁻¹. This vibration increases obviously, which shows the increase in the number of double rings of T-atoms.

The very weak band around 1480-1380 cm⁻¹ may be affected by the non-structural alumina present in the pores. The broad weak band around 3000 to 4000 cm⁻¹ is attributed to the stretching vibration of hydrogen group of water molecules present in the pores of the AlPO₄ zeolites. The weak and sharp peaks at 1700-1500 cm⁻¹ result due to bending vibration of water.

The external linkage frequencies occur principally in two regions of the spectrum at 500 to 600 cm⁻¹. A medium intensity band in the former has been related to the presence of double ring polyhedra in the framework. Thus, all of the zeolite frameworks with D-4 and D-6 rings have a medium (or in a few cases mw or ms) band in the 500 to 400 cm⁻¹ region. The second main external linkage frequency can be assigned to a breathing motion of the isolated rings forming pore opening in zeolites.

The IR spectra of pure amino acids show no peaks around 3100 to 3500 cm⁻¹. But, a broad peak at 2900 to 3100 cm⁻¹ is observed, while that of AlPO₄ without any amino acids shows broad peak at 3000 to 3500 cm⁻¹. But in the AlPO₄ with amines, a sharp peak at 3580 cm⁻¹ appears. This may be due to the formation of amines as shown in the scheme. The peak around 1645 to 1659 cm⁻¹ shows large change.
from AlPO₄-alanine to AlPO₄-glycine. This shows an increase in hydrogen bond formation when alanine is used as structure directing agent. The intensity of the band absorbed at 1645 to 1659 cm⁻¹ signifies the large-scale hydrogen bond.

**Positron annihilation lifetime measurements (PALS)**

The positron annihilation studies were carried out to know the free volume of the pores interconnecting channels in the hydrothermally synthesized AlPO₄ zeolites containing aminoacids. The zeolite sample under study was made into two identical pellets of dimension 1 cm diameter and 1.2 mm thickness and used in positron lifetime measurements. Positron lifetime spectra were recorded using the positron lifetime spectrometer consisting of fast-fast coincidence unit with BaF₂ detectors coupled to XP2020/Q photomultiplier tubes. The spectrometer has a time resolution of 220 ps.

Of the four lifetime components, τ₃ and τ₄ are the lifetimes of o-Ps, which annihilate in micropores of the zeolites. The respective intensities of τ₃ and τ₄ are I₃ and I₄, which represent the number of density of respective size micropores. The relation between o-Ps lifetime and the size of the pores (free volume cavities) is given by Nakanishi, et al.⁹,¹⁰ as:

\[
(\tau_4)^{-1} = 2 \left[1 - \left(\frac{R}{R_o} + \frac{1}{2\pi} \sin(2\pi\frac{R}{R_o})\right)\right]
\]

where \(R\) is the radius of the pores and \(R_o = R + \Delta R\), where \(\Delta R\) is a fitting parameter. A value of \(\Delta R = 1.656\ \text{Å}\) is used in evaluating the radius of the pores from the above equation. With the \(R\) values, the pore volume of the free volume cavity is calculated as \((4/3)\pi R^3\). The results so calculated are given in Table 3, exhibiting that the intensity changes in the presence of glycine and alanine acting as structure directing templates. With glycine, the AlPO₄ structure evolves with more micropores (radius of 1.36 Å) and for slightly bigger pores (radius of 3.14 Å). But with alanine, there is a drastic change in the sample. The bigger size pores which are present with glycine are totally absent and even the smaller pores reduced in their number density. Considering the XRD results, the structure with alanine has bigger cell volumes of 10908.175 Å³ which means it can accommodate larger molecules. The absence of \(\tau_4\) and \(I_4\) in this zeolite sample seems to be obvious.

**BET surface area analysis**

The BET surface area measurements were carried out for the AlPO₄ zeolite. 0.1 to 0.5 g of fine grained samples were taken in a glass sample holder tube. The samples were then degassed for 2 h at 70°C using nitrogen gas (15 psi pressure). Then, the sample tube was fixed to the analyser along with the balance tube and both the tubes were kept in the nitrogen bath. The

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_4\pm0.02) (ns)</th>
<th>(R_3) (Å)</th>
<th>(V_3) (Å³)</th>
<th>(f_{V3}=V_3*I_3)</th>
<th>(\tau_4\pm0.02) (ns)</th>
<th>(R_4) (Å)</th>
<th>(V_4) (Å³)</th>
<th>(f_{V4}=V_4*I_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO₄-blank</td>
<td>0.792; 17.3</td>
<td>1.27</td>
<td>8.5</td>
<td>147.0</td>
<td>2.10; 7.4</td>
<td>2.95</td>
<td>107.2</td>
<td>793.2</td>
</tr>
<tr>
<td>AlPO₄-glycine</td>
<td>0.835; 20.0</td>
<td>1.36</td>
<td>10.5</td>
<td>10.5</td>
<td>2.33; 6.1</td>
<td>3.14</td>
<td>130.0</td>
<td>793.0</td>
</tr>
<tr>
<td>AlPO₄-alanine</td>
<td>1.18; 5.5</td>
<td>1.96</td>
<td>30.3</td>
<td>30.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 2 — Scanning electron micrograph of AlPO₄: (a) blank, (b) glycine, and (c) alanine.
sample and balance tubes were evacuated initially followed by the nitrogen gas purging (15 psi pressure) for the adsorption. Average specific surface area from the 6 adsorption cycles was calculated using the Micromeritics software.

The specific surface area for AlPO₄-blank is 09.05 m²/g; for AlPO₄-glycine is 11.25 m²/g; and, for AlPO₄-alanine, it is 34.68 m²/g.

**Scanning electron micrographs**

In order to study the morphology and size of AlPO₄-alanine and AlPO₄-glycine zeolites structures, SEM was taken (Fig. 2). The structure shows a broad range of size distribution. The micrographs reveal surface morphology of the crystallites. The blank AlPO₄ zeolites agglomerate, whereas AlPO₄ glycine crystallizes like a flower and AlPO₄ alanine crystallizes in the tabular forms. As indicated by the micrographs, the nanostructures grown by hydrothermal method are obtained in different shapes and sizes. Amino acids appear to be the dominant processing factors in controlling the morphology of the obtained crystallites.

**Conclusions**

The synthesis of AlPO₄-alanine and AlPO₄-glycine zeolites have been carried out under hydrothermal conditions at 150°C and autogenous pressure. The hydrothermal crystallization process has been understood through the proposed reaction mechanism. The pH of the solution was strongly influenced by the alanine and glycine in the formation of AlPO₄– zeolites. Based on the XRD and FTIR spectroscopic studies, it can be inferred that the cell volume increases sufficiently with addition of the alanine and glycine, indicating a large-scale hydrogen bond network within the unit cell. The free volume has been determined through the positron annihilation studies. It has been proved that the AlPO₄-alanine has larger pore than the AlPO₄-glycine. It is also confirmed from the BET surface area analysis, that the surface area is more in AlPO₄-alanine as compared to that of the AlPO₄-glycine and AlPO₄-blank. Scanning electron micrographs reveal that amino acids plays an important role in the morphological and structural changes.

**References**