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Synthesis of 7-hydroxy-4-methyl coumarin over Lewis acid metal ion-exchanged ZAPO-5 molecular sieves

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ABSTRACT

Zinc aluminophosphate (ZAPO-5) molecular sieve was synthesized hydrothermally and ion-exchanged with Lewis acid metal ions such as Ga^{3+}, In^{3+}, La^{3+} and Ce^{3+} by wet method. The materials were characterized by XRD, FT-IR, BET, ICP-AES, ^{27}Al and ^{31}P MAS NMR, SEM, TPD (ammonia) and TGA. XRD patterns of ion-exchanged molecular sieves appeared almost the same as that of parent ZAPO-5 thus illustrating absence of structural degradation during ion-exchange. However, BET surface area and ICP-AES analysis indicate a small amount of non-framework oxide present in the ion-exchanged catalysts. ^{27}Al and ^{31}P NMR account for the incorporation of zinc in the framework of AlPO-5. The thermograms of metal ion-exchanged ZAPO-5 showed a weight loss between 550 °C and 600 °C for all ion-exchanged materials. This is assigned to the decomposition of $M(OH)_2^+$ into MO^+ species. The total acidity of the materials decreased after ion-exchange as revealed from TPD (ammonia) study. It also showed selective ion-exchange of strong acid sites by Ga^{3+}, In^{3+}, La^{3+} and Ce^{3+} ions. Their catalytic activity was tested in the solvent free synthesis of coumarin using resorcinol and ethyl acetoacetate in the liquid phase. Lewis acid ion-exchanged catalysts showed higher activity than the parent ZAPO-5. The Lewis acid metal ion could act as a template which brings the reactants to its co-ordination sphere and subsequently reacts to form coumarin.

1. Introduction

Microporus aluminophosphate (AlPO) molecular sieves have attracted much attention due to their catalytic and sorptive properties [1–5]. The drawback of parent AlPO molecular sieve is the absence of acid sites. Hence incorporation of Bronsted acid sites becomes necessary. The incorporation of divalent cations such as Mg^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, etc. into AlPO and SAPO resulted MAPO and MSAPO, respectively [6–8]. Such isomorphous substitution introduced charge imbalance in the framework which is balanced by protons, thus generating Bronsted acidity and offering catalytic activity and ion-exchange capability [9]. Among the aluminophosphate molecular sieves AlPO-5 has attracted much attention due to its large pore size with 0.7 nm pore opening. It is composed of 12-membered rings of regular alternation of Al and P in the tetrahedral framework [10]. Catalytic applications of both transition and non-transition divalent metal ions substituted AlPO-5 molecular sieves have been reported already [11,12]. Although there are many reports on the catalytic activity of metal ions substituted AlPO-5 molecular sieves with Bronsted acid sites as catalytically active sites, Lewis acid ion-exchanged ZAPO-5 catalysts yet to receive considerable importance. However, Lewis acid ion-exchanged zeolites have been reported to be catalytically active for many reactions of industrial importance [13,14]. However, there is no literature report on Ga^{3+}, In^{3+} and rare-earth metal ions exchanged ZAPO-5 molecular sieves. Hence it is our interest to prepare Lewis acid ion-exchanged ZAPO-5 molecular sieves and to study their catalytic activity in the synthesis of coumarin derivatives. The most widely used method for the synthesis of coumarin derivatives is Pechmann reaction which involved the use of conc. sulphuric acid as the catalyst [15]. This process is not only hazardous but also requires long reaction time. In addition, it produces by-product and solid waste due to neutralization of the spent sulphuric acid. To circumvent this problem, heterogeneous catalysts such as Nafoin/silica composites [16], zeolite H-BEA [17], Amberlyst-15 [18] and other solid acids [19,20] were used in the preparation of 7-hydroxy-4-methyl coumarin. The yield of the product over SAC80 (80% Nafion in the composite) was 96% [17]. The newly developed Amberlyst-type catalysts such as Amberlyst-15, -35, -36, chlorinated Amberlyst and surface-sulphonated Amberlyst were also employed as alternative catalyst for the Pechmann reaction. Although a wide variety of catalysts have been used for the synthesis of coumarin derivatives, Lewis acid metal ion catalysed route has not been reported so far. The present study attempted Lewis acid ion-exchanged ZAPO-5 molecular sieves for the synthesis of coumarin using ethyl acetoacetate and resorcinol as precursors. The reaction was carried out in the liquid

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phase at different temperatures and the results are presented in this manuscript.

2. Experimental

2.1. Synthesis of ZAPO-5

Hydrothermal synthesis of ZAPO-5 was carried out using a gel composition of $0.1ZnO:1TEA:1Al_2O_3:1P_2O_5:40H_2O$ adopting already reported procedure [21] Aluminium isopropoxide (Merck), phosphoric acid (Merck) (88%) and zinc sulphate (Merck) were used as sources for Al, P and Zn respectively. Aluminium isopropoxide (28.37 g) was soaked in 30 ml distilled water for 24 h in a stainless steel autoclave (316 type) and vigorously stirred for 1 h. While stirring, 1.99 g zinc sulphate dissolved in 7.8 ml phosphoric acid and 20 ml distilled water was added drop by drop and continued the stirring for additional 1 h. Triethylamine (9.7 ml) was added drop wise to it and the pH of the gel was found to be 4.4. The autoclave was tightly closed and kept at 175 °C under autogeneous pressure for 24 h. Then it was cooled to room temperature to obtain the solid product. The product was washed several times with distilled water and dried in an air oven at 110 °C for 12 h. It was then calcined at 550 °C for 8 h to remove the template.

The ion-exchanged materials were prepared by stirring 2 g calcined ZAPO-5 with corresponding metal nitrate solution (30 mL; 0.1 M) for 12 h at 80 °C. The solid was filtered, washed thoroughly with distilled water and dried at ambient temperature. The same procedure was repeated thrice. These samples were used for characterisation and catalytic studies.

2.2. Physicochemical characterization

The powder X-ray diffraction patterns of the samples were recorded on a PANalytical X'pert PRO diffractometer using nickel filtered Cu Kα ($\lambda = 0.154$ nm) radiation and a liquid nitrogen cooled germanium solid state detector. The diffractograms were recorded in the 2θ range from 5° to 40° in steps of 1.2 min^{-1} with a count time of 10 s at each point. Fourier transform infrared spectra (FT-IR) of the materials were recorded on a FT-IR spectrometer (Nicolet Avatar 360) using KBr pellet technique. About 15 mg of the sample was pressed (under a pressure of 2 tons cm^{-2}) into a self-supported wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) of the materials was performed on a high resolution thermogravimetric analyser (Perkin Elmer diamond series) under nitrogen atmosphere in the temperature from 50 to 800 °C at a heating rate of 10 °C min^{-1}. ^{27}Al and ^{31}P MAS NMR spectra were recorded using NMR spectrometer (Bruker MSL 300). The size and morphology of the samples were recorded using a scanning electron microscope (SEM) (JEOL 640). Surface area, pore volume and micropore area of the samples were analysed by nitrogen physisorption method at −196 °C using ASAP 2010 porosimeter from Micromeritics Corporation (Norcross, GA, USA). The density and strength of acid sites were determined by temperature programmed desorption (TPD) of ammonia on a Micromeritics chemisorb 2750 pulse chemisorption system. About 0.08 g sample was pretreated in an oxygen stream at 450 °C for 3 h. Ammonia was adsorbed at 100 °C and the physisorbed ammonia was removed by applying vacuum. The temperature was then increased upto 600 °C in a helium stream (20 ml min^{-1}) at a heating rate of 10 °C min^{-1} and the desorption was monitored by thermal conductivity detector (TCD) [22]. The elemental analysis was performed for ZAPO-5 and ion-exchanged ZAPO-5 using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with the Labtum Plasma 8440 instrument.

The liquid products obtained in the reaction were analysed by a gas chromatograph (Shimadzu GC-17A; crosslinked 5% phenyl methyl siloxane capillary column, FID detector). Further, the products were also confirmed using a gas chromatograph coupled with Turbo mass spectrometer (GC–MS Perkin–Elmer Auto system XL (EI, 70 eV)) using helium as the carrier gas at a flow rate of 1 ml/min.

3. Results and discussion

The powder X-ray diffraction patterns of ZAPO-5 and metal ion-exchanged ZAPO-5 catalysts are shown in Fig. 1. The patterns of ZAPO-5 coincided with already reported one [21]. All the ion-exchanged XRD patterns are almost similar to the patterns of ZAPO-5 and hence there is no structural degradation taken place during ion-exchange. Further, there are no patterns corresponding to non-framework metal oxide in the XRD patterns of ion-exchanged ZAPO-5 molecular sieves and hence there are no distinct peaks corresponding to any of the metal oxides of metal ions used for ion-exchange as they might be finely dispersed state without the formation of bulk oxide phase. However, the metal oxides, even if present, in low amount may not be in sufficient dimension to be detected by XRD.

The FT-IR spectrum of calcined ZAPO-5 catalyst is shown in Fig. 2a. The broad envelope between 3000 and 3700 cm^{-1} is due to O–H stretching vibration of water, defective P–OH groupings, surface hydroxyl groups and bridged hydroxyl groups. The presence of water is confirmed by its OH_2 bending vibration close to 1630 cm^{-1}. The water content appears to be different in these catalysts. The broad absorption band around 1200 cm^{-1} is due to tetrahedral asymmetric vibrations of P-O-Al and P-O-M groups. The corresponding symmetric vibration gives a peak close to 750 cm^{-1}. The peak around 500 cm^{-1} is due to the bending mode of T-O-T. These are the characteristic vibrations of ZAPO-5 molecular sieve [21]. The spectra of LaZAPO-5, CeZAPO-5, GaZAPO-5 and InZAPO-5 are shown in Figs. 2b–e. The spectral characteristics of ion-exchanged ZAPO-5 are almost similar to ZAPO-5. However, the intensity of O-H stretching vibration is higher than ZAPO-5. This indicates that ion-exchanged catalysts hold more amount of adsorbed water than ZAPO-5. This unusual observation is attributed to co-ordination of water molecules with MO^+ species present in metal ion-exchanged ZAPO-5.

Thermogravimetric analysis of metal ion-exchanged ZAPO-5 was carried out between 30 and 800 °C. There is a characteristic

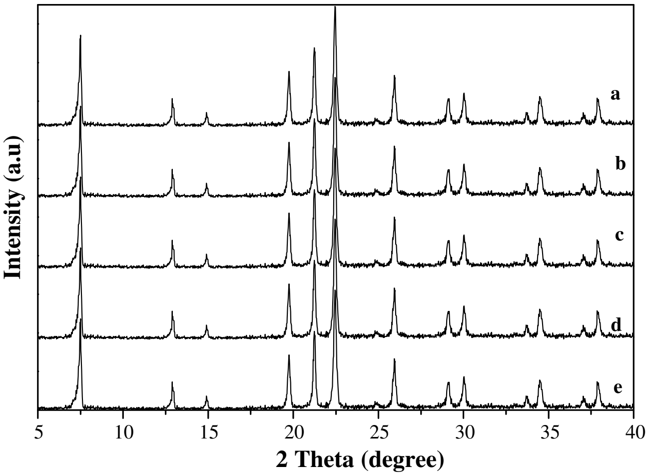

Fig. 1. XRD patterns of (a) ZAPO-5,(b) LaZAPO-5,(c) CeZAPO-5,(d) InZAPO-5 and (e) GaZAPO-5.