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Synthesis and MASNMR Characterization of VPI-5 Molecular Sieve

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The synthesized VPI-5 sample was characterized by XRD, SEM, FTIR, TG/DTA, ^{27}Al, ^{31}P and 3Q MASNMR techniques, which shows that the sample was highly crystalline. Carbon and nitrogen analysis reveals that the sample contains no template molecules; however, TG/DTA analysis shows the presence of physisorbed template molecules. MASNMR results show the presence of two different types of aluminium and phosphorus, 3Q MASNMR shows the presence of two types of environmentally different tetrahedral aluminium, which are not observable by ordinary MASNMR along with known octahedral aluminium.

Key Words: VPI-5, Synthesis, XRD, SEM, TG/DTA, FTIR, MASNMR, 3Q-MASNMR

INTRODUCTION

Since the first discovery of zeolite, numerous natural and synthetic zeolites[1, 2], silica polymorphs, aluminophosphate based molecular sieves[3, 4] and microporous compounds built from MO_4 tetrahedra (where M is neither aluminium nor silicon, *e.g.*, gallophosphate microporous crystals[5, 6]) have been brought to light. These materials are prepared hydrothermally and some of them possess new framework structures. VPI-5[7] is an extra-large ring aluminophosphate microporous material consisting of 18 tetrahedral (18T) atoms. Although there are several studies on its characterization[8–14] only a few studies[15] were on its synthesis. The synthesis of VPI-5 at lesser duration *i.e.*, at 2 h is reported[16]. Herein, the modified synthesis along with its XRD, SEM, TG/DTA, FTIR, ^{27}Al, ^{31}P and 3Q-MASNMR characterization is reported.

EXPERIMENTAL

Synthesis of VPI-5: 3.58 g of pseudoboehmite (74.2% Al_2O_3, Vista Chemicals, USA) was mixed with 10 mL of distilled water. 5.75 g (85%, S.D. Fine, India) was added dropwise to the above mixture. The resulting thick white paste was aged for overnight at room temperature. 2.969 g of di-*n*-propyl amine (98%, Aldrich, India) along with 10 mL of distilled water was added dropwise to the white paste. The mixture was stirred well. The resulting active gel was charged into a teflon-lined steel autoclave. Crystallization was carried out for 2 h at 415 K. The autoclave was quenched in cold water and the product removed was washed several times with distilled water and dried at ambient temperature. The resulting solid material was subjected to various physicochemical characterizations. The other molecular sieves having properties similar to VPI-5 are given in Table-1.

TABLE-1
SYNTHESIS OF MOLECULAR SIEVES (PROPERTIES SIMILAR TO VPI-5 FROM AQUEOUS AND NON-AQUEOUS MEDIA)

S.No.	Gel composition	Aging	Temperature (°C)	Time	Product
1.	$Al_2O_3 : P_2O_4 : 1.16DPA : 45H_2O$	8 h	142	4h	VPI-5
2.	$Al_2O_3 : 1.8P_2O_5 : 2.32HEM : 45H_2O$	12 h	200	2d	NCL-2
3.	$Al_2O_3 : 1.8P_2O_5 : 4.5HEM : 45EG$	24 h	200	15d[a]	NCL-6
4.	$0.3TiO_2 : Al_2O_3 : P_2O_5 : 1.16HEM : 45H_2O$	—	200	2d	NCL-9
5.	$Al_2O_3 : 1.8P_2O_5 : 4.5HEM : 45EG$	24 h	200	15d	NCL-10
6.	$Al_2O_3 : 1.8P_2O_5 : 4.5HEM : 45EG$	48 h	200	15d	NCL-11
7.	$Al_2O_3 : 1.8P_2O_5 : 4.5HEM : 45EG$	24 h	200	15d	VPI-5

DPA = di-*n*-propylamine, HEM = hexamethyleneimine and EG = ethylene glycol
[a] with stirring

The sample synthesized during the course of the work was analyzed for qualitative identification by X-ray powder diffraction (Rigaku, Model D/MAX III VC, Japan; Ni filtered Cu-K_α radiation, $\lambda = 1.5404$ Å; graphite crystal monochrometor; computer controlled automated diffractometer). The morphology of the aluminophosphate synthesized was investigated using a scanning electron microscope (Jeol, JSM 5200). The framework region (1300–400 cm^{-1}) of the synthesized aluminophosphates was analyzed using a Nicolet 60SXB FTIR instrument in the diffuse reflectance mode using a 1 : 300 ratio of the sample to KBr mixture. Simultaneous TG/DTA analyses of the crystalline phases were performed on an automatic derivatograph (Setaram TG-DTA 92). The thermograms were recorded in flow of air with heating rate 10 K/min.

MASNMR spectra were recorded in the solid state with a Bruker DRX 500 spectrometer operating at a field of 7 tesla. ^{27}Al spectra were recorded at a frequency of 78.2 kHz, with a pulse length of 2 μs and a spinning speed of 3–5 kHz. ^{31}P spectra were recorded at a frequency of 202.45 MHz with pulse length 1.5 μs and the recycle delay is 4 s. The ^{27}Al triple quantum experiments were performed using a three pulse sequence incorporating a z-filter[17]. The z-filter modification ensured that the echo and anti-echo pathways were symmetrized during the conversion step to get a pure absorption mode 2D spectra with negligible phase distortion. MAS spinning speed of 13.5 kHz was employed along with rotor synchronization during the triple quantum evolution period (t_1) to eliminate spinning side bands appearing in the isotropic dimension. After a shearing, ^{27}Al 3Q-MAS contour plots were analyzed by a graphical procedure[18].

RESULTS AND DISCUSSION

X-ray powder diffraction (XRD) pattern of the synthesized VPI-5 is shown in Fig. 1. The XRD pattern of VPI-5 was prepared by other methods, although peak intensities differ. The synthesis of VPI-5 was facilitated in a lesser duration compared to the former reported one[9]. This may be due to the following reasons. In the present case, the aluminophosphate paste was aged for overnight. Aging

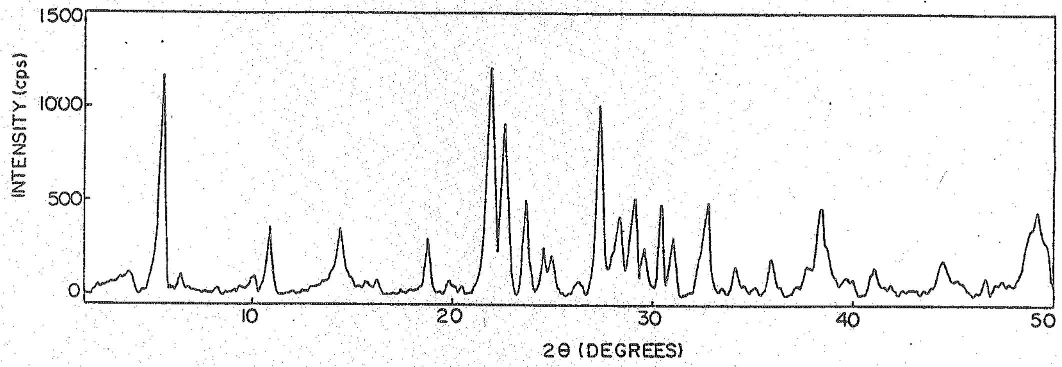

Fig. 1. X-ray powder diffraction pattern of VPI-5

may cause the formation of aluminophosphate layers which on addition of template and water become well dispersed particles and are ready for crystallization. So within 2 h of crystallization the process was completed. The other VPI-5 like aluminophosphate molecular sieves are formed on varying the aging and stirring parameters (Table-1). In aqueous media titanium facilitates such phases. Increase in template concentration (2.32 molar ratio) also causes similar phases. Irrespective of aluminium source whether catapal-B or aluminium isopropoxide will give that phase. Scanning electron microscopy (SEM) shows that the VPI-5 exists as layers (Fig. 2) and also indicates that the product is pure. FTIR spectrum shows (Fig. 3) three bands at 1272–955, 801–625 and 478.3 cm^{-1} are the characteristic of aluminophosphate molecular sieves. The asymmetric stretching vibrations of the P-O-Al unit occur at 1267.1, 1170.5 and 1072.3 cm^{-1} and symmetric stretching vibrations of P-O-Al are at 744.5 and 600 cm^{-1}. The band at 478.3 cm^{-1} arises from the vibration of the P-O-Al bending vibrations of the aluminophosphate framework.

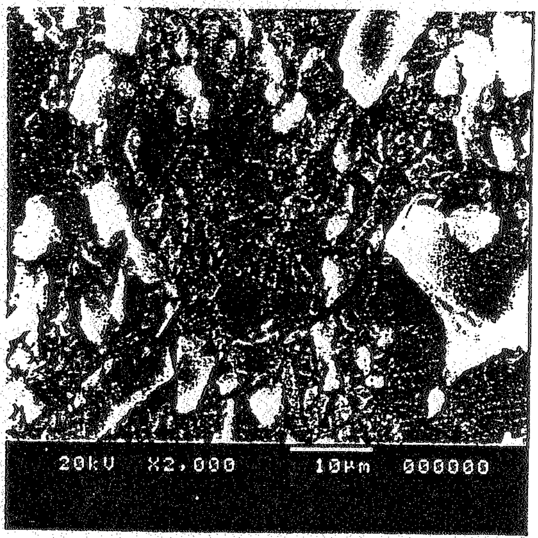

Fig. 2. SEM spectra of VPI-5

Thermogravimetric analysis indicated losses of 26.14% m/m from 25 to 731°C. This mass loss corresponds to the amount of organic molecules and water adsorbed by VPI-5 (Fig. 4). The exothermic peak at 251°C is caused by a phase

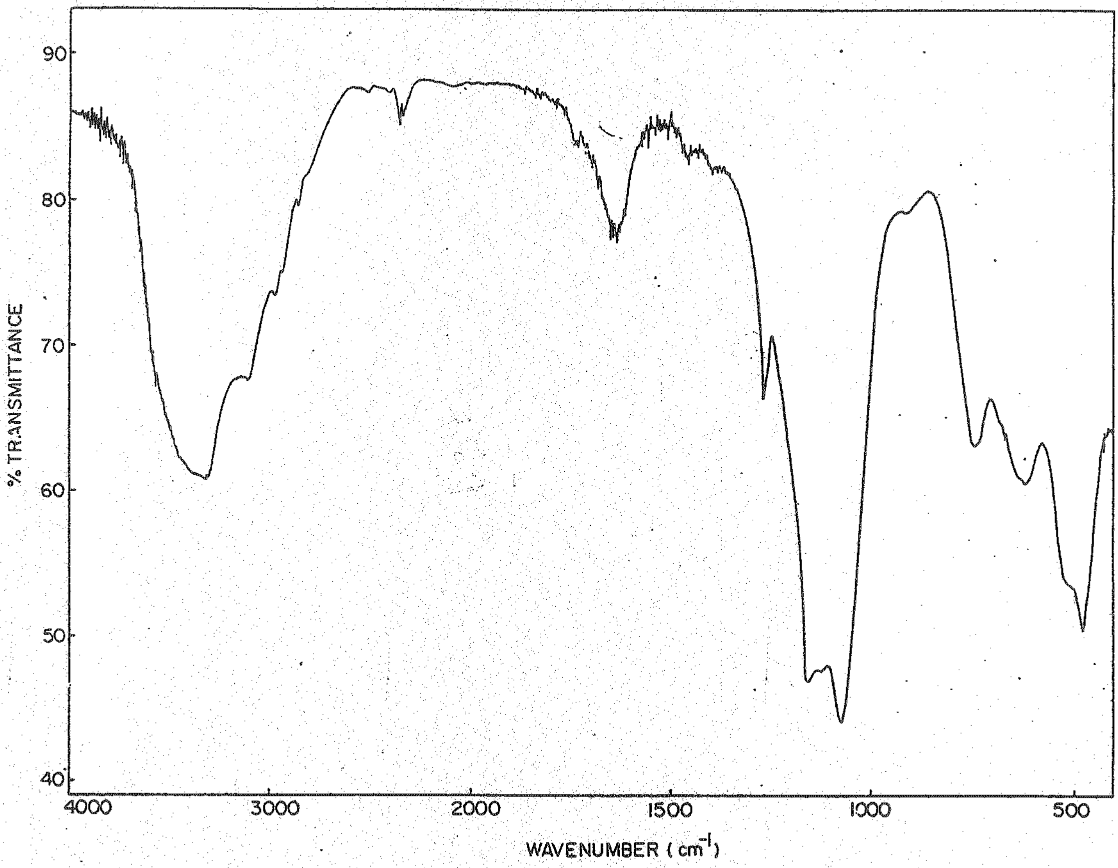

Fig. 3. FT-IR spectra of VPI-5 in the framework region

change. Carbon and nitrogen analysis shows the absence of any organic material in the solid. It is known from the earlier report that the VPI-5 molecular sieve contain template (0.4 (molar ratio) di-*n*-propyl amine)[10]. However, another reference[8], from chemical analysis and TGA/DSC techniques, says that there is no template molecule (tetrabutylammonium hydroxide) present in VPI-5 molecular sieve but it contains some water. Practically there is not much difference between di-*n*-propyl amine and tetrabutyl ammonium hydroxide in size. The present carbon and nitrogen and FTIR analyses on same molecular sieve show the absence of any template (di-*n*-propylamine) molecules. However, the TG/DTA analysis shows that the presence of small amount of template molecules (*ca.* 5%), is calculated from the higher temperature elimination (200–731°C). The reason for two different reports on same molecular sieve is not known. This may be due to the earlier crystallization of the molecular sieve.

The crystal structure of hydrated VPI-5 (space group $P6_3$)[19] reveals the presence of three crystallographically inequivalent Al and P sites in the aluminophosphate framework, two of them located at the connection of six- and four-membered rings [4/6 sites Al(2), P(2) and Al(3), P(3)] and the third in fused four-membered rings [4/4 site Al(1), P(1)]. While Al(2) and Al(3) are tetrahedrally coordinated to four framework oxygens, Al(1) is octahedrally coordinated to four framework oxygens and to two water molecules. In agreement with this structure, the ^{31}P MAS (magic angle spinning) NMR spectrum of hydrated VPI-5 consists of three resonances of equal intensity at δ –24.8 (P^A), –28.6 (P^B) and –34.2 (P^C)[20] and two resonance could also be resolved in the ^{27}Al MAS NMR, isotropic chemical shifts of δ 36 (Al^A) and –20(Al^C)[21] (Fig. 4). van Eck and Veeman[22] have shown that chemical shift line Al^C can unambiguously be attributed to the octahedral Al(1) site and the P^{31} peak P^C must be assigned to P(1). The other peak Al^A has been assigned to Al(3) respectively, by Grobet *et al.*[20] whose interpretation is correct; an assignment of the ^{31}P peak P^A to site P(2) and P^B to site P(3) would follow from the correlation spectrum. A shoulder peak at –33 ppm for ^{31}P MASNMR is due to phosphorus pentoxide impurities and small peak at 3 ppm in ^{27}Al MASNMR is due to side bands of the tetrahedrally co-ordinated aluminium[21]. However, peak for Al(2) is not traceable by ordinary MASNMR.

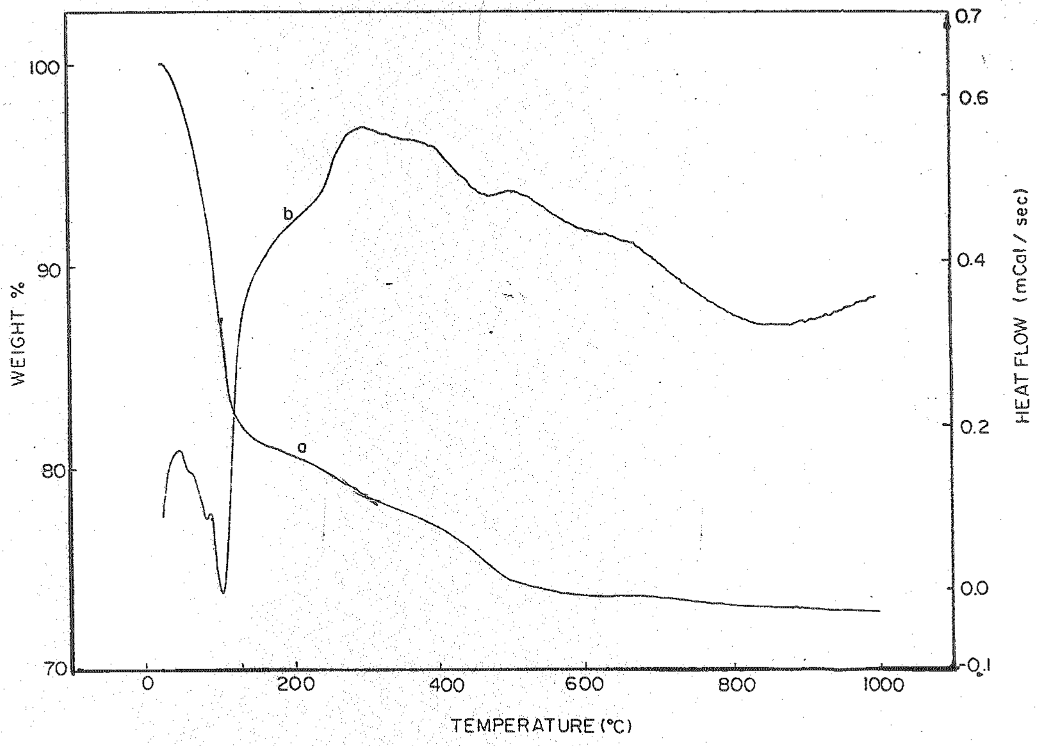

Fig. 4. TGA (a) and DTA (b) curves of VPI-5

Fig. 6 shows ^{27}Al 3Q-MASNMR spectra of VPI-5. The ^{27}Al MASNMR spectra depict Al purely in tetrahedral coordination due to the appearance of signals in the 6.411 to 51.0 ppm region. However, no clues are provided about the signal multiplicity due to crystallographic non-equivalence. This is due to residual second order quadrupolar broadening, which is not eliminated under MAS. The residual second order quadrupolar broadening is eliminated in the triple quantum MAS experiment. This is achieved by a two-dimensional correlation of orientation dependent triple quantum frequencies with the corresponding single quantum frequencies detected during the acquisition period (t_2). After scaling, the centre of gravity of the contour is located at (45, 35), (42, 35) and (–10, –30). Two different splittings in the 3Q MASNMR appear for equivalent tetrahedrally coordinated aluminium and another lone peak for octahedrally coordinated aluminium. A weak peak at (10, –5) is due to side bands of tetrahedrally coordinated aluminium.

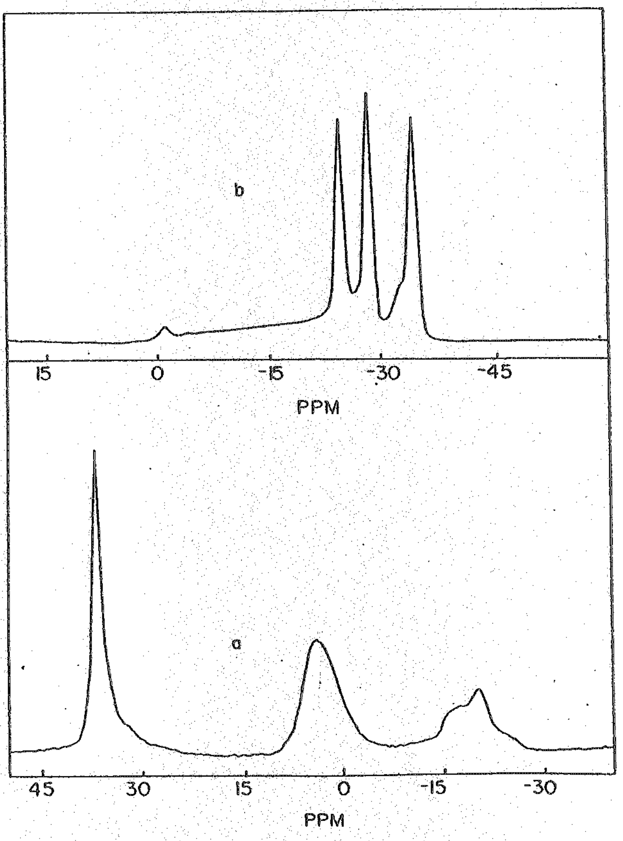

Fig. 5. ^{27}Al MASNMR (a) and ^{31}P MASNMR (b) of synthesized VPI-5

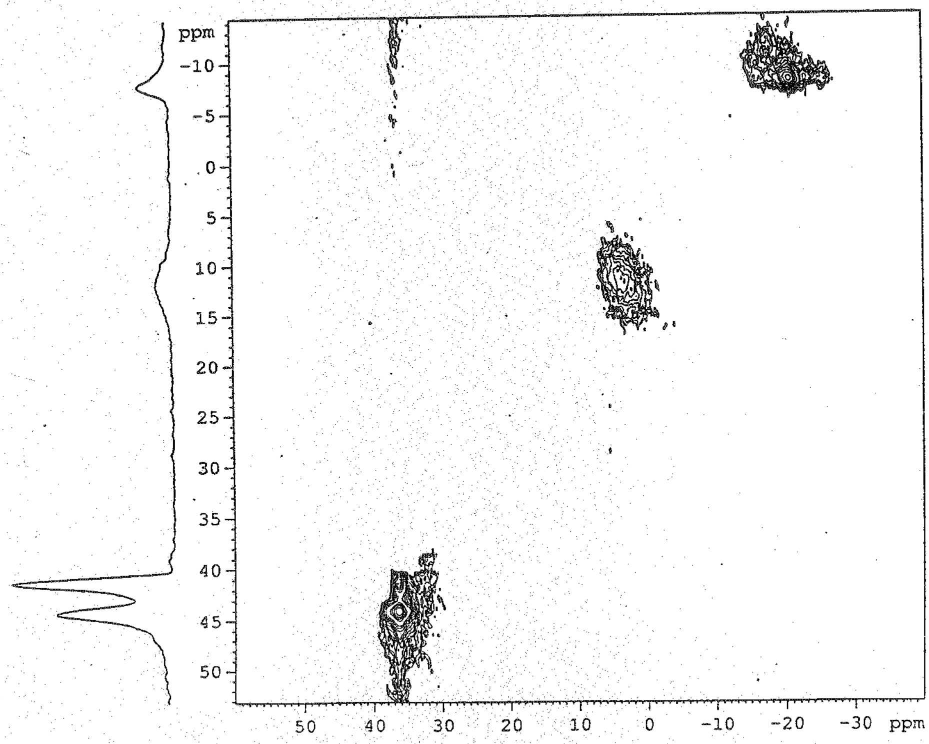

Fig. 6. ^{27}Al 3Q MASNMR of synthesized VPI-5
(VPI-5 new sample 3Q-MAS at 12.5 kHz with ^{1}H couping)

In conclusion, the synthesized VPI-5 was characterized by various physicochemical techniques. XRD, SEM and FTIR spectroscopic techniques show that the sample is well crystalline. Carbon and nitrogen analysis shows that there is no template present in the VPI-5 as-synthesized sample. However, TG/DTA analysis reveals the presence of some adsorbed template molecules. ^{27}Al and ^{31}P MASNMR indicate the presence of two different types of aluminium and three different types of phosphorus. One of them is located at the connection of six and four-membered rings are tetrahedrally coordinated to four framework oxygens, second located in fused four-membered rings and octahedrally coordinated to four framework oxygens and to two water molecules. However, the 3Q MASNMR shows the presence of other environmentally different tetrahedral aluminium atoms.

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