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Synthesis and Characterization of VPI-5 Molecular Sieve from Non-aqueous Systems

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The extra large pore aluminophosphate molecular sieve, VPI-5 has been synthesized from non-aqueous media using hexamethyleneimine template for the first time. Aqueous media VPI-5 samples have been prepared for comparison. X-ray diffraction pattern shows that the synthesized material is similar to reported VPI-5. SEM photograph shows that the morphology is even. TG/DTA and carbon and nitrogen analysis shows that there is 37.12% weight loss due to the loss of the template and water molecules. However, the VPI-5 samples synthesized from aqueous media contain no template. FT-IR spectrum of the sample in framework region is similar to the reported pattern. MAS NMR shows that the sample contains three different aluminium and phosphorus sites.

Key Words: Aluminophosphate, AlPOs, VPI-5, XRD, SEM, TG/DTA, FT-IR, MAS NMR.

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 crystal[5, 6]) have been brought to light. These materials are prepared hydrothermally and some of them possess new framework structures. VPI-5 for example is an extra-large ring aluminophosphate microporous material consisting of 18 tetrahedral (18T) atoms[7]. Recently, a synthetic gallophosphate molecular sieve with a 20T-atom pore opening, cloverite was reported[8]. This is the largest ring among the natural and synthetic zeolite and zeolite-like materials. More recently a microporous crystalline material possessing a 20 T-atom channel, designated as JDF-20 was synthesized[9].

Aluminophosphate molecular sieves are generally prepared from aqueous hydrothermal systems through crystallization of an active aluminophosphate gel containing organic amine or quaternary ammonium templating agents[3, 10, 11], while zeolites[12–14] can be synthesized from organic or mixed solvent systems in which water is a minor component. However, until now few kinds of aluminophosphates have been synthesized from non-aqueous systems[15–18].

In the present study, the author reports the novel synthetic procedure using non-aqueous medium to crystallize VPI-5 and some of the relevant characterizations.

EXPERIMENTAL

VPI-5 was synthesized in the presence of template hexamethyleneimine from a predominantly non-aqueous system using ethylene glycol as the solvent. Aluminium triisopropoxide and phosphoric acid (85 wt. % H_3PO_4) were used exclusively as the aluminium and phosphorus starting materials, respectively. The typical synthesis procedure is as follows. 6.05 g of aluminium triisopropoxide (98%, Aldrich, U.S.A.) is slurried in solvent ethylene glycol (45.50 g, 98%, S.D. Fine, India). 7.27 g of hexamethyleneimine (98%, Aldrich, U.S.A.) is added to the aluminous slurry. 6.024 g of orthophosphoric acid (85%, S.D. fine, India) is added dropwise to the mixture. The whole mixture is stirred until it becomes homogeneous (1 d) forming the final gel, which is charged into the autoclave and heated in an oven at 453 K for 15 d. The autoclave is removed from the oven and allowed to cool and products recovered by filtration with copious amounts of water or another solvent and dried in ambient air. The conditions for synthesis of VPI-5 from aqueous media are given in Table-1 for comparison.

TABLE-1

SYNTHESIS OF VPI-5 MOLECULAR SIEVES FROM AQUEOUS AND NON-AQUEOUS MEDIA

S. No.	Gel composition	Aging (h)	Temperature (°C)	Time
1.	$Al_2O_3 : P_2O_4 : 1.16DPA : 45H_2O$	8	142	4 h
2.	$Al_2O_3 : 1.8P_2O_5 : 4.5HEM : 45EG$	24	200	15 d

DPA = di-*n*-propylamine and HEM = hexamethyleneimine.

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 monochromater; computer controlled automated diffractometer). The morphology of the aluminophosphate synthesized was investigated using a scanning electron microscope (JEOL, JSM 5200). The framework region (400–1300 cm^{-1}) of the synthesized aluminophosphates was analyzed using a Nicolet 60SXB FTIR instrument in the diffuse reflectance mode using nujol paste. Simultaneous TG/DTA analysis of the crystalline phases was performed on an automatic derivatograph (Setaram TG-DTA 92). The thermograms were recorded in flow of air with heating rate 10 K/min. MAS NMR spectra were recorded in the solid state with a Bruker DRX 500 spectrometer operating at a field of 11.7 tesla[27]. All spectra were recorded at a frequency of 130.3 MHz, 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 a pulse length of 1.5 μs and the recycle delay was 4 s. 1 M $Al(NO_3)_3$ and 1 M H_3PO_4 solutions (for aluminium and phosphorus) were used as standards.

RESULTS AND DISCUSSION

The XRD pattern of VPI-5 synthesized using hexamethyleneimine template from non-aqueous media is given in Fig. 1, which shows that the synthesized sample is pure and highly crystalline. The first high intensity peak at 17.24 Å shows that the aluminophosphate is an extra large pore molecular sieve[19–21]. The 2θ values were fitted into the Taupin program. Results show that the crystals were in orthorhombic system (Table-2) with P222 Latice type. Stoichiometry of the prepared VPI-5 in calcined form is $Al_2O_3 : 0.99P_2O_5$. Scanning electron micrograph is given in Fig. 2. It shows that the morphology of the sample is layered one with

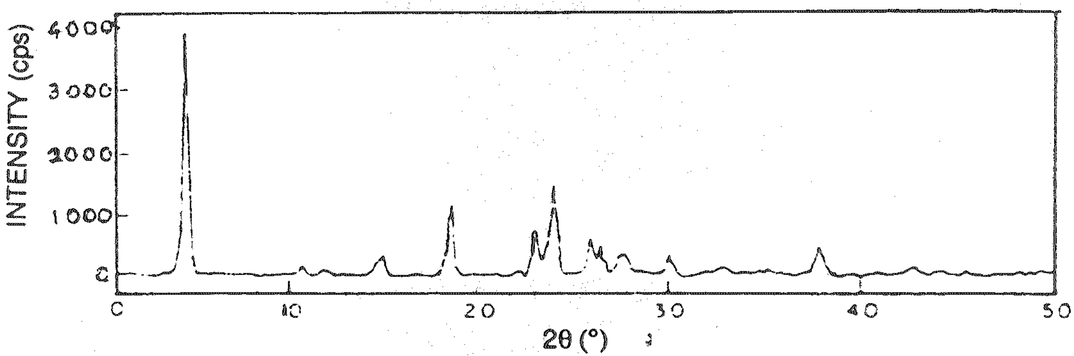

Fig. 1. X-ray diffraction pattern of VPI-5 synthesized from non-aqueous media

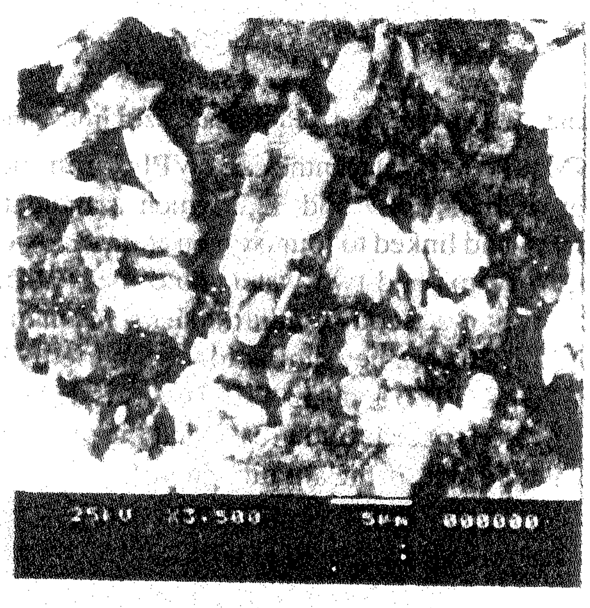

Fig. 2. Scanning electron microscopic photograph of VPI-5 synthesized from non-aqueous media

particle size 2.5 × 5.0 µm. The infrared spectrum of VPI-5 synthesized from non-aqueous media shows three bands at 1261–1000, 758–721 and 545–478 cm^{-1}, which are characteristic of aluminophosphate molecular sieves containing four and six membered rings[21, 22]. The spectrum of VPI-5 is more complex than those of $AlPO_4$-5 and $AlPO_4$-11.

The thermogravimetric analysis for VPI-5 indicates (Fig. 3) that the weight loss (up to *ca.* 37.18%) is caused by the removal of water and hexamethyleneimine. The weight loss at relatively high temperature, *ca.* 663.5°C (hexamethyleneimine, b.p. 138°C at 748 mm), implies interaction between hexamethyleneimine and the framework. VPI-5 synthesized from aqueous media contains no template molecules in its structure. However, VPI-5 synthesized from non-aqueous media contains more template. The carbon and nitrogen analysis shows that the molecular sieve contains 24.24% of C and 3.85% of N. The template content is 0.275 molecule per 100 g equivalent of the material and the analysis indicates that there are three ethyleneglycol along with three template molecules in its structure. The results were in contrast to the reported ones for SAPO-35 synthesized in ethylene glycol media[17].

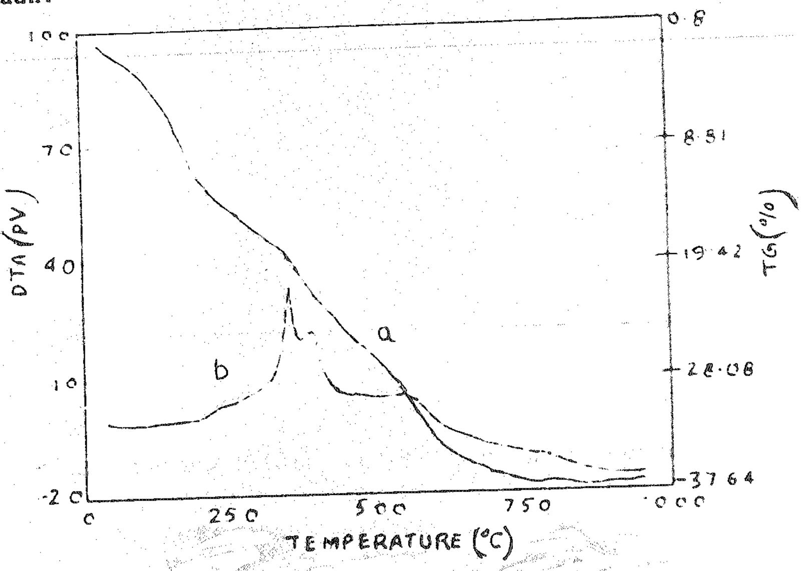

Fig. 3. TGA (a) and DTA (b) curves of VPI-5 synthesized from non-aqueous media

The ^{27}Al MAS NMR spectra of synthesized VPI-5 from non-aqueous media shows a resonance at δ 39.0, –26.7 and 32.2 which is indicative of aluminium tetrahedrally coordinated and linked to four oxygen atoms and octahedrally coordinated with four oxygen atoms and two water molecules[23]. The ^{31}P spectrum of VPI-5 synthesized from non-aqueous media (a sharp resonance δ –26.6 (P(1)), –30.4 (P(2)) and –37.2 (P(3)) is rather similar to the reported VPI-5 from aqueous media (δ –23.3 (P(1)), –27.2 (P(2)) and –33.1 (P(3))[25]. It is deduced from the crystal structure of hydrated VPI-5 (space group P(3)[24], that the presence of three crystallographically inequivalent P sites in the aluminophosphate framework, two of them located at the connection of six- and four-membered rings [4/6 sites P(2) and P(3)] and the third in fused four membered rings [4/4 site P(1)]. While P(2) and P(3) are tetrahedrally coordinated to four framework oxygens, P(1) is octahedrally coordinated to four framework oxygens and water.

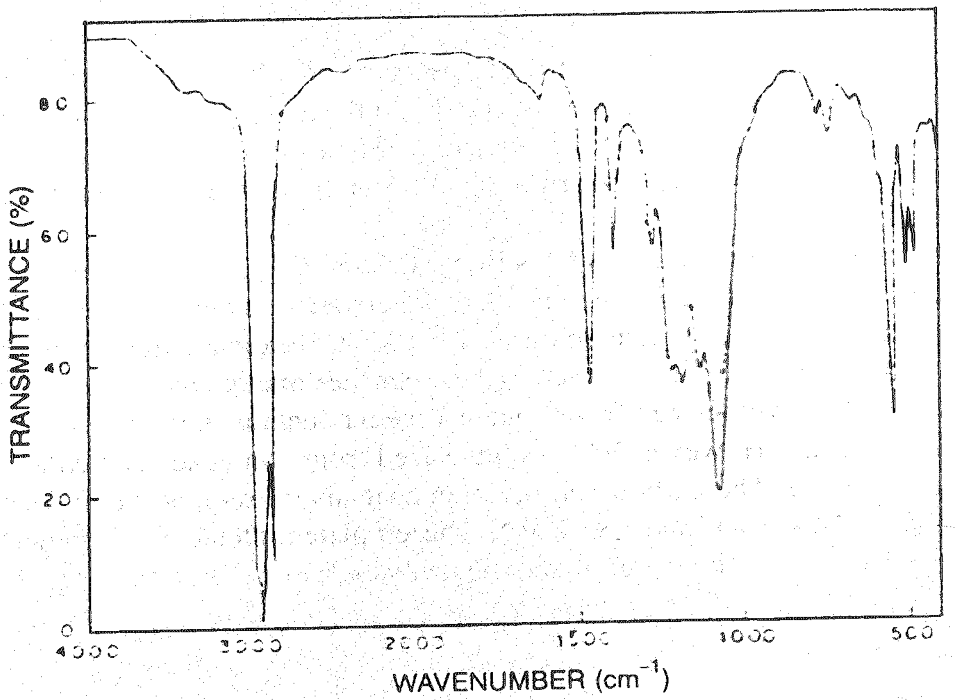

Fig. 4. FT-IR spectrum of VPI-5 synthesized from non-aqueous media in the framework region

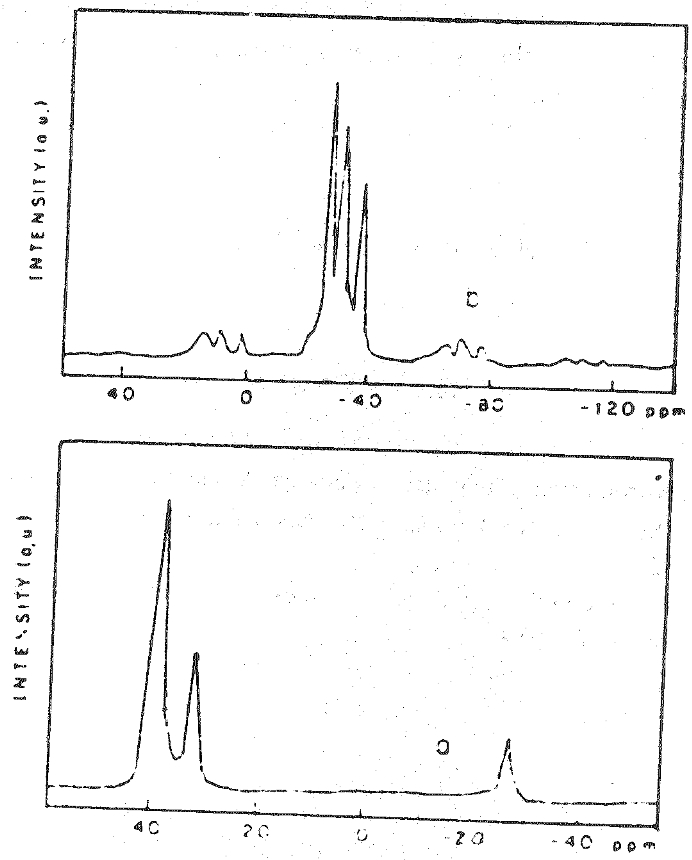

Fig. 5. ^{27}Al (a) and ^{31}P (b) MAS NMR spectrum of VPI-5 synthesized from non-aqueous media

The solvent employed in the synthesis of $AlPO_4$-31 is essentially non-aqueous. Water is present in H_3PO_4, hexamethyleneimine and other reagents in small amounts and probably does not play a significant role. An important aspect of the synthesis of VPI-5 is the use of hexamethyleneimine as the templating agent, in marked contrast to synthesis in aqueous systems. The latter usually employs linear chain molecules, such as di-*n*-propylamine, di-*n*-butylamine and tetrabutyl ammonium hydroxide, as the templating agent. It is proposed that half a template molecule is present in one unit cell along the c-direction. Hexamethyleneimine owing to its heterocyclic ring has little chance to act as a template during the synthesis of VPI-5 in aqueous systems. In our system we believe that hexamethyleneimine and the solvent interact during the reaction leading to the formation of VPI-5 and its successful synthesis suggests that other suitable templating agents for different $AlPO_4$-*n* structures in non-aqueous media may be found. This was confirmed by the carbon and nitrogen analysis, which shows the presence of three template molecules along with three ethyleneglycol present in unit cell.

Conclusion

In conclusion, the extra large pore aluminophosphate, VPI-5, is synthesized from non-aqueous media using hexamethyleneimine template for the first time and characterized using various physico-chemical techniques such as XRD, SEM, TG/DTA, FT-IR and MAS NMR methods. Aqueous media VPI-5 samples were prepared for comparison. XRD, SEM analysis shows the crystallinity of the synthesized sample. TG/DTA gives more weight loss, *i.e.*, 37.18%. Carbon and nitrogen analysis shows that the samples synthesized from aqueous media contain no template in contrast to the non-aqueous media samples. FT-IR analysis in framework region shows that the spectra is similar to the reported one from aqueous media. ^{27}Al and ^{31}P MAS NMR shows that the samples contain three different aluminium and phosphorous sites.

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