Characterization of Amorphous $AlPO_4$ Surface Sites

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Summary: $AlPO_4$ surface possesses weakly acidic AlOH and POH groups generated due to water chemisorption on the surface. The presence of these groups on the surface were identified from the well-defined peaks in the infra red region at 510, 1000-1200, for PO bending/stretching respectively and 1650, 3400 and 3780 cm^{-1} for AlOH and POH. Heat treatment at 300 °C affects only the Bronsted acidic sites i.e., weakly acidic AlOH and POH at 1650, 3400 cm^{-1} and disappearance of the band at 1400 cm^{-1} whereas the lattice nature remains unaffected. Water adsorption again enhanced the bands at 1650 and 3400 cm^{-1} along with re-appearance of the band lost at 1400 cm^{-1}.

Introduction

Inorganic solids, such as zeolites, metal oxide/ hydroxide and metal arsenate in amorphous, semi crystalline and crystalline forms have been widely studied as catalysts, molecular sieves, chromatographic columns, ion exchangers etc [1-3]. Apart from these solids metal phosphate has also been in market as protective coatings against corrosion, molecular sieves and catalysts such as in dehydrogenation, dehydration and isomerization reactions [4-6]. These inorganic solids have often been characterized using IR/ FTIR spectrometry which helps understand the presence and mechanism of surface sites [7, 8].

Moffat *et al.,* [9] investigated water adsorption mechanism on BPO_4 using IR spectrometry and postulated the presence of BOH and POH groups on the surface which were presumed to be due to partially dissociation of water molecules on the surface.

The IR spectrum for Al substituted hydroxyapatite was interpreted by Ishikawa *et al.,* [8]. The bands at 3784, 3744, 3735 and 3712 cm^{-1} showed the appearance of the Al-OH groups. Previous studies [10] for Si-substituted $AlPO_4$ showed the bands at 3735 cm^{-1} for terminal Si-OH groups, 3666 for terminal POH/ AlOH, 3362 for bridged Si-OH-Al.

$AlPO_4$ a chemical combination of AlO_4 and PO_4 tetrahedron exist both in amorphous and crystalline forms, occurs both naturally as well as synthesized possessing variable properties such as acidity, pore size and shapes. The catalytic activity and extent of sorption is related to the surface Bronsted and Lewis acidic sites. The FTIR studies investigated so far reported the presence of weakly acidic AlOH and POH groups on the surface [11, 12].

The present study deals with application of FTIR spectroscopic technique for determining type of groups on the amorphous $AlPO_4$ surface and effect of heating on such groups.

Results and Discussion

Figure 1 shows the FTIR spectra of $AlPO_4$. This spectra shows a weak band at 3780 cm^{-1}, very broad band at 3450 cm^{-1}, a small band at 2330 cm^{-1}, a sharp band at 1650 cm^{-1}, sharp and broad band at 1000-1200 cm^{-1}, weak band at 800 cm^{-1}, a broad band at 640 cm^{-1} and a sharp band at 510 cm^{-1}. The band observed at 1000-1200 cm^{-1} and 510 represents P-O banding and stretching vibrations of PO_4 units respectively. A small band at 1380 cm^{-1} is due to anti-symmetric stretching of POH group. OH bending of the matrix is attributed to the band at 1650 cm^{-1} while 3450 cm^{-1} band is due to OH stretching vibrations. These bands arise due to chemisorption of H_2O on neutral $AlPO_4$ surface, resulting in acidic AlOH and POH sites according to reaction 1,

$$AlPO_4 + H_2O \Leftrightarrow Al(OH)(HPO_4) \qquad [1]$$

Similar conclusions for $AlPO_4$ were reported in the literature [13]. Individual identification of AlOH is not possible as the bands overlap each other.

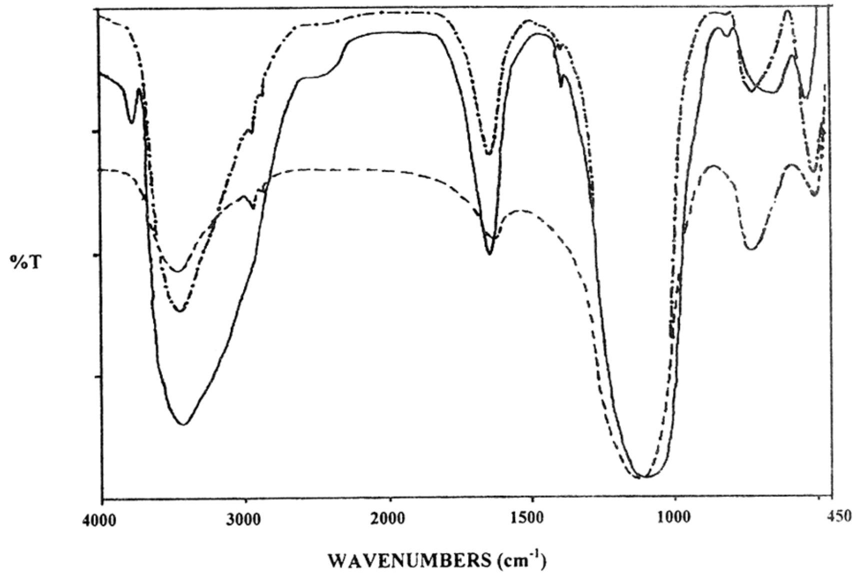
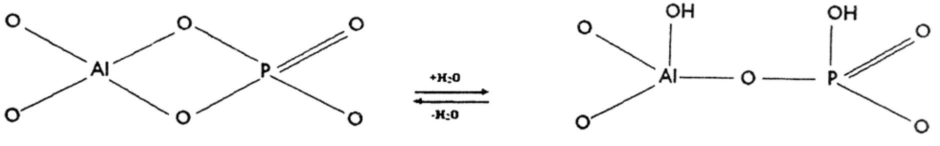


Fig. 1: FTIR spectra of $AlPO_4$, ——— = $AlPO_4$ dried at 105 °C, – – – = $AlPO_4$ treated at 300 °C for 04 hours, -·-·- = $AlPO_4$ after water adsorption at 26 °C

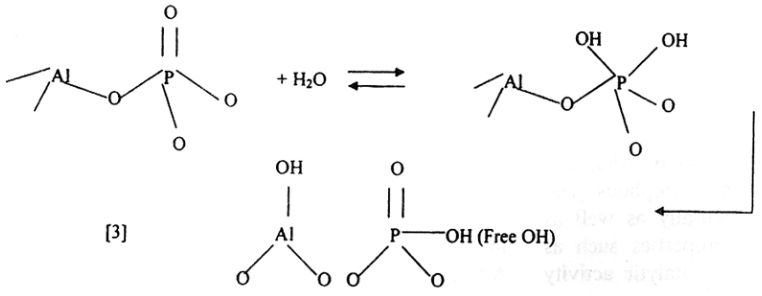
The broadness of 3450 cm^{-1} band suggests that H-bonding interactions are involved, possibly from adjacent OH groups. The sharp band at 3780 cm^{-1} is attributed to some form of free or unperturbed OH (no hydrogen bonding is involved) that is AlOH and POH. Bands at similar position were reported [11, 12] in a number of $AlPO_4$. This represents some isolated OH groups on the surface, or adjacent OH groups with one OH hydrogen bonded leaving the other OH group relatively unperturbed.

Mechanism of water adsorption

$AlPO_4$ is considered as a mixed oxide composed of AlO_4 and PO_4 sites. Both these sites can be assumed to explain the reactivity and catalytic properties of $AlPO_4$ towards water molecules. The



[2]



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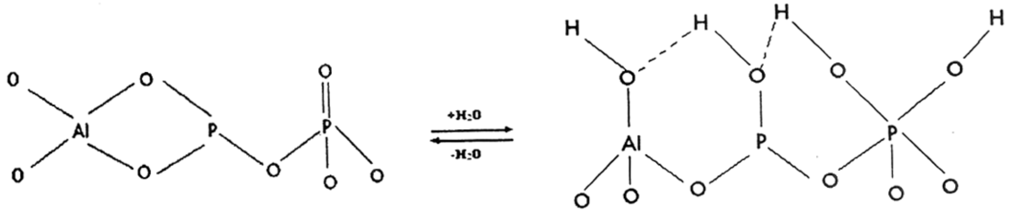

[4]

dissociation of water on the solid surface may be presumed to be according to the following reactions.

Reaction 2 is responsible for appearance of the broad band at 3450 cm^{-1}. AlOH and POH on the surface are in close vicinity and therefore, interactions of hydrogen bonding cannot be ruled out.

In reaction 3 some of the free OH groups in the form of AlOH and POOH may not interact through hydrogen bonding due to lying far distant from each other. This reaction 3 appears in the form of band at 3780 cm^{-1}. Water dissociation on the surface may also takes place according to reaction 4 where H bonding is also prominent. This type of arrangement of P atoms may be due to polymerization of P groups with heat treatment of AlPO$_4$ and was supported in the literature [11].

The spectrum of AlPO$_4$ after heat treatment shows that the bands for P-O bending and stretching appear at similar positions. However, a decrease in the intensity of OH bending/stretching has been noted. Similar decrease in OH bending and stretching was reported in barium phosphate and Co substituted AlPO$_4$ [9, 14]. Further, the bands become sharpen after heat treatment. Two band of very low intensity at 2847 and 2925 cm^{-1} also appeared with heat treatment and were assigned to OH stretching which were previously overlapped due to presence of densely population of water molecules both physically as well as chemically bonded. These observations show the loss of some physical and chemical bound waters after heat treatment. The band at 1380 cm^{-1} completely disappears. The proton of POH and OH group of AlOH a form of chemisorbed water shown in reaction 2 (right hand side) are removed with heat treatment leaving bare PO group. This removal of chemisorbed water leads to the rearrangement of AlPO$_4$ structure shown in reaction 2 (left hand side). The band at 640 cm^{-1} has shifted to 720 cm^{-1} and become sharper while the band at 800 cm^{-1} has disappeared with heat treatment. The origin of these bands may also be due to loss of H_2O molecules from the matrix. The shift of PO band at 640 to higher frequencies upon dehydration may be because of the hydrogen bonding of the hydrate water molecules to the oxygen in the phosphate anions which when removed results in a shift of PO band towards higher frequencies. The origin of the 800 cm^{-1} band can be assigned to the PO bending of hydrogen bonding of physisorbed water molecules. Removal of these physisorbed water molecules completely leaves the PO group with no hydrogen bonding and therefore no sign of 800 cm^{-1} band in the IR region.

The FTIR spectra after water vapor treatment for four days show an increase in intensity of OH bending and stretching at 1635 and 3450 cm^{-1} pointing towards water re-adsorption on the surface leading to an increase in the number of weakly acidic O-H sites. Most of these groups were previously lost which in the present case has re-appeared. This appearance shows the adsorption of water on the same sites from which these groups were removed and thus support our proposed mechanism in reactions 2, 3 and 4. In addition an increase in P-O bending vibrations at 510 cm^{-1} is also noted. The increase of P-O bending points towards the physical type of interactions of H_2O adsorption. Hydrogen bonding of water molecules with oxygen of the P-O group enhances the intensity of PO bending and stretching. The 1380 cm^{-1} band reappears after water adsorption. The weak band at 800 cm^{-1} has also reappeared after water vapor adsorption indicating the regeneration of acidic POH sites.

It is thus concluded, that the amorphous Al (III) phosphate has weakly acidic AlOH and POH groups on the surface and that the concentration of these groups decrease with heat treatment. Removal of physical adsorbed as well as condensation of chemically adsorbed water molecules from the adjacent AlOH and POH groups occurs with heat treatment. The surface groups may regenerate after water adsorption.

Experimental

The solid $AlPO_4$ was provided by Merck in amorphous form and was heated at 105°C for 24 hours prior to studies. A portion of $AlPO_4$ was heat treated at 300°C for four hours in a furnace model HT 16147 Naber industrieofenbau W. Germany.

Double distilled water was used wherever needed.

FTIR spectras of $AlPO_4$ was taken by FTIR spectrometer model Perkin Elumer 16pc.

5 mg of solid was mixed with 1gm of KBr (A.R grade) and were ground to fine powder. The powder was shaped into transparent disk under an applied pressure of 10 tons for 3 minutes. After the interval the pressure was slowly relieved and the disk was subjected to IR radiations setting a resolution of 4 cm^{-1} and 5 scans.

Water adsorption was carried out by taking 0.2 g $AlPO_4$ in 20 ml distilled water using a 50 ml pyrex glass flask. The flask was kept in water bath set at a temperature of 25 °C for four days. During the equilibrium time the flask was shaken for 5 minutes after every 24 hours. After equilibration for 04 days the suspension was filtered through a Whatman filter paper (Schleicher & Schuell Rundfilter) and was dried in air.

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