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Research Paper

Mesoporous 12-tungstophosphoric acid/activated bentonite catalysts for oxidation of 2-propanol

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ABSTRACT

In the present study, the effect of 12-tungstophosphoric acid (HPW) immobilisation on the catalytic activity of $H_3PW_{12}O_{40}$/mesoporous acid-activated bentonite catalysts (AAB) was investigated. The catalysts were characterised by XRD, IR, SEM and BET, and the activity of acid-activated bentonite catalysts with various loadings of HPW were studied in the conversion of vapour-phase 2-propanol. The results indicated that the conversion of 2-propanol increased substantially as the temperature increased from 343 K to 553 K. Alternatively, the conversion and selectivity of the reaction increased with an increase in the HPW concentration. Moreover, the proposed catalysts enhanced the oxidation of 2-propanol to acetone and suppressed the acid-catalysed dehydration of propanol to propylene.

1. Introduction

Heteropolyacids (HPAs) are used as homogeneous and heterogeneous catalysts for oxidation and acid-catalysed reactions due to their unique physicochemical properties. In addition, HPAs can be used as model systems to study catalytic processes (Kozhevnikov, 1997; Timofeeva, 2003, L. Zhang et al., 2010). Unlike metal oxides and zeolites, HPAs possess a discrete and mobile ionic structure. Moreover, HPAs display strong Brønsted acidity and appropriate redox properties, which can be tuned by varying the chemical composition of the catalyst. Consequently, acid catalysis and catalytic oxidation are the two main areas of HPA catalysis. The most common HPA catalysts are Keggin HPAs, which contain heteropoly anions with a molecular formula of $[XM_{12}O_{40}]^{n-}$ (α-isomer), where X is the heteroatom (P^{5+} and Si^{4+}) and M is the addenda atom (Mo^{6+} and W^{6+}). Keggin anions consist of a central tetrahedron XO_4 surrounded by edge- and corner-sharing metal-oxygen octahedra (MO_6). Among various structural classes, Keggin-type HPAs, such as Keggin phosphotungstic acid ($H_3PW_{12}O_{40}$ and HPW), have received considerable attention due to their high acidity and ease of preparation (Kozhevnikov, 2007).

One of the main disadvantages of HPA catalysts is that their surface areas are relatively low. To increase the surface area of the catalysts, HPA has been supported on inorganic materials via conventional impregnation. For example, several mesoporous materials have been extensively investigated as HPA supports (Mastikhin et al., 1995; Nandhini et al., 2004; Bokade and Yadav, 2007; Rafiee et al., 2009; L. Zhang et al., 2010). Among these materials, clay is an excellent support due to its thermal stability, relative high surface area, large pore volume and uniform pore size distribution. Moreover, clay can be modified to possess a positive charge. In particular, bentonite and acid-treated bentonite are promising supports because their pore structure and morphology can be easily controlled (Yadav and Doshi, 2002; Nehate and Bokade, 2009; Garade et al., 2010; D. Zhang et al., 2010; Zhou, 2010). Furthermore, commercial acid-treated bentonite exhibits high activity for the decomposition of 2-propanol to isopropyl ether and/or propene (Haffad et al., 1998). The direct selective oxidation of alcohols could be used to manufacture a variety of useful oxygenates (Mavrikakis and Barteau, 1998). Unfortunately, the oxidation of alcohols to carbonyl compounds is not selective enough for practical applications. Currently, only the selective oxidation of methanol to formaldehyde is an industrially viable process (Yadav, 2005).

In this study, 12-tungstophosphoric acid/mesoporous acid-activated bentonite catalysts were used to model the conversion of vapour-phase 2-propanol. Moreover, the catalytic activities of acid-activated bentonite, HPW and HPW-AAB catalysts were studied.

2. Experimental

2.1. Materials

The results of our previous investigations on the modelling and optimisation of bentonite activation via response surface methodology (Rožić et al., 2010 were applied to modified bentonite, which was used

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as a support in the current study. Bentonite obtained under the optimal conditions possessed the following chemical composition (% by wt.): $SiO_2 = 73.66$; $Al_2O_3 = 12.28$; $Fe_2O_3 = 4.73$; $CaO = 0.70$; $MgO = 1.99$; $Na_2O = 0.60$; $K_2O = 0.30$; and $TiO_2 = 0.57$; ignition on loss = 5.17. Polycrystalline $H_3PW_{12}O_{40} \times 6H_2O$ was prepared from commercial phosphotungstic acid (microscopy grade $H_3[P(W_3O_{10})_4]_{aq}$, Fluka AG, CH-9470 Buchs, #79690) by heat treatment at 353 K for 1 h.

2.2. Catalyst synthesis

12-tungstophosphoric acid/mesoporous acid-activated bentonite was prepared according to the method described in the literature (Bokade and Yadav, 2007). HPW was dissolved in methanol, and the resulting solution was added slowly to 5, 10 or 20 wt.% of acid-activated bentonite. To remove residual methanol, wet samples were dried in a water bath and further dried in an oven for 2 h at 100 °C. The catalyst was stored in a sealed bottle until use.

2.3. Characterisation

The crystallinity of the samples was determined by powder X-ray diffraction (XRD) on a Philips PW 1710 with CuK_α radiation (40 kV, 30 mA, and $\lambda = 0.154178$ nm) at a 2θ scan range of 3–70°.

The BET specific surface area was determined via N_2 adsorption–desorption isotherms, which were obtained at 77 K with an automatic adsorption apparatus (Sorptomatic 1990 Thermo Finningen). The specific surface area of the catalysts was calculated by fitting the adsorption data to the linear range of the BET equation (relative to p/p_0 (0.05–0.35)). The pore size distribution was calculated according to the BJH method using N_2 desorption isotherms (Barrett et al., 1951).

Infra-red (IR) spectra were measured with a Perkin-Elmer 983 G IR-spectrometer between 4000 and 250 cm^{-1}. The KBr pressed-disc technique (2 mg of sample and 200 mg of KBr) was used to produce IR samples.

The morphological characteristics of the samples were investigated via scanning electron microscopy (JEOL, model JSM 6460-LV) at 25 keV.

2.4. Catalytic activity

The oxidation of 2-propanol was performed in a fixed bed catalytic reactor made of stainless steel tubing with an outer diameter of 6 mm, an inner diameter of 4 mm and a length of 115 mm. The catalysts were housed in a quartz wool holder located in the middle of the reactor, and thermocouples were placed on the top and bottom of the catalyst bed. The reactor was loaded with 50 mg of catalyst, which corresponded to a catalyst volume of 0.07 cm^3. Liquid 2-propanol was stored in a temperature controlled saturator, and a mass flow-controlled stream of air was passed through the saturator to achieve the desired partial pressure of 2-propanol. The inlet and outlet concentrations of hydrocarbons were analysed with an FID detector equipped with a 6.5 ft × 1/8 in stainless steel column containing 23% SP 1700 on chromosorb PAW. The flow rate of air through the catalyst bed was equal to a space velocity of 21,500 h^{-1}, and the temperature was varied between 343 and 553 K at a constant inlet concentration of 2.2 vol.% in air. The temperature was maintained with an accuracy of ±0.2 K, and the concentration of reactants was determined with an accuracy of ±0.2%. The reproducibility of the results was verified by repeating each test.

3. Results and discussion

3.1. Characterisation

Prior to the catalytic studies, the purity and mesoporous structure of the catalysts were evaluated. Fig. 1 shows the X-ray powder diffraction patterns of mesoporous acid-activated bentonite (AAB), HPW and HPW-AAB catalysts with HPW loadings of 5, 10 or 20%. Bulk HPW hexahydrate possesses a cubic structure and was characterised by the corresponding reflections in the XRD patterns. In addition, the presence of smectite (Sm), illite (I), feldspar (F) and quartz (Q) was evident in the XRD patterns of acid-activated bentonite. Impregnation with HPW caused a slight decrease in the intensity of quartz reflections at 2θ of 20.9 and 26.7. Moreover, the intensity of the quartz reflections was proportional to the HPW loading.

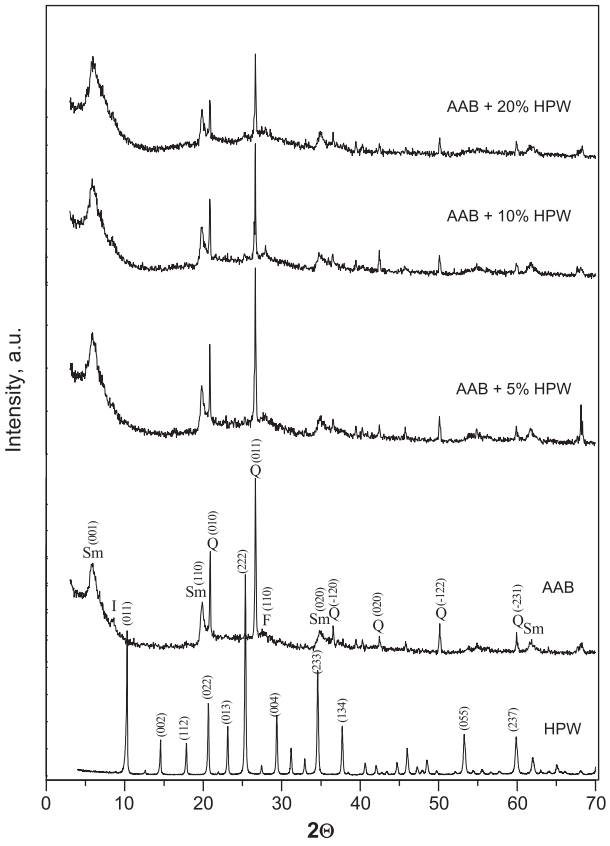

Fig. 1. XRD patterns of 12-tungstophosphoric acid, acid-activated bentonite and HPW-AAB catalysts with various loadings of 12-tungstophosphoric acid.

Similar to the results obtained from immobilised $H_3PW_{12}O_{40}$ on mesostructured acid-activated bentonite, reflections of the polyacid were not detected, indicating that HPW was in an amorphous state and was randomly distributed on the bentonite surface or incorporated in the pores of the support.

The textural properties of the support (AAB) and the catalysts are provided in Table 1. The results revealed that mesoporous acid-activated bentonite possessed a relatively large surface area (272 m^2/g) and pore volume (0.2473 cm^3/g).

As shown in Table 1, the HPW loading had a significant effect on the textural properties of the materials. Namely, the specific surface

Table 1
Pore characteristics of the support (AAB) and supported catalysts with various loading of HPW obtained from N_2 adsorption and desorption analysis.

Sample	BET surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Micropore volume ($cm^3\,g^{-1}$)	Pore diameter (nm)
AAB	272	0.2473	0.1175	3.65
AAB + 5% HPW	246	0.2114	0.1070	3.65
AAB + 10% HPW	188	0.1951	0.0810	3.62
AAB + 20% HPW	130	0.1207	0.0594	3.66