

t-Butylation of phenol over mesoporous aluminophosphate and heteropolyacid supported aluminophosphate molecular sieves

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Abstract

Mesoporous aluminophosphate (AIPO) has been synthesized hydrothermally using cetyltrimethylammonium bromide (CTAB) as structure-directing agent in the presence of tetramethylammonium hydroxide (TMAOH) at room temperature. Phosphotungstic acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW) was supported on the synthesized mesoporous AIPO at various loadings viz., 10, 20 and 40 wt.% to yield PW/AIPOs and characterized by XRD, TGA and FT-IR. XRD patterns confirm that HPA retains the Keggin structure on the AIPO surface and forms finely dispersed heteropoly acid (HPA) species. HPA crystal phase was not developed even at HPA loading as high as 40 wt.%. Catalytic activities of both parent AIPO and HPA loaded AIPOs were studied by carrying out *t*-butylation of phenol with *tert*-butanol in vapour phase in the temperature range 190–250 °C. The products obtained were *o*-*tert*-butyl phenol (*o*-*t*-BP), *p*-*tert*-butyl phenol (*p*-*t*-BP) and *tert*-butylphenyl ether (*t*-BPE) with high selectivity towards *p*-*t*-BP. The effects of feed ratio and WHSV towards conversion of phenol were studied and finally the time on stream studies were also carried out to compare the activities of the catalysts. PW/AIPO catalysts were found to yield higher conversion than parent AIPO due to the increase in Bronsted acid sites. Hence, PW/AIPO compositions are promising catalysts exclusively for acid type conversion of large organic molecules.

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Keywords: Mesoporous aluminophosphate (AIPO); Heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$; Alkylation of phenol; *t*-Butylation; Bronsted acid sites

1. Introduction

Catalytic applications of heteropolyanions have attracted increasing interest in the last decade [1]. Catalysts based on polyoxometalates related to the Keggin structure have been chosen for the study because of their extreme stability in solution as well in solid state. Heteropolyacids (HPAs) have been widely used both in acid and oxidation catalysis [2,3]. They are known to possess a strong purely Bronsted acidity, the acidity being stronger than in many mineral acids or conventional solid acids such as amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{H}_3\text{PO}_4/\text{SiO}_2$, HX and HY zeolites [4,5]. The acid strength of crystalline HPAs decreases in the series $\text{PW} > \text{SiW} > \text{PMo} > \text{SiMo}$. Usually relative catalytic activities of HPAs are consistent with this order both in

homogeneous and heterogeneous systems [6,7]. In the present study phosphotungstic acid, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (PW), the strongest HPA in the Keggin series [3] has been used. As bulk HPA has low surface area ($<10 \text{ m}^2/\text{g}$), an inert support material, namely, mesoporous aluminophosphate molecular sieve having pore dimension in the range of 20–100 Å has been chosen so that disadvantage of HPA can be overcome in supported HPA. Aluminophosphates possess strict alternance of AlO_4^- and PO_4^+ tetrahedra having neutral framework and hence does not possess sufficient acidity for catalytic reactions. In the present investigation, it was aimed to use concomitantly the high acidity of HPA and the large surface area of mesoporous AIPO towards alkylation reactions. PW/AIPO compositions containing 10–40 wt.% PW were prepared by impregnating pure mesoporous AIPO with PW and were characterized by XRD and FT-IR. As alkylation of phenol is an industrially important reaction, *t*-butylation of phenol using *t*-butanol

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has been carried over these catalysts to assess their catalytic performance.

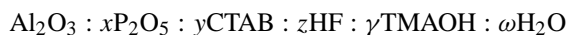
2. Experimental

2.1. Materials

Aluminium isopropoxide (Merck) and phosphoric acid (88% Merck) were used as the sources for aluminium and phosphorus, respectively. Hydrofluoric acid (48% Merck) was used as a co-solvent in order to disperse the gel effectively. Cetyltrimethylammonium bromide (Ottokemi) was used as template. Other materials included tetramethylammonium hydroxide (25 wt.% in H₂O, Merck), absolute ethanol (Heymann), *tert*-butanol (Merck) and phenol (Merck) were used as such without any further purification.

2.2. Preparation of catalysts

Mesoporous AlPO was synthesized hydrothermally from a gel composition of



where $x = 1\text{--}1.5$; $y = 0.25\text{--}0.5$; $z = 0.35\text{--}0.85$; $\gamma = 1.25\text{--}1.75$; $\omega = 150\text{--}300$

In a typical synthesis, aluminium isopropoxide was mixed with dilute phosphoric acid under vigorous stirring in which ethanol was employed as solvent. The slurry was continuously stirred until a homogeneous mixture was obtained. To the mixture appropriate amount of HF was added and the stirring continued. CTAB was then added and the stirring continued further. Finally, TMAOH was added dropwise into the above mixture until pH 9.5 was reached. The gel obtained in the above process was again subjected to stirring for 24 h at room temperature and the resulting product was filtered, washed with deionized water and dried in an oven at 70 °C.

2.3. Surfactant removal

About 500 mg of the as-synthesized samples, dispersed in 50 ml of 2 M ammonium chloride, was refluxed for 2 h [8]. The sample was then filtered during which majority of the organic part (surfactant) was extracted without any destruction of the mesostructure and dried at 70 °C. The sample was then subjected to calcination at 450 °C for 3 h.

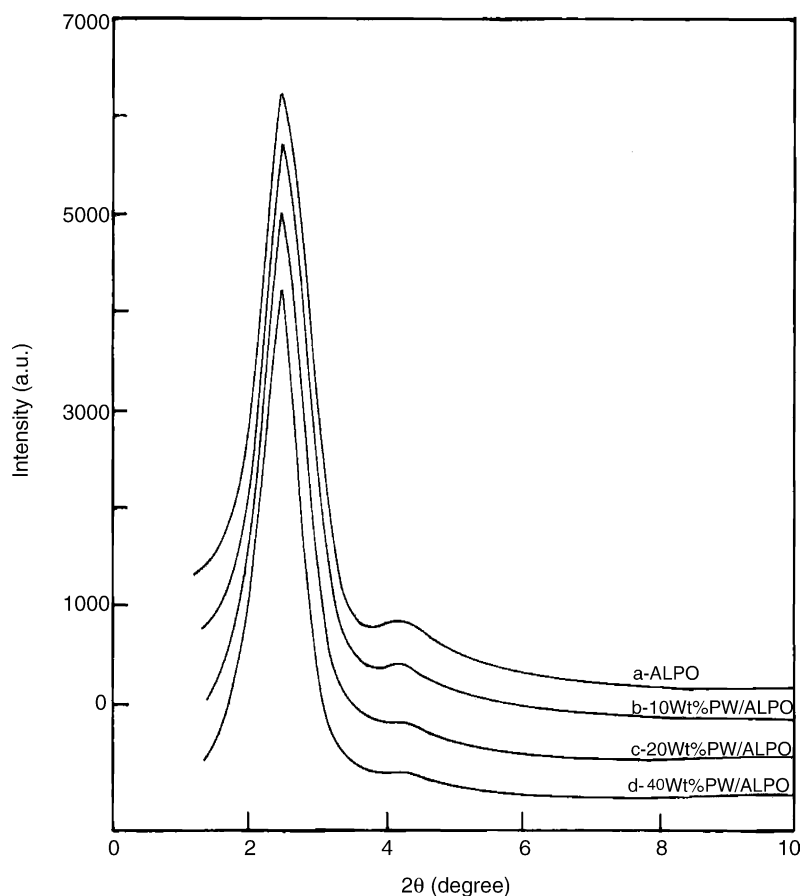


Fig. 1. XRD patterns of (a) AlPO, (b) 10 wt.% PW/AlPO, (c) 20 wt.% PW/AlPO and (d) 40 wt.% PW/AlPO.

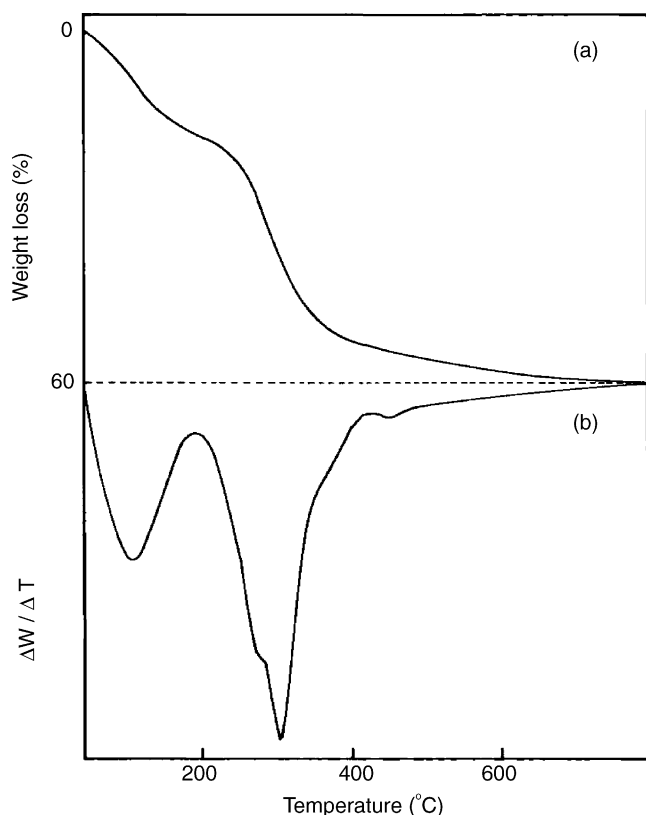


Fig. 2. (a) TG and (b) DTG analysis of as-synthesised AIPO.

2.4. HPA supported mesoporous AIPO

The supported catalyst was prepared by the impregnation of phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O}$) on mesoporous AIPO by adopting the already reported procedure [9]. The supported HPAs with PW loadings 10, 20 and 40 wt.% obtained were stored in a desiccator over P_2O_5 .

2.5. Characterization

Low angle X-ray powder diffraction (XRD) patterns were carried out on a Siemens D 5005 diffractometer using monochromatized $\text{Cu K}\alpha$ radiation. Patterns were recorded over the range $0\text{--}30^\circ$ (2θ) in steps of 0.03° with a count time of 15 s at each point. Thermogravimetric analysis of the as-synthesised mesoporous AIPO was carried out in Mettler TA 3000 thermal analyser. The samples were heated in air at a heating rate of $20^\circ\text{C}/\text{min}$ in the temperature range $35\text{--}800^\circ\text{C}$. FT-IR spectra were recorded on Nicolet-Avator 360 using KBr pellet technique.

2.6. Catalytic studies

Vapour phase alkylation of phenol with *t*-butanol was carried out in a fixed bed vertical flow type glass reactor ($40\text{ cm} \times 2\text{ cm}$). The reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital tem-

perature controller cum indicator. The chromel–alumel thermocouple was used to measure the temperature of the catalyst bed. About 0.5 g of the catalyst was placed in the middle of the reactor and supported on either sides with a thin layer of quartz wool and ceramic beads in order to maintain constant flow of the reactants into the catalyst. Reactants were fed into the reactor through the inlet using a syringe infusion pump. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The liquid products were analysed with Shimadzu GC-17A Gas Chromatograph using DB-5 capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) equipped with flame ionization detector.

3. Results and discussion

3.1. Characterization

In order to check the purity and mesoporous nature of the synthesised materials before subjecting them to catalytic studies, the following characterisation studies have been carried out. Fig. 1 shows the X-ray powder diffraction patterns of the parent mesoporous AIPO and PW/AIPO catalysts with various HPA loadings (PW/AIPO of 10, 20 and 40 wt.%). The XRD peaks confirm the hexagonal mesoporous nature of the materials. The samples exhibit an intense peak at about 2° (2θ) with a d spacing of $32.68\text{ }\text{\AA}$ due to (1 0 0) plane and a weak peak due to (1 1 0) plane between 4° and 5° (2θ). These peaks can be indexed for hexagonal unit cell.

On HPA loading, the intensity of the peak at $32.68\text{ }\text{\AA}$ decreases as expected. However, with HPA content increasing from 10 to 40 wt.%, no patterns from PW crystal phase were obtained [10]. Therefore, the XRD data indicate that PW is finely dispersed on the AIPO surface, no HPA crystallinity being observed at any of the loadings.

The thermogravimetric analysis of as-synthesised sample of mesoporous AIPO done between 35 and 800°C shows three distinct stages of weight losses as shown in Fig. 2. The first weight loss, which occurred below 175°C is due to desorption of H_2O . The second major weight loss which occurred around 200°C is due to oxidative desorption of template. Finally, the third weight loss between 400 and 600°C is due to the condensation of uncondensed defective $-\text{OH}$ groups in the framework.

The FT-IR spectra of as-synthesised and extracted mesoporous AIPO are shown in Fig. 3. The broad envelope around 3425 cm^{-1} is due to $-\text{OH}$ stretching of H_2O . The corresponding bending mode is observed around 1642.05 cm^{-1} . In the as-synthesised sample the peaks observed at 2920.96 and 2851.59 cm^{-1} are assigned to symmetric and asymmetric stretching modes of the $-\text{CH}_2$ group of the locked in template. The corresponding bending mode for the as-synthesised material is observed at 1487.12 cm^{-1} . Whilst these $-\text{CH}_2$ stretching and bending mode peaks are absent in the extracted mesoporous AIPO indicating the complete removal of the template. The T–O–T asymmetric stretching is

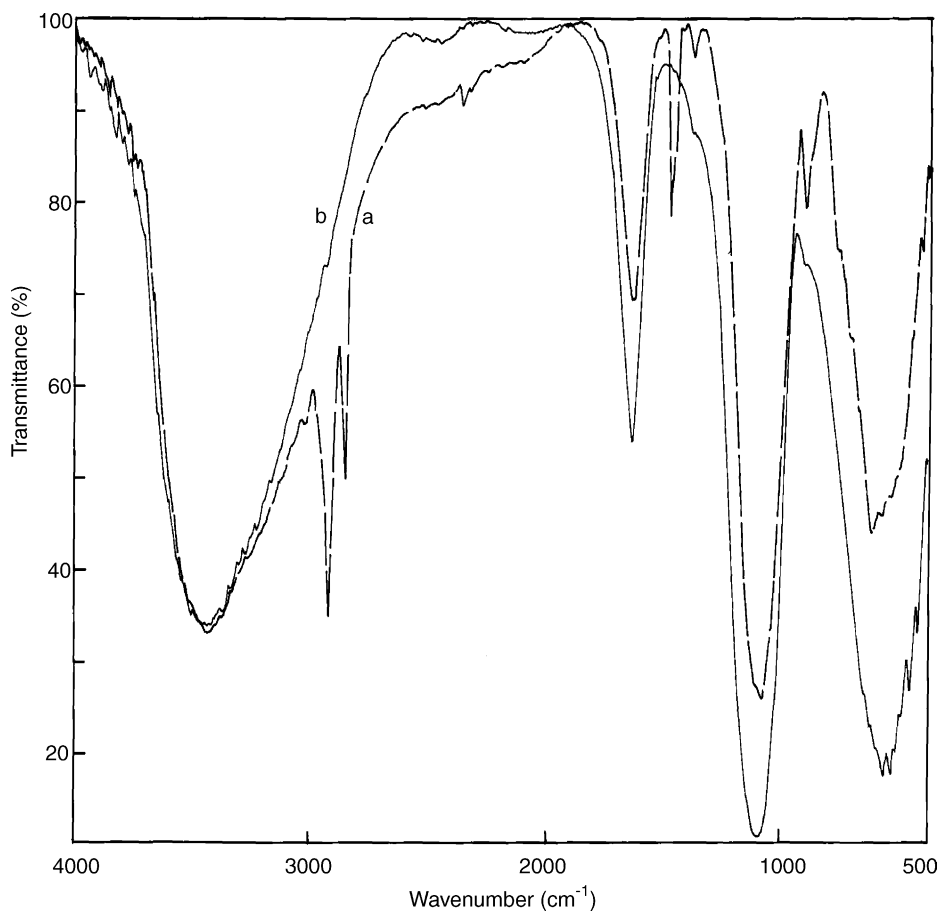


Fig. 3. FT-IR spectra of (a) as-synthesised AlPO and (b) extracted and calcined AlPO.

positioned at 1082.95 cm^{-1} and the corresponding symmetric stretching mode is observed at 624.74 cm^{-1} . The T–O–T bending mode is positioned at 407.79 cm^{-1} . The peak at 911.88 cm^{-1} is due to defective –OH, which is uncondensed –OH group formed during Al–O–P bond formation.

Fig. 4 illustrates the FT-IR spectra of PW/AlPO catalyst with different loadings. All the catalysts show the typical IR bands at 1080 (P–O in the central tetrahedral), 982 (terminal W=O), 893 and 812 cm^{-1} (W–O–W) asymmetric vibrations associated to Keggin ion, indicating that the primary structure of the heteropolyacid is preserved after supporting it on the mesoporous AlPO [10].

3.2. *t*-Butylation of phenol

As alkylation of phenol is an industrially important reaction, *t*-butylation of phenol using *tert*-butanol has been chosen to study the catalytic activity of the synthesised catalysts.

3.2.1. Catalytic studies on parent AlPO

The reaction has been performed over mesoporous aluminumophosphate in the temperature range 190 – $275\text{ }^{\circ}\text{C}$. Study of the influence of feed ratio (phenol: *tert*-butanol) has revealed inadequacy of $1:1$ and $1:2$ to effect ring alkyla-

tion. This may be due to non-adsorption of both the reactants or adsorption of any one of them, preferably phenol on the Bronsted acid sites of the catalyst [11]. Hence, in order to achieve effective co-adsorption of both the reactants on the Bronsted acid sites, the feed ratio has been further increased to $1:3$ with $\text{WHSV} = 5.25\text{ h}^{-1}$. The products obtained were *o*-*t*-butyl phenol (*o*-*t*-BP), *p*-*t*-butyl phenol (*p*-*t*-BP) and *t*-butylphenyl ether (*t*-BPE) as confirmed by a combined gas chromatography–mass spectrograph (Perkin-Elmer Elite Series PE-5, capillary column ($30\text{ cm} \times 0.25\text{ mm} \times 1\text{ }\mu\text{m}$) with tubular mass spectrometer (EI, 70 eV) with helium as carrier gas at a flow rate of 1 ml/min).

Phenol conversion and selectivity of products with respect to temperature are shown in Figs. 5 and 6. The decrease in phenol conversion at higher temperature (viz. 225 , 250 and $275\text{ }^{\circ}\text{C}$) may be due to desorption of *tert*-butanol and coke formation as reported earlier for microporous zeotype molecular sieves [12]. High selectivity towards *p*-product compared to thermodynamically favourable *m*-product may be due to the fact that the hydroxyl group of phenol is *o*-*p*-directing [13]. Further the moderate acidic nature of the catalyst is also found to be one of the main reasons for the observed high *p*-selectivity with increase in temperature [14]. Though the mesoporous AlPO framework is expected to be neutral,

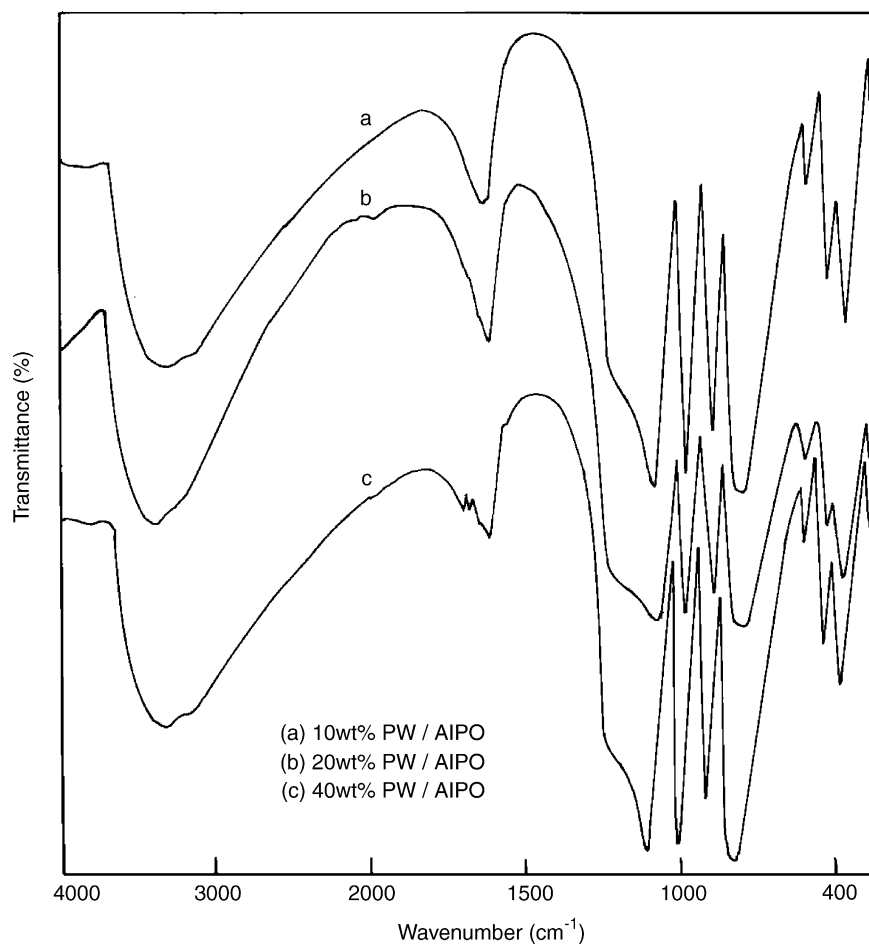


Fig. 4. FT-IR spectra of (a) 10 wt.% PW/AIPO, (b) 20 wt.% PW/AIPO and (c) 40 wt.% PW/AIPO.

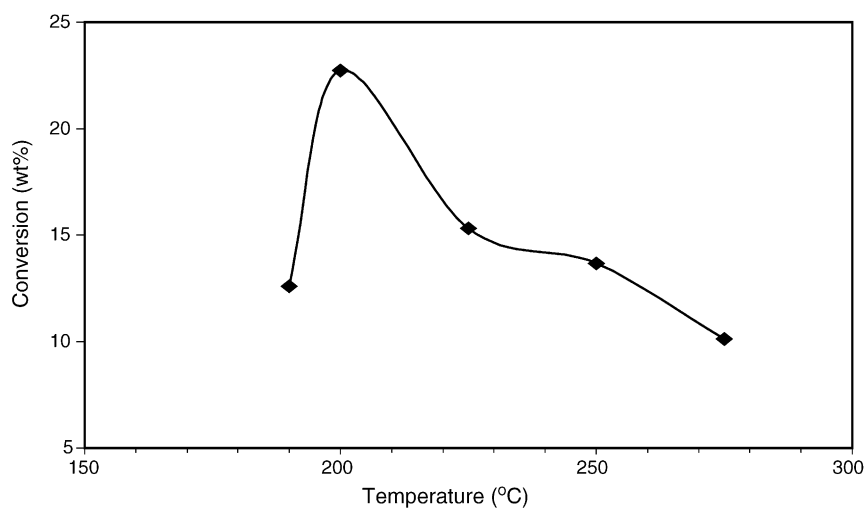


Fig. 5. Effect of temperature on phenol conversion over AIPO.

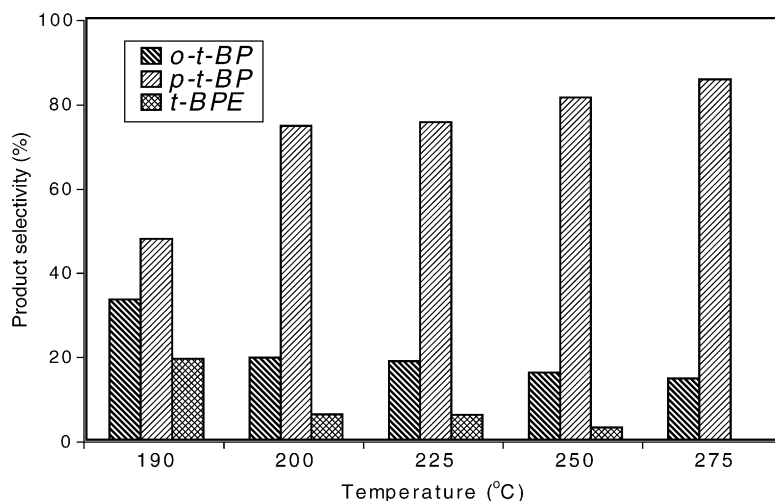
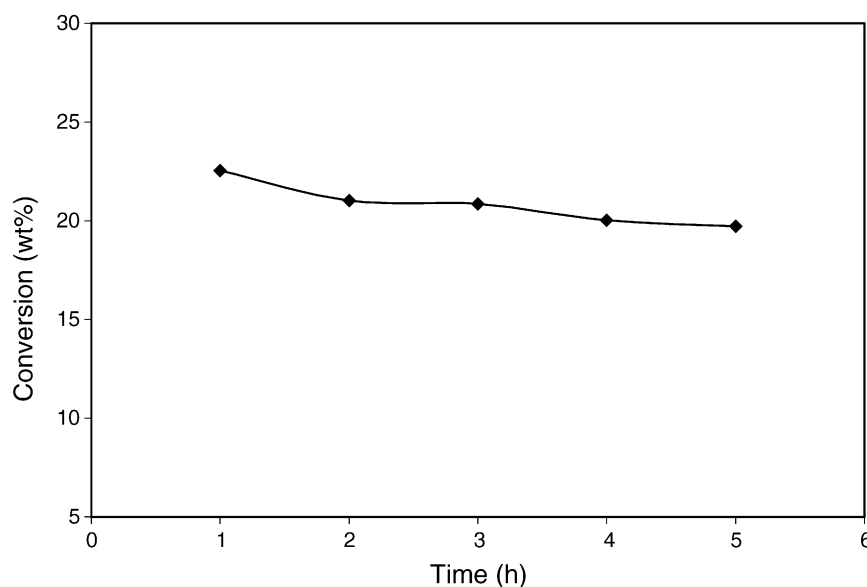


Fig. 6. Effect of temperature on product selectivity over AIPO.

Fig. 7. Effect of time on stream on conversion over AIPO at 200 °C; WHSV = 5.25 h⁻¹.

terminal P–OH groups and/or significant numbers of uncondensed free –OH groups present in it, assist the reaction requiring weak acidity.

In order to assess the catalytic activity, the effect of time on stream (TOS) over the catalyst was examined at 200 °C with WHSV = 5.25 h⁻¹ (Fig. 7). There is only a slight decrease in the conversion of phenol with time indicating the stability of the catalyst towards deactivation by coke formation.

3.2.2. Catalytic studies on HPA supported mesoporous AIPO

The acidity of parent AIPO is due to its defective sites. These acid sites are proved to be important for its activity to yield *p-t*-butyl phenol (*p-t*-BP) [14]. Conversion over 10, 20 and 40 wt.% HPA loaded catalysts is comparatively high due to their strong density of acid sites (Fig. 8). Conversion

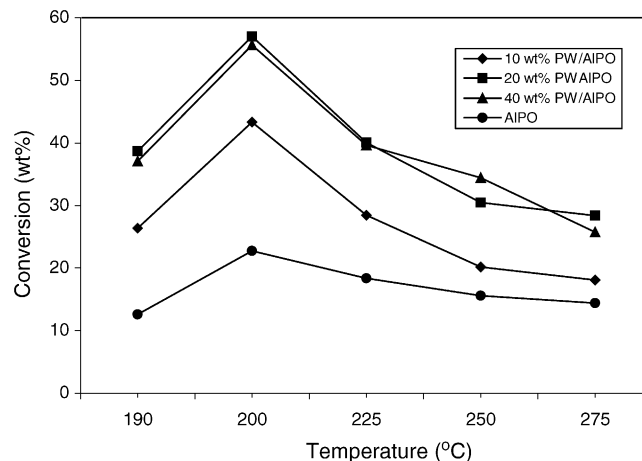


Fig. 8. Effect of temperature on conversion over AIPO and PW/AIPOs.

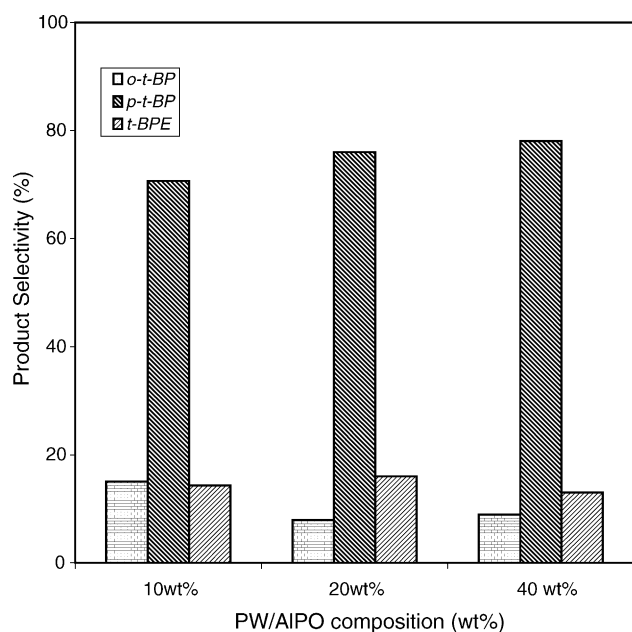


Fig. 9. Effect of product selectivity over PW/AIPOs at 200 °C; WHSV = 5.25 h⁻¹.

increases from 190 to 200 °C, but above 200 °C it decreases. The less conversion at 190 °C is attributed to molecular association that reduces adsorption and dissociation on the active sites. The decrease in conversion above 200 °C is due to blocking of active sites by thin film of polybutene oligomers as reported earlier [15,16].

The selectivity of the products formed in the reaction at 200 °C is illustrated in Fig. 9. The selectivity to *p-t-BP* increases from 10 to 20 wt.% loading but for 20 and 40 wt.% loading it is nearly equal. Hence, at 20 and 40 wt.% HPA loading there might be nearly equal level of strong Bronsted acid sites that yield *p-t-BP*. As the Bronsted acid sites are strong, phenol with non-centrosymmetric charge distribution may be preferentially adsorbed on any one of the ortho carbons in comparison to the para carbon. This is assisted by H-bonding between phenolic -OH and the catalyst surface. Hence, the electrophilic attack at the para position of phenol selectively occurs with the *t*-butyl cations chemisorbed close to it. High density of acid sites also favours close adsorption of phenol and *t*-butyl cations on the catalyst surface, thus, leading to high selectivity for *p-t-BP*. Hence, it is justified that at 20 wt.% loading there is fine dispersion of a layer of Bronsted acid sites by the closely packed Keggin structure on the mesoporous surface. So, on further increase in HPA loading to 40 wt.% there is no significant increase in the density of Bronsted acid sites [17].

The selectivity towards *o-t-BP* is less on all the HPA loaded catalysts than parent AIPO as the dense Bronsted acid sites of the loaded catalysts will facilitate the adsorption of phenol on the acid sites thus reducing the selectivity towards *o-t-BP*. *o-t-BP* and *t-BPE* are formed with same selectivity over 10 wt.% loaded AIPO, although the former is expected to have more selectivity due to two ortho carbons.

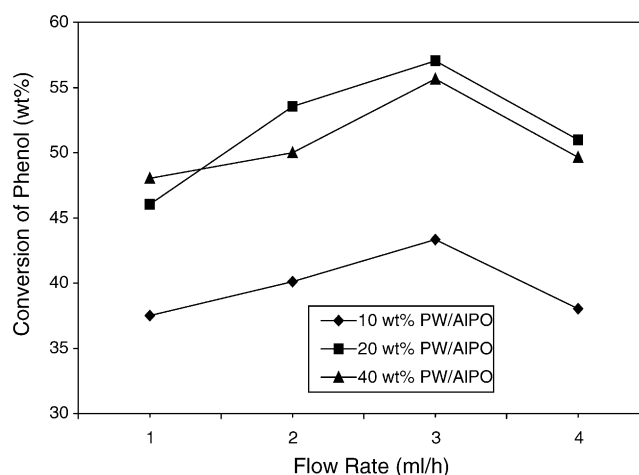


Fig. 10. Effect of WHSV on phenol conversion over PW/AIPOs at 200 °C.

This may be due to the chemisorption of part of vapour phase phenol that prevents its reaction with *t*-butyl cation to yield *o-t-BP*. Such a problem would not arise for *O*-alkylation. Hence, the selectivity of *o-t-BP* and *t-BPE* are nearly the same. The selectivity to *t-BPE* is more than *o-t-BP* over 20 and 40 wt.% loaded catalysts as more dense strong acid sites would favour chemisorption at the ortho position rather than alkylation.

In order to study the influence of contact time, WHSV was varied from 1.75 to 6.98 h⁻¹ at 200 °C. Increase in phenol conversion with increase in flow rate from 1 to 3 ml/h has been observed over all the catalysts as shown in Fig. 10 which is due to the enhanced adsorption of reactants [18]. On increasing the flow rate from 3 to 4 ml/h, conversion of phenol decreases over all the three catalysts. Hence, the flow rate of 3 ml/h at 200 °C with WHSV = 5.25 h⁻¹ was optimized for all the studies.

Fig. 11 shows the effect of WHSV on product selectivity when varied from 1.75 to 6.98 h⁻¹ at 200 °C. It is observed that selectivity towards *p-t-BP* is high at 5.25 h⁻¹ for all the catalysts and exclusively more for 20 wt.% PW/AIPO. This is due to the little or no adsorption of the *tert*-butanol on the catalysts at other WHSVs leading to lower conversions and selectivities [18]. Comparison of product selectivity for the flow rate of 3 ml/h shows the following order, *p-t-BP* > *t-BPE* > *o-t-BP*.

The influence of feed ratio on phenol conversion has been studied at 200 °C with WHSV = 5.25 h⁻¹ (Fig. 12). On comparison with parent AIPO, more conversion has been achieved on PW/AIPO catalysts with different loadings. In the parent AIPO there will be more crowding of the acid sites so also the adsorbed reactants/products in defective centers. As a result of this full exploitation of the acid sites would be difficult. Whilst in PW/AIPO catalysts there will be masking of the defective centers due to the formation of thin film of HPA over the catalyst surface thus enhancing the dispersion of Bronsted acid sites in the loaded catalysts. This provides almost no chance for crowded adsorption of

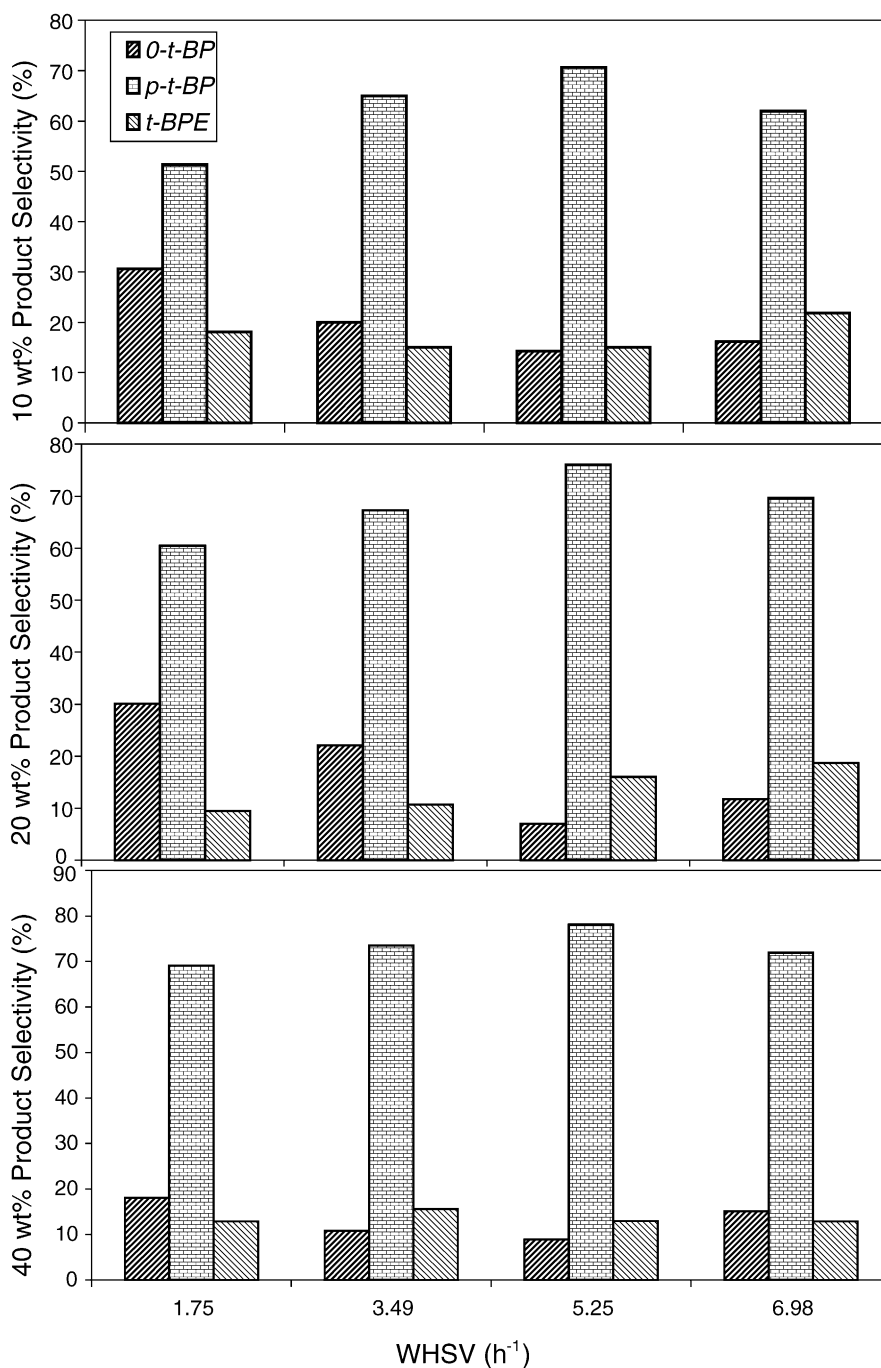


Fig. 11. Effect of WHSV on product selectivity over PW/AIPOs at 200 °C.

reactants/products that would mask the activity of free Bronsted acid sites. Hence, every site can exhibit significant activity thus leading to more conversion. Similar to parent AIPO, conversion increases with increase in alcohol content in the feed except with ratio 1:4 where the observed decrease in conversion might be attributed to dilution of phenol by *tert*-butanol in the vapour phase.

The influence of time on stream (TOS) on conversion of phenol has been studied over all the PW/AIPO catalysts at 200 °C with feed ratio of 1:3 and WHSV 5.25 h⁻¹. The re-

sults are depicted in Fig. 13. The conversion of phenol decreases gradually with increase in time on stream. Nearly similar conversion with increase in time on stream over 20 and 40 wt.% loading establishes similar level and distribution of acid sites on them. As there is no rapid decrease in conversion with time on stream, the products may freely diffuse and escape out of the pores. It is quite understandable that coke formation, a process involving repeated alkylation, could be more prevailing over HPA loaded catalysts as the active sites are more and very well dispersed [19,20].

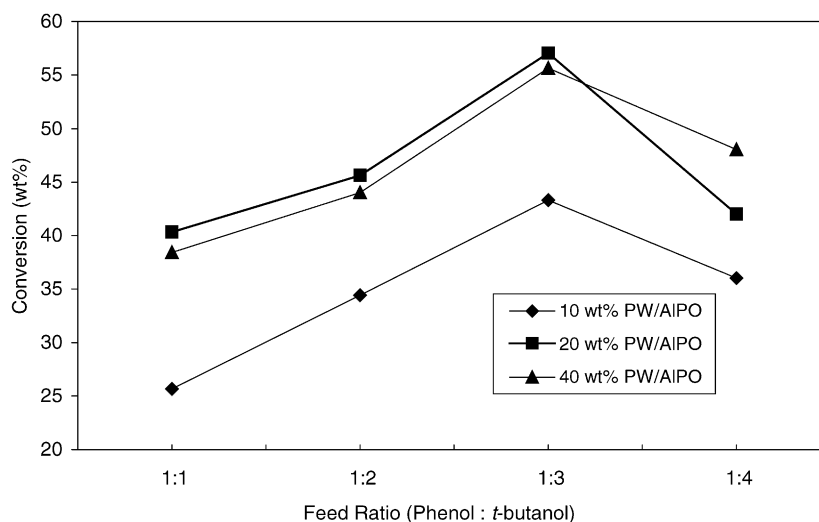


Fig. 12. Effect of feed ratio on phenol conversion over PW/AIPOs at 200 °C.

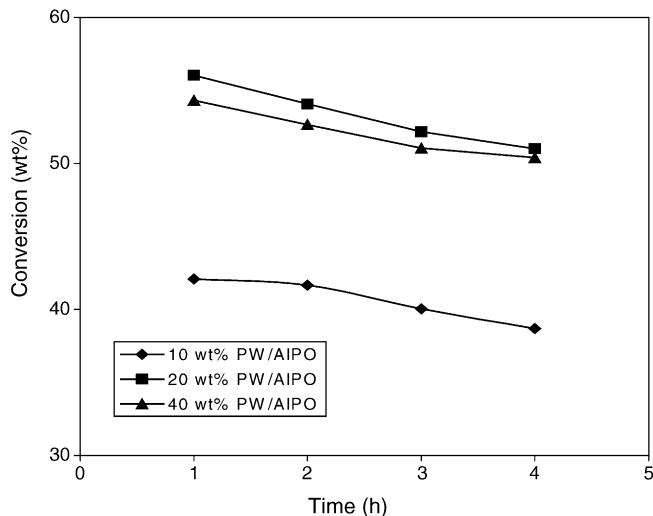


Fig. 13. Effect of time on stream on conversion over PW/AIPOs at 200 °C; WHSV = 5.25 h⁻¹.

4. Conclusion

Solid acid catalytic compositions of recently developed mesoporous aluminophosphate molecular sieve and Keggin type heteropolyacid PW have been prepared and characterized. HPA retains the Keggin structure on the AIPO surface and forms finely dispersed HPA species which is evidenced from the XRD patterns where there is no detectable crystal phase for HPA in all the loadings including 40 wt.%. PW/AIPO materials possess strong Bronsted acid sites, which are enhanced by HPA and it is found to be maximum in 20 wt.% PW/AIPO catalyst. These new catalytic compositions may be useful in acid-catalyzed conversion of organic compounds of large molecular size as against large pore size zeolites such as zeolite Y and beta, where such large molecular size reaction is difficult to achieve.

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