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Incorporation of zirconium in medium-pore aluminophosphate molecular sieves with AEL framework

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Abstract

Zirconium incorporated aluminophosphate molecular sieves ZrAPO-11 was synthesized by hydrothermal method. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy, thermogravimetric/differential thermal analysis (TGA/DTA), diffuse reflectance UV–visible spectroscopy, magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy (^{31}P and ^{27}Al). The acidity of the materials were determined by temperature programmed desorption (TPD) of ammonia. X-ray diffraction and scanning electron microscopy reveals formation of crystalline material in pure phase. Thermal analysis shows higher template content in zirconium containing samples than the corresponding AlPOs. MAS NMR suggests incorporation of zirconium in the framework. TPD reveals that the ZrAPO-11 samples were of higher acidity than $AlPO_4$-11.

Keywords: Molecular sieve; Aluminophosphate; ZrAPO-11; $AlPO_4$-11; Catalysis

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1. Introduction

Since their first synthesis in pure form by Wilson et al. in 1982 [1], the aluminophosphate molecular sieves have been finding importance as catalysts in various chemical reactions in the field of petrochemicals and fine chemicals [2–6]. Like zeolites they are microporous crystalline materials with high surface area. Their framework consists of alternating oxygen sharing AlO_4 and PO_4 tetrahedra. The pore sizes and the electronic confinement inside the pores are ideal for guest–host chemistry. Substitution of metal in the aluminophosphate framework is a challenging task which gives rise to the formation of metal substituted aluminophosphate molecular sieves [7–12]. In these frameworks the metal remains in a highly dispersed state, which is expected to enhance its catalytic activity. Incorporation of transition metal into the aluminiphosphate framework leads to the formation of redox molecular sieves [13], which can be applied as catalyst in oxidation–reduction reactions. Out of the various metals, zirconium is an important transition metal and zirconium based materials are finding application as catalysts and catalyst support [14,15]. Zirconium containing aluminophosphate molecular sieves are not well studied, although in recent years some research groups had reported synthesis of ZrAPO-5, ZrAPO-11 and ZrSAPO-11 [16–18]. Medium pore molecular sieves can act as host to a number of molecules of interest. So we tried to synthesize zirconium substituted molecular sieves ZrAPO-11 and compare its properties with $AlPO_4$-11. Though the synthesis of ZrAPO-11 was reported earlier [18], substitution of zirconium into the framework was not established un-ambiguously, particularly incorporation of zirconium in the AEL framework was not supported by MAS NMR. We are reporting the synthesis and characterization of ZrAPO-11 with MAS NMR for the first time.

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Table 1
Gel composition and synthesis condition

Sample	Gel composition					Reaction condition		
	Al_2O_3	P_2O_5	ZrO	DPA	H_2O	pH	Temperature (K)	Time (H)
$AlPO_4$-11	1.0	1.0		1.15	55	4.20	453	24
ZrAPO-11/1	1.0	1.0	0.05	1.0	40	7.04	453	36
ZrAPO-11/2	1.0	1.0	1.0	1.0	40	7.02	453	36

2. Experimental

Pseudoboehmite (Catapal B, Vista) and aluminium isopropoxide (Aldrich) were used as source of aluminium in the synthesis of $AlPO_4$-11 and ZrAPO-11 respectively. Orthophosphoric acid (85%, E. Merck) was used as the phosphorous source. Zirconyl nitrate (Loba-Chemie) was used as the source of zirconium while *n*-dipropylamine (DPA) (E. Merk) was used as the template. All the samples were synthesized hydrothermally in Teflon-lined autoclaves under autogenous pressure. The $AlPO_4$-11 was synthesized by mixing 9.189 g of pseudoboehmite to a mixture of 15.373 g of orthophosphoric acid and 61 ml of water followed by addition of 7.758 g of *n*-dipropylamine drop by drop until a uniform mixture was obtained. Similarly ZrAPO-11/1 was prepared by stirring 8.110 g of aluminium isoprppoxide and 0.680 g of zirconyl nitrate (1.360 g in case of ZrAPO-11/2) with 13.225 g of orthophosphoric acid, 50 ml water and 6.845 g of *n*-dipropylamine. Finally, the pH of the mixture was adjusted and transferred into an autoclave and heated in an air oven at required temperature for specified period of time (synthesis conditions given in Table 1). The product obtained was separated, washed and then dried at 373 K for 12 h. The as-synthesized samples were calcined slowly at the rate of 2 K per minute up to 823 K and then heated isothermally for 18 h. Two samples of ZrAPO-11 (1 and 2) with different zirconium contents and one sample of $AlPO_4$-11 were studied. The samples were dissolved in sulphuric acid (H_2SO_4:H_2O = 2:1) and chemical analysis was carried out using an atomic emission spectrometer (Perkin–Elmer P-1000) fitted with an ICP source. X-ray powder diffraction patterns of the samples were recorded on a Rigaku Miniflex diffractometer using nickel-filtered CuK_α radiation. The scanning electron microscopy was carried out using a JEOL JSM-840A scanning electron microscope. The thermogravimetric and differential thermal analyses (DTA–TGA) were carried out in dry air flow, heating the sample at a rate of 10 K per minute in the temperature range of 289–1273 K using Universal V2.5H TA thermal analyzer. The BET-surface area of the calcined samples were determined with Quantachrome Autosorb-1C instrument. Diffuse reflectance UV–visible spectra of the samples were obtained using a Shimadzu UV-2550 spectrophotometer. The MAS NMR studies were carried out on a Bruker DRX 500, using single pulse excitation technique, at 202.45 MHz for ^{31}P and 130.3 MHz for ^{27}Al with acquisition delays of 3 s and 1 s respectively. Standard 4 mm zirconia rotors with spinning speeds of 10–12 kHz were employed. Phosphoric acid (85%) was used as reference for ^{31}P, while hexahydrated aluminium (1 M) was used as reference for ^{27}Al. Temperature programmed desorption (TPD) of ammonia was carried using 10% NH_3 in helium, employing a Micromeritics (Autochem 2910) instrument. Initially the sample (~100 mg) is heated at 773 K in He flow for 2 h and cooled to 373 K, prior to the adsorption of ammonia. To remove the physisorbed ammonia, the sample was heated at 373 K in helium for 1 h. The desorption experiment was carried out by heating the sample to 1073 K at a programmed heating rate of 10 K min^{-1}.

The catalytic activity of the synthesized products were investigated by carrying out hydroxylation of phenol with the catalyst using hydrogen peroxide (30%, E. Merk) as oxidizing agent. The catalytic reaction was carried out in a 100 ml glass round-bottom flask fitted with a water-cooled condenser. The mixture of the substrate (Phenol, E. Merk) and solvent (Acetonitrile, E. Merk) was heated to the reaction temperature and then catalyst was added. Finally required amount of hydrogen peroxide was added slowly. The reaction mixture was stirred vigorously and the reaction was continued for a definite period of time. The products were taken out time to time and analysed using a Varian gas chromatograph (CP-3800) equipped with a FID. The separation of various products was achieved using a capillary column BP-1. To investigate if the zirconium environment in the synthesized material is different, zirconium impregnated catalyst was prepared by adding an aqueous solution of zirconyl nitrate to calcined $AlPO_4$-11. The mixture was dried slowly by heating under constant stirring. The dry product was finally calcined at 823 K for 12 h. The zirconium loading in the impregnated catalyst ZrAPO-11/imp was same as ZrAPO-11/2.

3. Results and discussion

3.1. Chemical analysis

Chemical analysis of the ZrAPO-11 samples confirms presence of zirconium (Table 2). Ideally, the ratio Al/P in aluminophosphate and (Al + Zr)/P in the zirconium substituted samples should be unity assuming that zirconium replaces aluminium in the structure. In case of $AlPO_4$-11 the Al/P ratio was found to be greater than 1. This might imply the presence of some extra-framework aluminium in the sample. In the case of ZrAPO-11 on the other hand, total (Al + Zr) is less than P in the sample.