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Synthesis and characterization of a novel class of molecular sieves namely organophosphate

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Abstract : A novel class of molecular sieves namely organophosphates are reported for the first time. The molecular sieves are similar to zeolites in many properties. One among them was *n*-propylamino phosphate and it is similar to ZSM-5 (MFI) zeolite. Characterization by various instrumental techniques shows interesting properties. Attempt to synthesize organosulphate results in less stable materials. Secondary and tertiary amines did not produce solid product. A plausible mechanism on its synthesis is also proposed. It is soluble in water but insoluble in most of the organic solvents.

Keywords : *n*-Propylaminophosphate, MFI, basic catalyst.

Introduction

Argauer and Landolt[1] from Mobil Oil Corporation, in 1972 was reported the first patent on the synthesis of a pentasil aluminosilicate zeolite, termed as ZSM-5. The structure of ZSM-5 is constructed using five member ring building units. The combination of these building units results in a framework containing two intersection channel system, one sinusoidal and the other straight (5.3 × 5.6 Å and 5.1 × 5.5 Å). The pore openings are elliptical 10-member rings. There are 12 unique T atom sites in ZSM-5. This structure is successfully described in the orthorhombic space group Pnma. It is also known that the molecular sieve is prepared in broad range of SiO_2/Al_2O_3 ratio i.e. 5-100. Further it is reported to synthesise by using tetrapropylammonium bromide and tetrapropylammonium hydroxide templating agents. Later, it is reported to synthesise in the SiO_2/Al_2O_3 range > 200[2,3]. There are several literatures on the synthesis of ZSM-5 type molecular sieves by using a wide variety of amines[4-8] as templates which include ethylene diamine[9,10]. The role of organic structure-directing agents has been discussed by several authors[11,12] as it plays an important role in the kinetics of nucleation and crystallization. Both solid phase and liquid phase transformations have been proposed[12] as possible mechanisms.

ZSM-5 is an industrially important catalyst, applicable to several organic transformations. There are several attempts made to reduce the crystallization period and cost of reagents and to improve the yield. However the result is poor. Here we have succeeded to synthesise the ZSM-5 like molecular sieve (*n*-propylaminophosphate) through instant reaction by efficient way. We have attempted to synthesise other organo inorganic molecular sieves. The results are interesting. There is a possibility to synthesise a family of similar molecular sieves by varying the amine. The *n*-propylaminophosphate was also characterized by different physicochemical techniques such as X-ray diffraction, scanning electron microscopy, thermogravimetry/differential thermal analysis, Fourier transform infrared spectroscopy, nitrogen adsorption, UV-Visible, X-ray photoelectron spectroscopy, ^{31}P Magic angle spinning Nuclear Magnetic Resonance spectroscopy and catalytic properties. The results are compared with ZSM-5 synthesized using ethylene diamine.

Experimental

In a typical procedure the *n*-propylaminophosphate was synthesized as follows. 1 : 4 molar ratios of orthophosphoric acid (85%, s.d. fine, India) and *n*-propylamine (98%, Aldrich, USA) were mixed well. A thick white solid resulted. The ground solid was dried at 80 °C for 12 h. The solid was subjected to various physicochemical characterizations. Similar synthesis was carried out using different amines.

ZSM-5 was synthesized using ethylene diamine as follows. 0.825 g of sodium aluminate (99%, s.d. fine, India) was mixed well with 2.1 g of sodium hydroxide (99%, s.d. fine, India) and 129 g of distilled water. This mixture was stirred well until the entire solid is dissolved and this was taken as solution A. Another solution B was made by thorough mixing of 46.47 g of silica sol (30%, s.d. fine, India) and ethylene diamine (C_2DN, 18.3 g, 99%, Aldrich, USA). Solutions A and B were mixed well to make clear mixture ($6.0Na_2O : Al_2O_3 : 15.2SiO_2 : 592H_2O : 19.7C_2DN$) and charged into a Teflon lined steel autoclave. Crystallization was carried out at 177 °C for 6 days.

The samples synthesized during the course of the work under different conditions were analyzed for qualitative phase identification by X-ray powder diffraction (Rigaku, Model D/MAX III VC, Japan, Ni filtered Cu-Kα radiation, λ = 1.5404 Å). The morphology of the organophosphate was investigated using a scanning electron microscope (JEOL, JSM 5200). Simultaneous thermogravimetry/differential thermal analysis of the crystalline phases were performed on an automatic derivatograph (Setaram TG-DTA 92). The Fourier transform infrared spectra were recorded in the diffuse reflectance mode using a 300 : 1 ratio sample in KBr (Nicolet 60SXB). The adsorption and desorption measurements were carried out using an Autosorb-1 instrument. The ultraviolet-visible diffuse reflectance spectra were recorded using a Pye Unichem (SP-8-100) spectrometer in the 200–800 nm regions. X-Ray photoelectron spectroscopy was measured at 10^{-8} mm using a Vg Scientific, ESCA-II MK3 instrument. All spectra were corrected at carbon C1s. Magic angle spinning nuclear magnetic resonance spectra were recorded in the solid state with a Bruker DRX 500 spectrometer.

Results and discussion

The X-ray diffraction patterns of ZSM-5 and *n*-propylaminophosphate are given in Fig. 1. Both are looking similar (Table 1, MFI type structure) except small changes in peak intensities[16]. In general the first two peaks of ZSM-5 were small compared to middle range peaks. However on calcination at 550 °C, the first two peaks

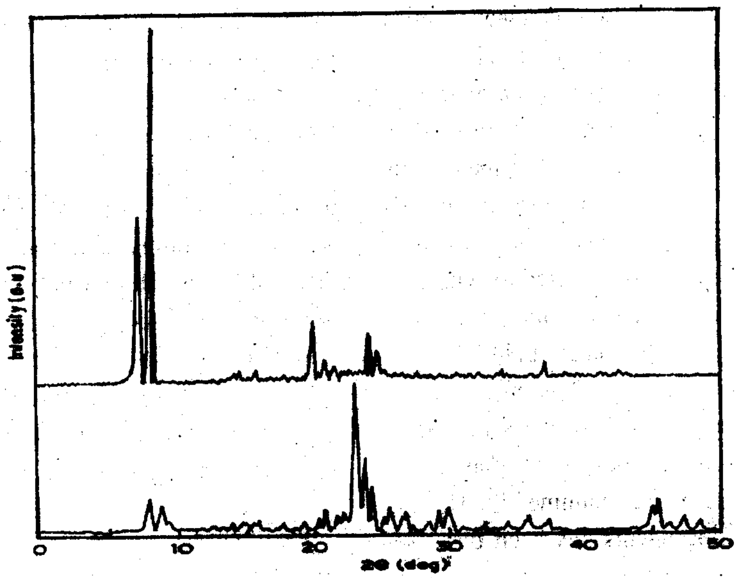
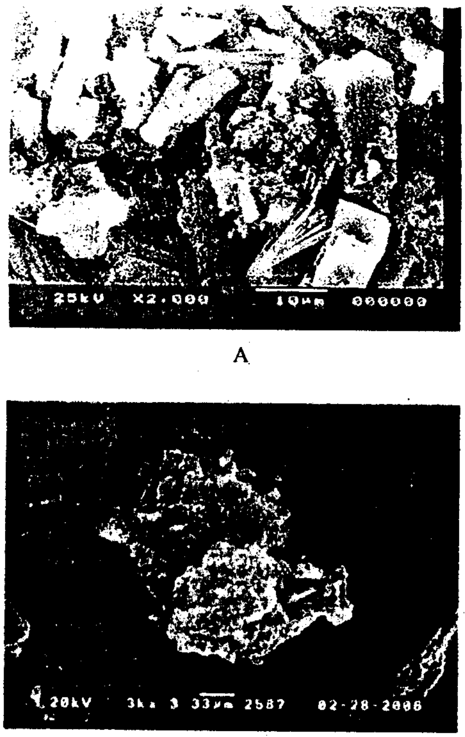


Fig. 1. X-Ray diffraction pattern of ZSM-5 (down) and *n*-propylaminophosphate (upper).

Table 1. X-Ray diffraction peak position of MFI type molecular sieves

Sl.	Organophosphate		ZSM-5	
no.	2θ	I/I_0	2θ	I/I_0
1.	6.7	47	7.8	24
2.	7.2	100	8.8	20
3.	20.0	18	22.8	100
4.	21.0	6	23.8	50
5.	21.6	4	24.1	33
6.	25.9	13	28.8	16
7.	26.8	7	30.0	19
8.	37.5	5	45.3	21

intensity was rising higher. So it is derived that this phenomenon is due to the presence of water. As organophosphates do not containing water, the synthesized sample itself contains the first two peaks in higher intensity. This is a unique nature of the organophosphate. This phenomenon is verified by XRD studies on hydrated ZSM-5 samples after calcination. *n*-Butyl amine also gives similar (ZSM-5 like) material. Aniline gives AFI ($AlPO_4$-5) and *p*-nitro aniline gives AFO ($AlPO_4$-41) structure. Secondary and tertiary amines did not give any solid product. Attempt to synthesize organosulphate results in less stable material. The organophosphates are soluble in water. However, they are mostly insoluble in organic solvents. We also succeeded in incorporating manganese in organophosphate. Synthesis of organo silicates is well on the way.



A

B

Fig. 2. Scanning electron micrograph of (A) ZSM-5 and (B) *n*-propylaminophosphate.

Scanning electron micrographs of ZSM-5 and *n*-propylaminophosphate are given in Fig. 2. The morphology of ZSM-5 is different from *n*-propylaminophosphate. Fig. 2a of ZSM-5 shows intergrown platelets (15 × 2 μm) and Fig. 2b of *n*-propylaminophosphate shows mostly cuboids (15 μm). It is not expected that both the synthesis give same morphology and particle size as the synthesis parameters are different.

Fig. 3 shows the thermogravimetric and differential thermometric analysis curves for ZSM-5 and *n*-propylaminophosphate. The thermogravimetry of ZSM-5 shows two different weight losses at 25–130 °C (4.52%) and 130-661 °C (8.59%). The first endothermic loss is due to the loss of physisorbed material and second one is due to loss of oxidatively decomposition of the entrapped template (organic amine). *n*-Propylaminophosphate loses exothermically at 25–800 °C (80%). This may be due to oxidative decomposition of the organic amine. The weight loss at higher temperature shows the strong interaction of template with phosphate molecules. Elemental analysis shows that the ZSM-5 contain three ethylene diamine molecules per unit cell and *n*-propylaminophosphate has elemental composition, $(C_3H_7NH)_3PO$.

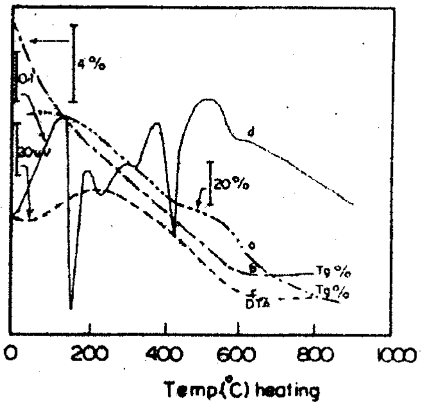


Fig. 3. Thermogravimetric (a, c)/differential thermal analysis (b, d) of (a, c) ZSM-5 and (b,d) *n*-propylaminophosphate.

The Fourier transform infrared spectra of synthesized ZSM-5 and *n*-propylaminophosphate in the framework region are given in Fig. 4. The peak positions and their assignments of *n*-propylaminophosphate and ZSM-5 are given in Table 2[17]. The highly characteristic peaks due to

Table 2. Fourier transform infrared spectroscopic vibrations of MFI type molecular sieves

Sample	T-O-T, asymmetric stretching		T-O-T, symmetric stretching		Double ring (cm^{-1})	T-O-T, bending (cm^{-1})
	Inner (cm^{-1})	Outer (cm^{-1})	Inner (cm^{-1})	Outer (cm^{-1})		
Organophosphate	1300	1000	750	–	550	500
ZSM-5	1250	1100	800	–	550	500

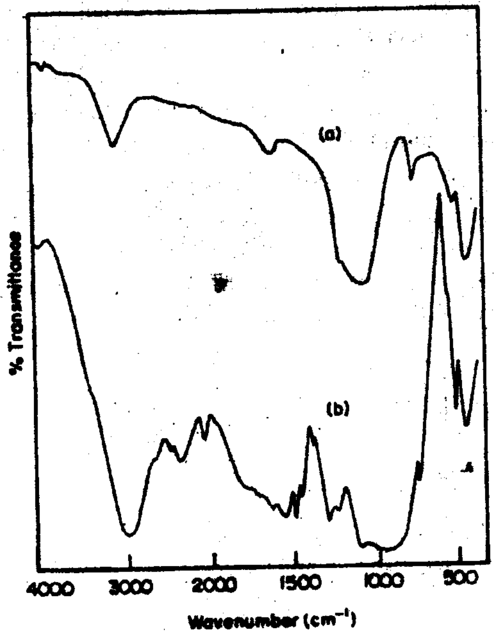


Fig. 4. Fourier transform infrared spectroscopic analysis of (a) ZSM-5 and (b) *n*-propylaminophosphate.

double ring vibrations and T-O-T bending vibration are similar in both the molecular sieves. Compared to ZSM-5, the *n*-propylaminophosphate peaks shifted to lower values due to expansion in pores.

Nitrogen adsorption curves for ZSM-5 and *n*-propylaminophosphate are given in Fig. 5. The N_2 adsorption isotherms of ZSM-5 are characteristics of micropore materials with uniform pore size[18] and type II. These isotherms show an inflection near p/p_0 0.72–0.96, indicating the capillary condensation within the pores. The presence of hysteresis, characteristic of multilayer adsorption dominating the process of filling and emptying the voids, indicates the pore size[19]. The BET surface area, is 300 m^2/g[20]. The adsorption isotherms of *n*-propylaminophosphate are of type III. The surface area is 100 m^2/g when it is activated at 100 °C before measurement. Activation at room temperature did not show any adsorption. This indicates that the pores are activated on

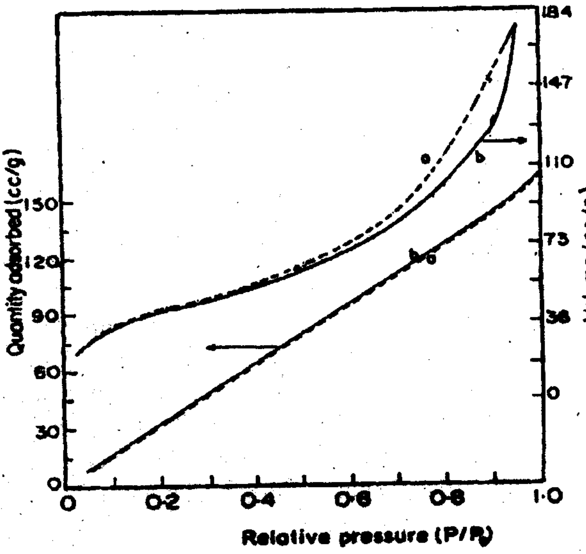


Fig. 5. N_2 adsorption curves of ZSM-5 (upper) and *n*-propylaminophosphate (down).

thermal treatment. Normally zeolites are activated at 400 °C in vacuum to remove the volatile impurities. The X-ray diffraction pattern of *n*-propylaminophosphate is reproducible after its thermal treatment up to 200 °C. As we know, the X-ray diffraction stability is essential for nitrogen adsorption, so we have activated the sample at 100 °C.

Fig. 6 shows the ultraviolet and visible spectra of *n*-propylaminophosphate. Two small peaks at 280 and 320 nm were observed. This may be due to P-O$^-$ species or tetrahedrally co-coordinated phosphorous species. ZSM-5 did not show any peak in this region.

The binding energy data from X-ray photoelectron spectroscopic analysis of ZSM-5 and *n*-propylaminophosphate are given in Table 1. Two different environmentally different Al or P species are observed in both the molecular sieves.

The Magic angle spinning nuclear magnetic resonance spectra of ZSM-5 and *n*-propylaminophosphate are

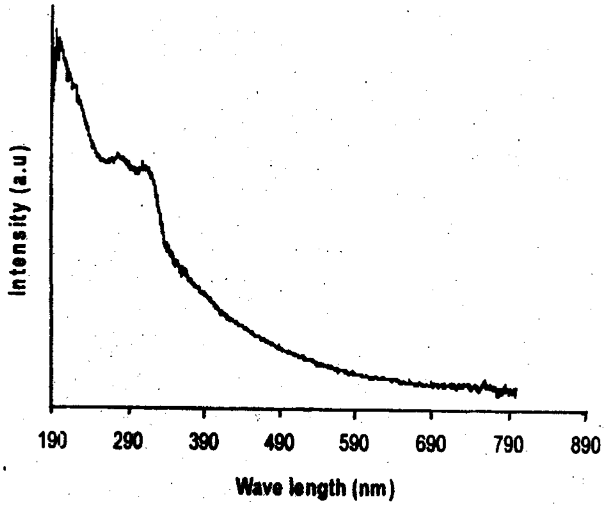


Fig. 6. Ultraviolet-visible spectra of *n*-propylaminophosphate.

given in Fig. 7. ^{27}Al MASNMR spectra of ZSM-5 show a single symmetrical line at 53.2 ppm along with small peak at 7.9 ppm for tetrahedral and octahedrally coordinated aluminium species. ^{29}Si MASNMR of the same sample shows the presence of Si : [3Al : Si] (–92.5 ppm), Si : [2Al : 2Si] (–101.8 ppm) and Si : [3Si : Al] (–107.0 ppm) species. The ^{31}P MASNMR of *n*-propylaminophosphate shows a peak around –29.0 ppm for tetrahedrally coordinated phosphorous atoms. However, the other two small peaks appeared for side bands.

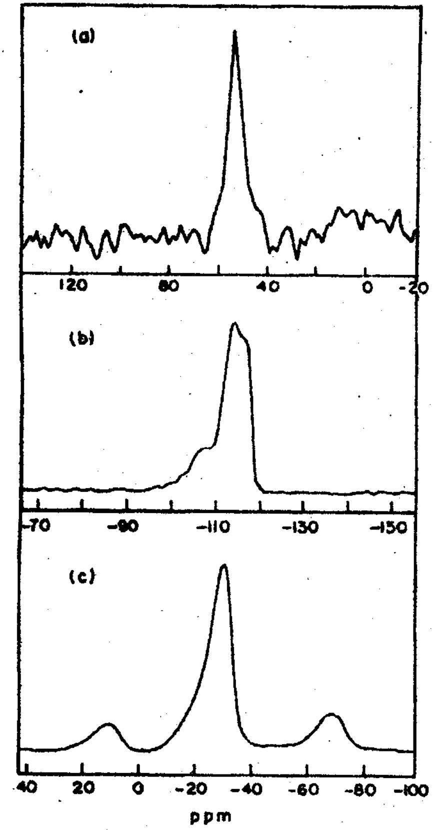


Fig. 7. (a) ^{27}Al, (b) ^{29}Si and (c) ^{31}P Magic angle spinning nuclear magnetic resonance spectra of ZSM-5 and *n*-propylaminophosphate.

Table 3. Binding energies of ZSM-5 and *n*-propylaminophosphate

Sample	Al/P (eV)	Si (eV)	C (eV)	N (eV)	O (eV)
Organophosphate	134 and 135 (P)	–	287	399	532
ZSM-5	73 and 74 (Al)	102	286	401	533.6 and 533.9

Scheme 1 shows a plausible mechanism for *n*-propylaminophosphate synthesis. Orthophosphoric acid has three hydroxyl groups. This three hydroxyl groups can easily react with three amine groups. The similarity with oxygen and nitrogen creates organophosphate structure similar to zeolites. The need for two hydrogen in organic amine supports this proposal. The organophosphate structure is neutral by presence of alternate P^{5+} and P^{3+} ions. Being a strong reducing agent (organic amine), the formation of P^{3+} species takes place. Compared to zeolites and aluminophosphate molecular sieves, all are partially ionic. Organophosphate is soluble in water (in soluble in most of the organic solvents), aluminophosphate molecular sieves are soluble in dilute sulphuric acid and aluminosilicates (zeolites) are soluble in dilute hydrofluoric acid. This similarity supports our invention organophosphate as molecular sieves. As most of the liquid phase reactions occur at lower temperature (< 100 °C) in organic solvents, the lower thermal stability (upto 200 °C) will not hurdle its application as catalyst.

$3CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2 + P^{5+}O(OH)_3 \longrightarrow$
(*n*-Propylamine) (Orthophosphoric acid)

$-[(P^{3+}(R\text{-}N)\ (R\text{-}N)P^{5+}(O)(N\text{-}R)]_n-$
n-Propylaminophosphate
$(R = CH_3\text{-}CH_2\text{-}CH_2)$

Scheme 1. A plausible mechanism for *n*-propylaminophosphate synthesis.

Conclusions :

A novel class of molecular sieves namely organophosphates are reported for the first time. The molecular sieves are similar to zeolites in properties. Characterization of *n*-propylaminophosphate shows that the sample is similar to ZSM-5 in many properties. Attempt to synthesize organosulphate results in less stable materials. Tertiary and secondary amines did not produce solid product. A plausible mechanism of its synthesis is also proposed. *n*-Propylaminophosphate posses basic properties due to the presence of amine group. Beside it is insoluble in most of the organic solvents suggesting the possibility of its function as environmentally safe basic catalyst. Compared to ZSM-5, this catalyst is having good conversion is phthalic anhydride esterification reactions.

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