

An improved process for the synthesis of VPI-5 molecular sieve

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Abstract. VPI-5 was synthesized with lesser time duration. The synthesized sample was characterized by XRD, SEM, FT-IR, TG/DTA, ^{27}Al and ^{31}P MASNMR techniques, which shows that the synthesized sample was highly crystalline. Carbon and nitrogen analyses reveal that the sample contains no template molecules, however, TG/DTA analysis shows the presence of physisorbed template molecules. MASNMR results show the presence of three different types of aluminium and phosphorous. Two of them were present as in tetrahedral and the remaining one is present in octahedral environment.

Keywords. VPI-5; synthesis; XRD; SEM; TG/DTA; FT-IR; MASNMR.

1. Introduction

Since the first discovery of zeolite, numerous natural and synthetic zeolites (Breck 1973; Barrer 1982), silica polymorphs, aluminophosphate based molecular sieves (Wilson *et al* 1982; Lok *et al* 1984), and microporous compounds built from MO_4 tetrahedra (where M is neither aluminium nor silicon, e.g. gallophosphate microporous crystal (Parise 1985; Yang *et al* 1987)) have been brought to light. These materials are prepared hydrothermally and some of them possess new framework structures. VPI-5 (Davis *et al* 1988) is an extra-large ring aluminophosphate microporous material consisting of 18 tetrahedral (18T) atoms. Although there are several studies on its characterization (Davis *et al* 1989; Rocha *et al* 1992; Engelhardt and Veeman 1993; Ernst *et al* 1993; He and Klinowski 1994; Rocha *et al* 1996), only few studies (Schmidt *et al* 1992) were on its synthesis. Here for the first time we are reporting the synthesis of VPI-5 at lesser duration i.e. at 2 h compared to the former at 4 h (He and Klinowski 1994). Further the sample was characterized by XRD, SEM, TG/DTA, FT-IR, ^{27}Al and ^{31}P MASNMR techniques.

2. Experimental

VPI-5 was synthesized as follows: 3.58 g of pseudo-boehmite (74.2% Al_2O_3 , Vista Chemicals, USA) was mixed with 10 ml of distilled water. 5.75 g of ortho phosphoric acid (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 142°C. The autoclave was quenched in cold water and the product removed, washed several times with distilled water and dried at ambient temperature. The resulting solid material was subjected to various physicochemical characterization.

The sample synthesized during the course of the work was analysed for qualitative identification by X-ray powder diffraction (Rigaku, Model D/MAX III VC, Japan; Ni filtered Cu-K α radiation, $\lambda = 1.5404 \text{ \AA}$; graphite crystal monochromator; computer controlled automated diffractometer). The morphologies of the aluminophosphate synthesized was investigated using a scanning electron microscope (JEOL, JSM 5200). The framework region ($400\text{--}1300 \text{ cm}^{-1}$) of the synthesized aluminophosphates was analysed using a Nicolet 60SXB FT-IR 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-DTA92). 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.

3. Results and discussion

The X-ray powder diffraction (XRD) pattern of the VPI-5 so synthesized is shown in figure 1. The XRD pattern of VPI-5 is similar to the samples prepared using other methods, although peak intensities differ. The synthesis of VPI-5 was facilitated in lesser duration compared to former reported one (He and Klinowski 1994). This may

be due to the following reasons. In our case, the aluminophosphate paste was aged for overnight. Aging may cause the formation of aluminophosphate layers which on addition of template and water becomes well dispersed particles and are ready for crystallization. So within 2 h of crystallization the process was completed. Scanning electron microscopy (SEM) shows that the VPI-5 exists as layers and also indicates that the product is pure. The FT-IR spectrum shows (figure 2) three bands at 1272–955, 801–625 and 478.3 cm^{-1} , which are 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 occur 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.

The VPI-5 sample was subjected to thermal analysis on a differential thermal analysis (DTA) instrument under the flow of air at a rate of 10°C min^{-1} (figure 3). 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 absorbed by VPI-5. The exothermic peak at 251°C is caused by a phase change. Carbon and nitrogen analyses show the absence of any organic material in the solid. It is known from the earlier report that the VPI-5 molecular sieve contains

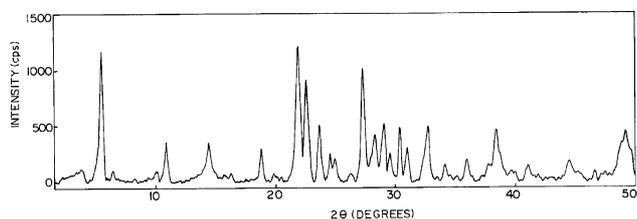


Figure 1. X-ray powder diffraction pattern of VPI-5.

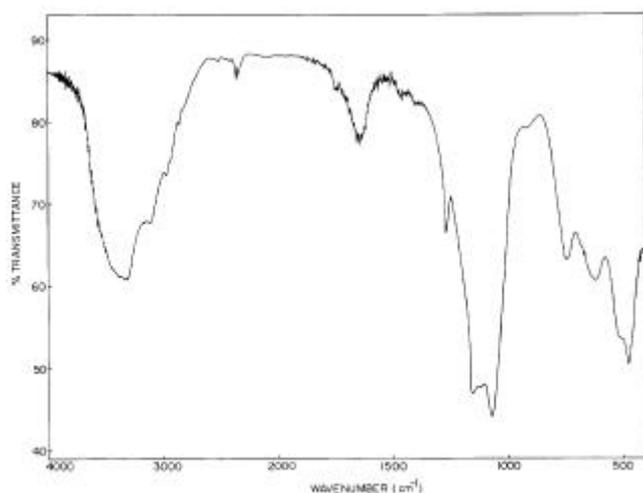


Figure 2. FT-IR spectra of VPI-5 in the framework region.

template (0.4 (molar ratio) di-*n*-propyl amine) (Robson and Lillerud 2001). However, another study (Davis *et al* 1989), from chemical analysis and TGA/DSC techniques indicate that there is no template molecule (tetrabutyl ammonium hydroxide) present in VPI-5 molecular sieve but it contains some water. Practically there is no much difference between di-*n*-propyl amine and tetrabutyl ammonium hydroxide in size. Our carbon, nitrogen and FT-IR analyses on same molecular sieve show the absence of any template (di-*n*-propyl amine) molecules. However, the TG/DTA analysis shows the presence of small amount of template molecules (~5%), 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. Techniques such as carbon and nitrogen analyses and FT-IR techniques are not precise enough to identify the trace amount of template molecules present in the sample, is clear.

The crystal structure of hydrated VPI-5 (space group $P6_3$) (McCusker and Baerlocher 1991) 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}) (Grobet *et al* 1989) and three resonance could also be resolved in the ^{27}Al MASNMR, isotropic chemical shifts of δ 36 (Al^{A}), 3 (Al^{B}) and – 20 (Al^{C}) (Grobet *et al* 1991) (figure 4). van Eck and Veeman (1993) have shown that chemical shift

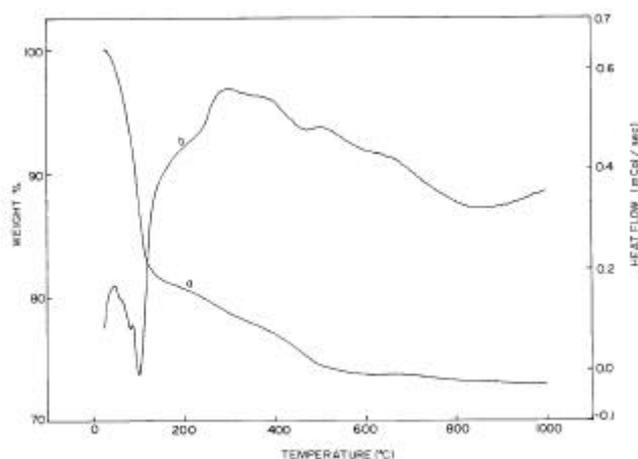


Figure 3. TGA (a) and DTA(b) curves of VPI-5.

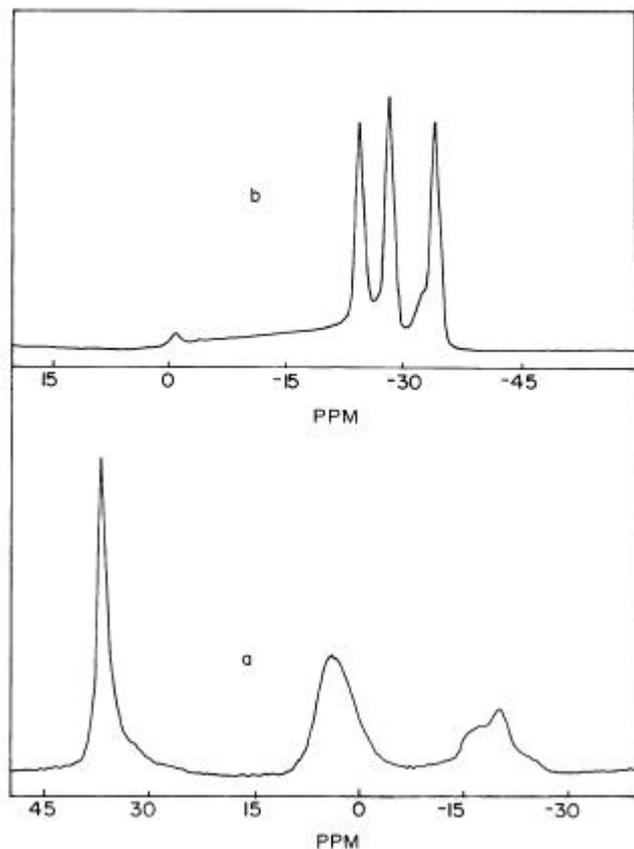


Figure 4. ^{27}Al MASNMR (a) and ^{31}P MASNMR (b) of as-synthesized VPI-5.

line Al^{C} can unambiguously be attributed to the octahedral $\text{Al}(1)$ site and the P^{31} peak P^{C} must be assigned to $\text{P}(1)$. The two peaks Al^{A} and Al^{B} have been assigned to $\text{Al}(2)$ and $\text{Al}(3)$, respectively, by Grobet *et al* and the interpretation is correct, an assignment of the ^{31}P peak P^{A} to site $\text{P}(2)$ and P^{B} to site $\text{P}(3)$ would follow from the correlation spectrum. A shoulder peak at -33 ppm for ^{31}P MASNMR is due to phosphorous pentoxide impurities and small peak at -17 ppm in ^{27}Al MASNMR is due to side bands of the tetrahedrally coordinated aluminium (Grobet *et al* 1991).

4. Conclusions

VPI-5 was synthesized at lesser time duration i.e. at 2 h, the earlier syntheses were minimum at 4 h. XRD, SEM and FT-IR spectroscopic techniques show that the synthesized sample is well crystalline. Carbon and nitrogen analyses show that there is no template present in the VPI-5 as-synthesized sample. However, TG/DTA analy-

sis reveals the presence of some adsorbed template molecules. ^{27}Al and ^{31}P MASNMR indicate the presence of three different types of aluminium and phosphorous. Two of them located at the connection of six and four-membered rings with tetrahedrally coordinated to four framework oxygens and third in fused four membered ring at octahedrally coordinated to four framework oxygens and to two water molecules.

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