Synthesis and characterization of a novel extra large pore aluminophosphate molecular sieve, NCL-6

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A novel extra large pore aluminophosphate molecular sieve NCL-6, has been prepared and characterized by various techniques such as XRD, SEM, TG/DTA, carbon and nitrogen analysis, FT-IR and MAS NMR are reported. X-Ray diffraction pattern shows that the synthesized sample is crystalline and have novel structure. SEM analysis indicate the phase purity and having granules morphology with $3 \times 5 \mu\text{m}$ particle size. FT-IR spectrum in the framework region shows that the sample is similar to the other known aluminophosphates. TG/DTA shows that the sample losses 30.45% due to the loss of water and organic molecules. Aluminium and phosphorous NMR shows that the presence of four different aluminium and three different phosphorous sites. The NMR are similar to VPI-5, NCL-2 and NCL-3.

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-5⁷, for example, is an extra-large ring aluminophosphate microporous material consisting of 18 tetrahedral (18T) atoms. Recently, a synthetic gallophosphate molecular sieve with a 20T atom pore opening, cloverite⁸, was reported. This is the largest ring among the natural and synthetic zeolite and zeolite-like materials. More recently, a microporous crystalline material possessing 20T-atom channel, designated as JDF-20⁹, was synthesized. This material has aluminophosphate composition whose channel is circumscribed with 20T-atoms. We report here the synthetic procedures used to crystallize NCL-6, and some of the relevant characterization data on NCL-6.

Results and discussion

Peak positions of X-ray powder diffraction pattern of the NCL-6 so synthesized do not fit to the any of the reported pattern^{10,11}. The first peak at 17.31° shows that the synthesized molecular sieve is a extra large pore sized. This pattern is stable upto 250°C . Elemental analysis of calcined sample shows the composition is Al_2O_3 ; 0.99 P_2O_5 . Scanning electron microscopy (SEM) shows that the NCL-6 exists as granules with particle size $3 \times 5 \mu\text{m}$, and

also indicates that the product is pure. The IR spectrum shows three bands at $1176.5\text{--}1080$, $880\text{--}757$ and $544.9\text{--}495.7 \text{ cm}^{-1}$ which are characteristic of aluminophosphate molecular sieves. The asymmetric stretching vibrations of the P-O-Al unit occur at 1176.5 and 1080.1 and symmetric stretching vibration of P-O-Al is at 880 and 757.0 cm^{-1} . The band 544.9 cm^{-1} is due to double ring vibrations and the peak at 495.7 cm^{-1} is due to P-O-Al bending vibrations. These are characteristic vibrations of the aluminophosphate framework. The NCL-6 sample was subjected to thermal analysis on a differential thermal analysis (DTA) instrument under a flow of N_2 at a rate of $10^\circ\text{C min}^{-1}$ (Fig. 1). Thermogravimetric analysis indicated losses of 30.45% m/m from 25 to 575°C . This mass loss corresponds to the amount of organic molecules and water adsorbed by NCL-6. The

Fig. 1. TG (a)/ DTA (b) analysis of NCL-6.

exothermic peaks at 405°C (298–462°C) and 570°C (462–692°C) gives weight loss 10.87 and 3.70% respectively are due to the oxidative decomposition of the template molecules. The higher temperature to eliminate the organic molecules indicate the strong interaction of template molecules with the aluminophosphate framework. Carbon and nitrogen analysis indicate the content are C = 15.93 and N = 2.55%.

The ^{27}Al MAS NMR spectra of the synthesized NCL-6 shows resonances at δ 44.6, 37.5, -4.8 and -21.7 is similar to NCL-2 except octahedrally co-ordinated aluminium at δ -4.8¹². Remaining peaks are due to aluminium in tetrahedral co-ordination. The ^{31}P MAS NMR spectrum of NCL-6 (two sharp resonance at δ -24.2, -28.8 and a diffuse peak at -34.6) is rather similar to VPI-5 (δ -23.3, -33.1 and -27.12), NCL-2 (δ -26.6, -30.4 and -37.22) and NCL-3 (δ -15.63, -23.26 and -27.88)¹³. The first two peaks are due to tetrahedrally co-ordinated phosphorous atoms and third one is due to octahedrally co-ordinated phosphorous atoms.

Conclusion :

A novel extra large pore aluminophosphate molecular sieve NCL-6 was synthesized and characterized by various physicochemical techniques such as XRD, SEM, TG/DTA, FT-IR and MAS NMR. X-Ray diffraction analysis shows that the sample is novel, pure and highly crystalline. SEM photograph shows that the sample is pure and having granules morphology with particle size $3 \times 5 \mu\text{m}$. FT-IR spectrum in framework region shows that the sample is similar to the other known aluminophosphates. TG/DTA shows that the sample losses 30.45% of the total weight due to the loss of adsorbed template and water molecules. There are two stages of oxidative decomposition occur in the sample. The ^{27}Al and ^{31}P MAS NMR shows the presence four types of aluminium and three types of phosphorous sites. The spectra is similar to VPI-5 and NCL-2 and NCL-3.

Experimental

NCL-6 was synthesized in the presence of template hexamethyleneimine (HEM, 98%, Aldrich, USA) from a predominantly non-aqueous system using ethylene glycol (EG, 99%, s.d. fine, India) as the solvent. Aluminium triisopropoxide (98%, Aldrich, USA) and phosphoric acid (85% H_3PO_4) were used exclusively as the aluminium and phosphorous starting materials, respectively. A typical synthesis procedure involves the following steps : (i) aluminium triisopropoxide (6.05 g) is slurried in solvent, ethyleneglycol (45.50 g), (ii) hexamethyleneimine (7.24 g) is added to the aluminous slurry, (iii) the phosphoric acid (6.024 g) added dropwise to the mixture, (iv) the whole mixture is stirred until it becomes homogeneous (24 h) forming the final gel having molar composition $\text{Al}_2\text{O}_3 : 1.8 \text{ P}_2\text{O}_5 : 4.5 \text{ HEM} :$

45 EG which (v) is charged into a Parr reactor and heated at 473 K for 15 days with stirring, the autoclave is removed from the reactor, and allowed to cool and products recovered by filtration with copious amounts of water or another solvent and dried in ambient air.

X-Ray diffraction patterns were recorded on a Rigaku (D/MAX III VC) instrument in the 2θ region of 5–45°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope : Chemical analysis was carried out by XRF using a Rigaku 3070 X-ray spectrometer. Carbon and nitrogen were estimated by microanalysis. The framework IR spectra were recorded in the diffuse reflectance mode using 300 : 1 ratio sample in KBr (Nicolet 60SXB). Simultaneous TG/DTA analysis of the crystalline phases were performed on an automatic derivatograph (Setaram TG-DTA 92). MAS NMR spectra were recorded in the solid state with a Broker DRX 500 spectrometer operating at a field of 11.7 Tesla. ^{27}Al 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 pulse length 1.5 μs and the recycle delay is 4 s. 1 M $\text{Al}(\text{NO}_3)_3$ and 1M H_3PO_4 solutions (for aluminium and phosphorous) were used as standards.

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