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Activated carbon–tungstophosphoric acid catalysts for the synthesis of *tert*-amyl ethyl ether (TAEE)

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Abstract

Catalytic activities of bulk tungstophosphoric acid (HPW) and its supported forms on activated carbon were investigated in the vapor phase etherification reaction of isoamylene with ethanol in a continuous flow reactor. Tungstophosphoric acid ($H_3PW_{12}O_{40}\cdot 11H_2O$) was supported on activated carbon having a surface area of 796 m^2/g, at two different loading levels (25% and 31%) by aqueous impregnation technique and the kinetic experiments were done in a temperature range between 353 and 370 K. Supported HPW catalysts containing the same amount of HPW yielded much higher conversion than bulk HPW at 353 K. Decrease of isoamylene conversion values with an increase in temperature on the supported catalysts was explained by the role of active carbon surface as a reservoir for the reactants. HPW was found to be highly immobilized on the active carbon surface keeping most of its activity after being excessively washed with ethanol. Results also indicated that activity of HPW was higher than the activities of both Amberlyst-15 and another heteropoly acid, namely molybdophosphoric acid.

Keywords: Heteropoly acid catalyst; Isoamylene; TAEE; Activated carbon; Impregnation technique; Tungstophoshoric acid; Molybdophosphoric acid

1. Introduction

All over the world, governments and regulatory agencies are taking legislative steps to reduce the impact of gasoline on the environment and on human health. Environmental considerations require new reformulations in gasoline. In these new generation fuels, the use of lead-containing engine knock suppressing additives was totally restricted and the levels of total aromatics and benzene were decreased below 25 and 1 vol.%, respectively. Another requirement of the reformulated gasoline is the level of oxygen content, which should be increased above 2 wt.%. These properties in the reformulated gasoline created a wide interest in oxygenated fuel blending components. High octane numbers, low vapor pressure and low atmospheric reactivity of oxygenates, such as tertiary ethers and alcohols attracted the interest of researchers and refiners [1–6]. Besides the high octane numbers, these oxygenates also cause reduction in CO and unburned hydrocarbon exhaust emissions.

Among the oxygenates, tertiary ethers are preferred to alcohols as gasoline blending components, because they have lower blending vapor pressure and alcohols may cause phase separation in fuel tanks in the presence of small amount of water. Among the ethers suggested as fuel blending components, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), *tert*-amyl ethyl ether (TAEE) and diisopropyl ether (DIPE) attracted the highest attention. Very recently, 2-methoxy-2,4,4-trimethylpentane was proposed as a novel gasoline oxygenate [7]. Tertiary ethers are produced by the reaction of *iso*-olefins with alcohols. By the reaction of isobutylene with methanol or ethanol, over an acidic catalyst, MTBE or ETBE is produced, respectively. In order to produce TAME or TAEE, isoamylenes must be used instead of isobutylene. Among these tertiary ethers, MTBE is the most popular one because it is cheaper and its properties are well known, but it creates environmental problems including water pollution [2,8,9]. Environmental considerations limited the use of MTBE as the octane enhancing gasoline blending oxygenate and diverted the attention to ethanol-based oxygenates such as ETBE and TAEE. Presence of significant amount of C_6 and C_5 reactive olefins (isoamylenes) in FCC light gasoline [9], brought about the possibility of direct etherification of gasoline with ethanol to

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produce TAEE and higher *tert*-ethers like *tert*-hexyl ethyl ether (THEE) [10]. One advantage of TAEE is that, ethanol can be produced by fermentation from renewable resources like sugarcane, sugarbeat, corn or molasses and also from crop and sugar wastes.

Generally, macroreticular acidic resins (Amberlyst-15) and zeolites are used for the etherification reactions between C_4 and C_5 *iso*-olefins and alcohols [11–18]. In recent studies, mesoporous catalysts [19] and nickel-based catalysts [20] were also proposed for the synthesis of oxygenates. Acidity of the solid catalysts is a major factor in such etherification reactions [5]. A promising alternate of such acidic macroreticular resins is the use of heteropoly acid components as the catalyst in these etherification reactions. Heteropoly acid (HPA) compounds and their salts are known to be active catalysts for many homogeneous and heterogeneous acid catalyzed reactions. A growing interest has been developed related to the chemical, physical properties and the catalytic activity of these compounds. They have very strong Brönsted acidity, approaching to superacid region, fairly high stability, and a structure with high proton mobility. The Hammett acidity H_0 of tungstophosphoric acid is -13.2 which is much stronger than 100% sulfuric acid ($H_0 = -11.94$). Besides their high acidity, redox properties and pseudo-liquid behavior of these compounds make them attractive catalysts for number of reactions. As a result, the reaction proceeds not only on the surface but also in the bulk of the crystalline heteropoly acid structure [21–26]. However, these materials have high solubility in polar solvents, which limits their use in number of liquid phase reactions. Also, they have very low surface area values in the order of a few square meters per gram. To increase the surface area of heteropoly acid catalysts and also to improve their stability, supporting of these compounds on high surface area materials is recommended. The major objective of the present work was to investigate the activity of tungstophosphoric acid catalyst supported on activated carbon and compare its activity with the activities of bulk tungstophosphoric acid, molybdophosphoric acid and Amberlyst-15 in the etherification reaction of isoamylene with ethyl alcohol in a continuous differential reactor. The effects of temperature and the loading procedure of heteropoly acid on the activity of such catalysts in TAEE synthesis were examined.

2. Experimental

2.1. Chemicals and catalysts

In this study, $H_3PW_{12}O_{40}\cdot xH_2O$ (HPW) and $H_3PMo_{12}O_{40}\cdot xH_2O$ (HPMo) from Acros Organics and Amberlyst-15 with an average particle diameter of 740 μm from Sigma [1] were used. The activated carbon, which is used as the support material is from KUREHA (Japan) in granular form with mesh size of 40–50 (425–300 μm). In the etherification reaction experiments, an isoamylene of mixture 2-methyl-2-butene (2M2B) (95%) and 2-methyl-1 butene (2M1B) (Merck) and absolute ethanol (Merck) were used.

2.2. Preparation of supported HPA catalysts

Before being utilized in impregnation experiments, the activated carbon (AC) was first washed in a solution of 0.1 M NaOH, then in 0.1 M HCl to eliminate the soluble acidic and alkaline impurities. Following a similar procedure as reported by Chimienti et al. [27] activated carbon particles were then treated with a 30 wt.% solution of HNO_3 and heated up to boiling in a reflux system for 2 h to make the carbon more acidic. HPW solutions with different concentrations were prepared by using a mixture of demineralized water and ethanol (96%), in a volumetric ratio of 1:1, as the solvent. The pretreated activated carbon particles were then impregnated by the prepared HPW solutions following a procedure similar to the procedures described in the literature [27–30]. The loading amounts of HPW were 25 and 31 wt.% and these catalysts were denoted as HPW25@AC and HPW31@AC, respectively. Further increase of HPW wt.% in the catalyst causes sharp decrease of pore volume and surface area due to pore plugging. After drying overnight, these catalysts were calcined at 453 and 403 K in a flow of air for 4 h, to see the possible effect of calcination temperature on the activity. In order to test the success of the impregnation procedure and catalyst stability in polar solvents, HPW31@AC was excessively washed in ethanol after the calcination step and the activity of this washed catalyst was compared with the activity of unwashed supported catalysts.

2.3. Characterization of catalysts

Thermogravimetrical analysis (DSC and TGA) of both bulk and supported heteropoly acid catalysts was carried out by using Dupont 951 Thermal Analyzer. The thermogravimetry experiments were performed under flowing nitrogen, using 18–25 mg samples and at a heating rate of 10 °C/min. The studied temperature range was 30–800 °C. The surface areas of the catalysts and the activated carbon support used in the experiments were determined from N_2-adsorption data obtained at 77 K by using BET equation using a surface area analyzer (ASAP 2000 of Micromeritics Co. Inc).

X-ray diffraction (XRD) for the identification of the crystalline phases was performed by Rigaku D/MAX2200 diffractometer with a Cu Kα radiation source. The scanning range of 2θ was set between 1° and 50° with a step size of 0.01°. FT-IR measurements of pure and supported HPW catalysts were performed by Bruker IFS 66/S instrument using KBr pellet technique. In addition to these techniques, the supported catalyst samples were characterized by X-ray photoelectron spectroscopy (XPS) using a SPECS instrument and energy-dispersive spectroscopy (EDS) using JEOL 6400 apparatus.

2.4. Catalytic reactions

Etherification reaction of isoamylene mixture with ethanol was carried out in vapor phase in a tubular reactor. Helium was used as the inert carrier gas and it was mixed with the reactants mixture in the evaporator at desired proportions. The composition of the feed stream to the reactor was adjusted as 14 vol.%

ethanol, 6 vol.% isoamylene and 80 vol.% helium. The composition of the reactor effluent stream was determined using a gas chromatograph (Varian Aerograph) equipped with flame ionization detector and the column was packed with 15% FFAP on Chromosorb AW.

In the first part of the experiments, the effect of temperature on the catalytic activities of bulk and supported HPW catalysts were investigated. In these experiments, 0.2 g of catalyst was placed into the tubular reactor and the temperature range was taken between 353 and 370 K.

In the second part of the experiments, etherification of isoamylene was investigated using different amounts of supported catalysts of different compositions, such that the amount of HPW charged to the reactor was kept constant at 0.2 g. These experiments were again carried out in the same temperature range. In addition to these catalytic tests, the deactivation of supported HPW catalysts was tested by carrying out successive etherification reactions in a temperature range between 353 and 370 K, with the same catalyst. Finally, the catalytic activity of alternative catalysts, namely Amberlyst-15 which is used for this reaction in number of other studies and HPMo catalyst, which is another Keggin type heteropoly acid, was investigated. Also in those experiments 0.2 g of catalyst was loaded to the reactor and the experiments were performed at a fixed temperature of 363 K.

3. Results and discussion

3.1. Catalyst characterization

The DSC result of bulk HPW is given in Fig. 1. When the catalyst was heated up to 130 °C, the molecules of crystalline water were removed from the structure of the catalyst:

$$H_3PW_{12}O_{40}\cdot nH_2O \Rightarrow H_3PW_{12}O_{40} + nH_2O \qquad T < 130\,^{\circ}C$$

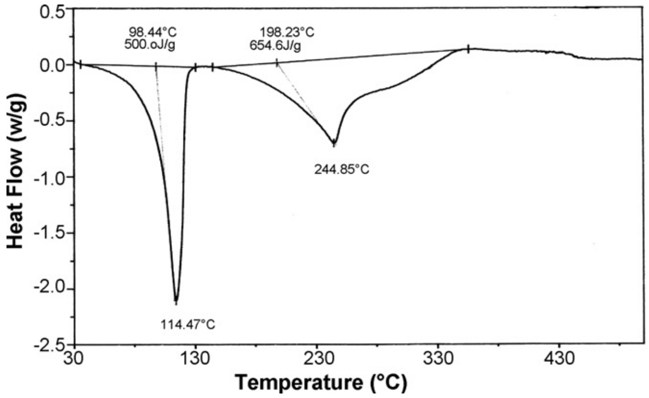

Fig. 1. DSC plot of bulk HPW.

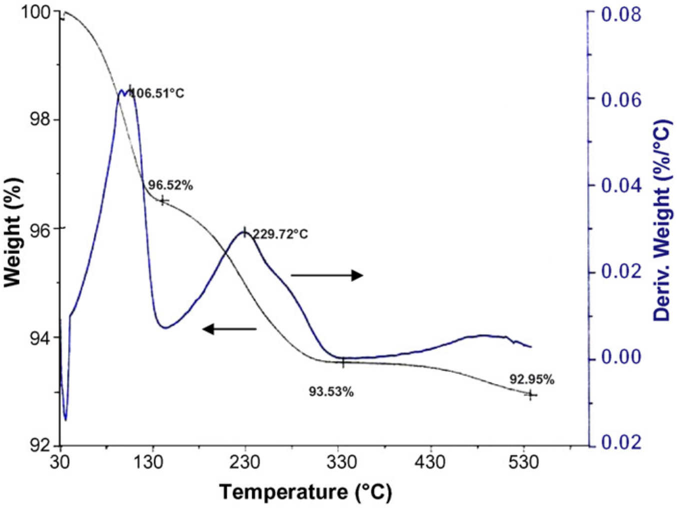

Fig. 2. TGA plot of bulk tungstophosphoric acid (HPW) catalyst.

TGA results of bulk HPW shown in Fig. 2 also justified these results. TGA results also indicated that n was equal to eleven in the HPW sample used in our work. When the catalyst was heated above 180 °C, it started to decompose and decomposition was completed at about 350 °C. The maximum of the DSC signal corresponding to the decomposition of anhydrous HPW was observed at about 245 °C, while the corresponding maximum in the TGA signal appeared at 229.72 °C These results are also in agreement with the NMR results reported by Thomas et al. [31]. According to those ^{1}H MAS NMR results, the signal observed at 2 ppm disappeared after calcination of HPW at 200 °C, indicating the removal of water and formation of anhydrous tungstophosphoric acid. However, the sharp signal observed at 8 ppm, which was attributed to the protons in anhydrous HPW, disappeared when sample was calcined at 300 °C. Our DSC and TGA results and NMR results reported by Thomas et al. [31] clearly indicated that decomposition of anhydrous HPW over 180 °C was also accompanied with the loss of acidity of the catalyst:

$$H_3PW_{12}O_{40} \Rightarrow 12WO_3 + 3/2H_2O + ½P_2O_5$$

$$180\,^{\circ}C < T < 350\,^{\circ}C$$

The TGA curve of the active carbon supported catalyst containing 25 wt.% HPW (HPW25@AC) also indicated similar results (Fig. 3). Loss of crystal water was completed at about 130 °C and decomposition of HPW started at around 180 °C, giving a maximum in TGA signal at about 323 °C (Fig. 3). This decomposition temperature of activated carbon supported HPW was about 90 °C higher than the maximum of the decomposition signal of bulk HPW, indicating higher stability of HPW supported on activated carbon than its bulk form.

The physical properties of the supported HPW catalysts and the active carbon support are given in Table 1. Tungstophosphoric acid itself has very low surface area, in the order of magnitude of 1–2 m^2/g. However, the BET surface area of the active carbon support used in our work was 796 m^2/g and about 68% of this area corresponded to the micropores. When HPW was supported on active carbon, some reduction of its surface area was observed (Table 1). The surface area of the sample containing 31% HPW and which was calcined at 130 °C was 501 m^2/g. This corresponds to about 63% of the surface area of fresh active carbon. Similar to the decrease of surface area, the total pore volume of the HPW31@AC was about 62% of the

Table 1
Physical properties of tungstophosphoric acid incorporated active carbon catalysts

Sample	Surface area (m^2/g)		Pore volume (cm^3/g)		Average pore diameter (nm)	
	BET	Micropore	Total	Micropore	Langmuir	BJH
Active carbon	796	545	0.395	0.256	1.46	3.5
HPW25@AC (calcined at 180 °C)	424	222	0.207	0.107	1.41	3.2
HPW31@AC (calcined at 130 °C)	501	350	0.245	0.165	1.44	3.2

fresh active carbon. The ratio of micropore area to the total BET area was about the same (about 0.68) for both fresh active carbon and for HPW31@AC. However, for the sample calcined at 180 °C, (HPW25@AC) the changes observed in the pore structure were more pronounced. Although HPW25@AC contained less HPW than HPW31@AC, its total surface area was less. Also, the ratio of micropore area to total surface area (about 0.52) and the ratio of micropore volume to total pore volume (about 0.52) values of HPW25@AC were smaller than the corresponding values obtained for HPW31@AC. A possible reason of these observations is the difference in calcination temperatures of these catalysts. As shown in the TGA curves, decomposition of HPW started at around 180 °C. Partial decomposition of HPW at 180 °C and plugging of some of the micropores by the decomposition products might be the reason of these observations.

The XRD patterns of bulk and supported HPW catalysts (HPW25@AC and HPW31@AC) are given in Fig. 4. The main peaks of the XRD patterns of supported catalysts and bulk HPW were quite similar. For bulk HPW, the XRD pattern showed sharp peaks at 2θ values between 20° and 40° (Fig. 4a). Also, three sharp peaks existed in the low Bragg angle range (less than 10°). On the other hand, the XRD patterns of the supported HPW catalysts showed that the intensity of the peaks decreased as compared to the peaks of bulk HPW and some small peaks were disappeared. The main conclusion reached from the XRD patterns is that the main characteristics of Keggin structure of HPW were essentially conserved in the supported catalyst. This conclusion was also supported by the FT-IR results obtained with supported and bulk HPW catalysts (Fig. 5). The typical FT-IR bands of bulk tungstophosphoric acid were observed at 1080 cm^{-1} (P–O), 983 cm^{-1} (W=O), 889 cm^{-1} (W–O–W in corner shared octahedral) and at 839 cm^{-1} (W–O–W in edge shared octahedral). Similar results were also reported by Bielanski and Lubanska [32] and Vazquez et al. [33]. Some shifts in the positions of these bands were observed in the supported catalysts. For instance for HPW31@AC which was calcined at 130 °C, the bands were observed at 1069, 1013, 967, 922 and 870 cm^{-1}, indicating the formation of some new bonds between the HPW and the active carbon support. Main bands observed for HPW25@AC, which was calcined at 180 °C, appeared at somewhat different positions than HPW31@AC, also indicating the importance of calcination temperature on the structure. For this sample an additional band was observed at 670 cm^{-1}. However, the bands observed for this sample also indicated that the changes in the characteristic Keggin structure were not high after calcination of the sample at 180 °C.

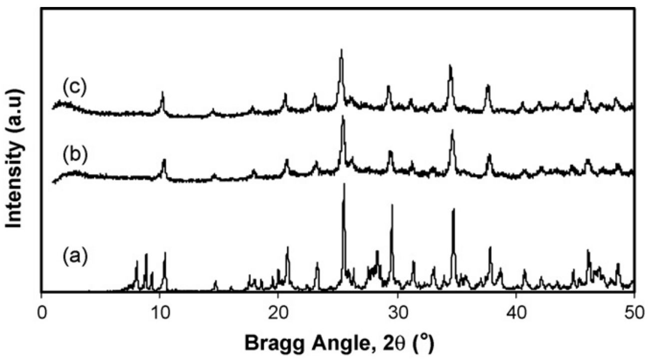

Fig. 4. XRD patterns of bulk and supported HPW catalysts: (a) bulk HPW, (b) HPW25@AC, and (c) HPW31@AC.

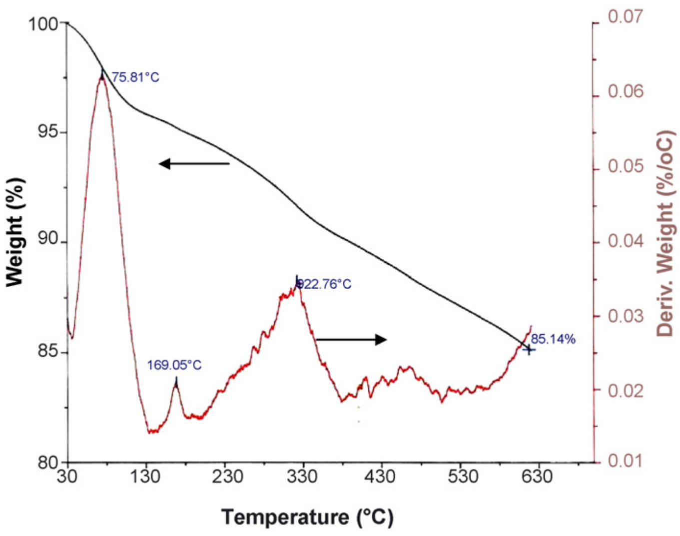

Fig. 3. TGA plot of HPW25@AC.

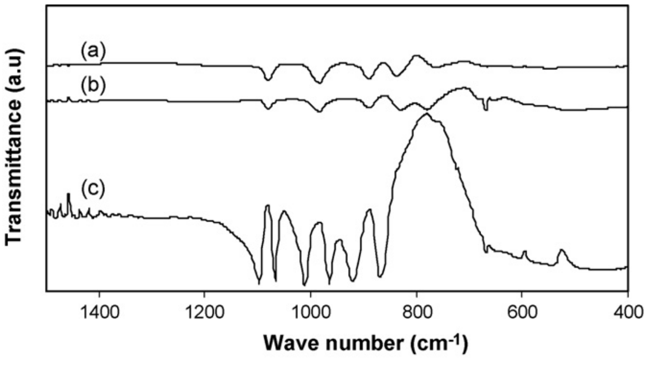

Fig. 5. FT-IR spectra of (a) bulk HPW, (b) HPW25@AC, and (c) HPW31@AC.

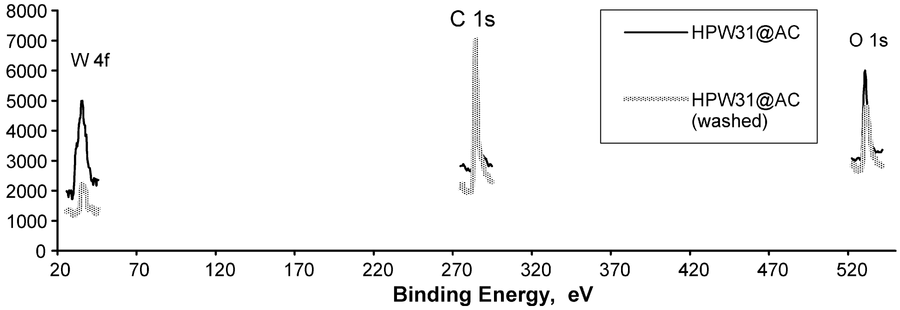

Fig. 6. XPS of HPW31@AC, before and after washing with ethanol.

The XPS and EDS of HPW31@AC before and after washing with ethanol were obtained to have an idea about the surface and bulk compositions of the washed and unwashed supported catalysts. The XPS of both washed and unwashed samples gave characteristic peaks of W^{6+} (4f), P (2p), C (1s) and O (1s) at 35.7, 133.3, 284.5 and 530.9 eV, respectively (Fig. 6). The signal of P was too small to make a quantitative analysis. However, the molar ratio of W/C at the surface of the unwashed supported catalyst was found as 0.13, which is about five times larger than the value estimated from the composition of impregnation solution. This result indicated that most of the HPA was deposited near the pore mouths of the supported catalyst. The EDS result indicated that P/W molar ratio in the supported catalyst (0.080) was about the same as the corresponding value in the impregnation solution (0.083), as expected. A more important conclusion was related to the composition of the catalyst which was excessively washed by ethanol. Results showed that even after excessive washing of the catalyst with ethanol, significant amount of HPW remained on the pore surfaces of the supported catalyst. The W/C molar ratio corresponding to the surface composition of the washed catalyst was found as 0.026, which was about the same as the value estimated from the impregnation solution composition.

3.2. Catalytic reactions

Isoamylene used in our work contained 95% 2M2B, the remainder of which was primarily 2M1B. Etherification reactions of 2M2B and 2M1B with ethanol and the isomerization reaction between 2M2B and 2M1B were expected to proceed simultaneously in the reactor [1,11,15]. However, the mole fractions of 2M2B and 2M1B in the feed mixture were close to equilibrium and fast equilibration of the isomerization reaction was expected over acidic resin catalysts [6]. Although isoamylene could be represented by a mixture of 2M2B and 2M1B, in the present study these two isomers were lumped together as isoamylene (IA) and conversion values were reported as conversion of IA to TAEE. Similar analyses were also reported in the works of Aiouache and Goto [34], Boz and Doğu [6] and Linnekoski et al. [11].

Fractional conversion values of isoamylene mixture obtained in a tubular flow reactor at different temperatures are shown in Fig. 7. In these experiments 0.2 g of supported catalysts containing different amounts of HPW and again 0.2 g of pure HPW were used.

The equilibrium conversion values were also calculated using the thermodynamic data reported in the literature [35,36]. For bulk HPW, the fractional conversion increased from 13.5% to 17.8% when the temperature was raised from 353 to 358 K. When the temperature was further raised up to 370 K, the conversion showed a decreasing trend similar to the trend of equilibrium conversion (Fig. 7). These results showed that, above 358 K reverse reaction became significant and thermodynamics became the controlling factor rather than reaction rate. The activities of the supported catalysts HPW25@AC and HPW31@AC were quite similar in the same temperature range. Although the amount of HPW within these catalysts were 25% and 31% of bulk HPW catalyst, these supported catalysts showed about the same activity as the bulk HPW (0.2 g) at 353 K. However, in contrast to pure HPW, fractional conversion of isoamylene showed a decreasing trend with temperature with those supported catalysts (Fig. 7). Such a decrease of etherification conversion with temperature was also reported by Kitchaiya and Datta [36], which was explained by thermodynamic considerations. In our case, conversion values are quite away from equilibrium. Possible reasons of this behavior will be discussed later in this manuscript.

In order to test the reproducibility, reaction experiments were repeated with fresh catalysts and also successive experiments were carried out with the same catalyst in the same temperature range. All these experiments showed that reaction results were highly reproducible. Typical experimental results obtained

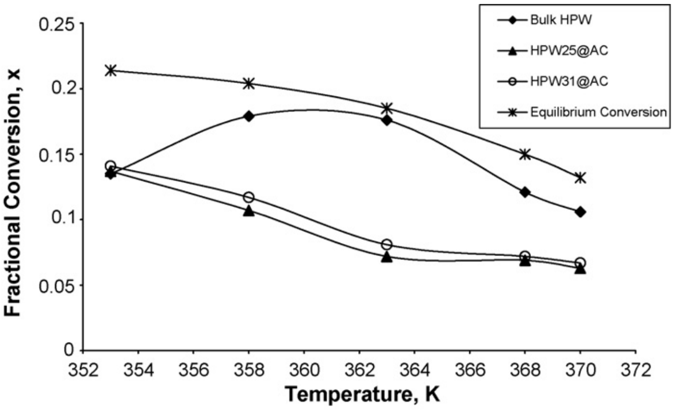

Fig. 7. Variation of fractional conversion of 2M2B with temperature in the presence bulk and supported HPW catalysts (0.2 g of catalyst packed into the reactor).

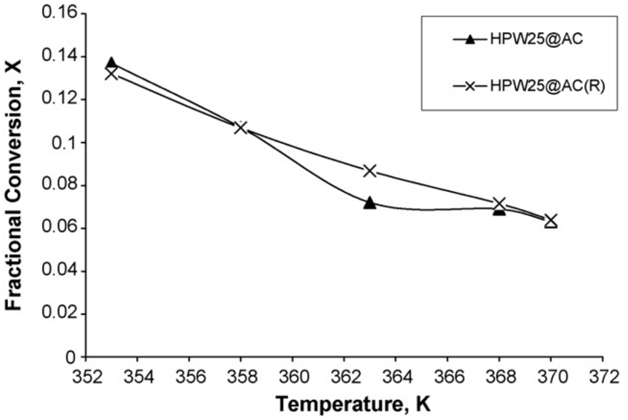

Fig. 8. Variation of conversion with temperature in the presence of HPW25@AC (reproducibility check).

with HPW25@AC in these reproducibility runs are shown in Fig. 8. All the data points reported in Figs. 7–9 correspond to the averages of at least five successive runs. A set of experiments carried out in the temperature range between 353 and 370 K were completed within about 12 h. To test the activity stability of the supported catalysts, some experiments were reported with the used catalyst in the same temperature range. Activity of the catalysts was quite reproducible in such repeated runs. Maximum decrease of isoamylene conversion values in the repeated runs (each taking place about 12 h) was less than 10%.

In the second set of experiments, catalytic etherification of isoamylene with ethanol was carried out with different amounts of supported catalysts (HPW25@AC and HPW31@AC) keeping the amount of HPW charged to the reactor as constant (0.2 g). For instance, 0.8 g of HPW25@AC contains 0.2 g of HPW. Similarly 0.64 g of HPW31@AC contains 0.2 g of HPW. Results of these experiments were compared with the results obtained with 0.2 g of pure HPW in Fig. 9. As shown in this figure, fractional conversion of isoamylene obtained with 0.8 g HPW25@AC and 0.64 g of HPW31@AC (both containing 0.2 g of HPW) were both much higher than the corresponding value obtained with 0.2 g of bulk HPW at 353 K. In fact, the conversion values approached to equilibrium conversion corresponding to this temperature. Activity comparison of HPW25@AC, HPW31@AC and bulk HPW obtained at 353 K was also illustrated in Fig. 10. These results indicated the higher utilization of active sites of HPW supported on a high surface area support, namely active carbon, than its bulk form. Ethanol and isoamylene are also expected to be adsorbed on the active carbon surface. In fact, the surface of active carbon may act as a reservoir for these reactants and the adsorbed reactant molecules may migrate on the surface to the active HPW sites. This may also explain the temperature dependence of fractional conversion observed with the supported catalysts. As shown in Figs. 7–9, with an increase in temperature, fractional conversion of isoamylene decreased in the experiments carried out with the supported catalysts. Decrease of adsorbed concentration of reactants on the active carbon surface (which act as a reservoir for the reactants) with an increase in temperature may explain the decrease in conversion with temperature. The conversion values obtained in these runs are away from the equilibrium conversions corresponding to the bulk fluid phase concentrations. However, in high surface area active carbon supported catalysts, significant pore diffusion resistances were expected in the micro- and mesopores of the catalyst and this would cause lower reactant concentrations within the pores. In such a case, local equilibration of the etherification reactions within the pores is also possible. This might also affect the temperature dependence behavior of conversion in the supported catalysts. These results indicated that the reaction mechanism and the rate determining process with the bulk and supported catalysts are not the same.

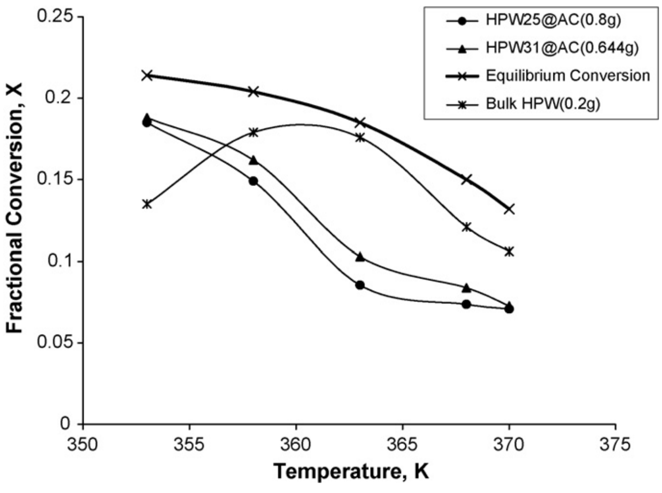

Fig. 9. Comparison of activities of catalysts for the same amount of HPW (0.2 g).

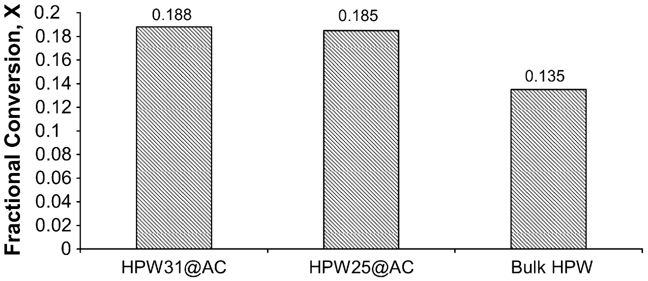

Fig. 10. Activity comparison of HPW25@AC, HPW31@AC and bulk HPW at 80 °C (0.2 g HPW).

In order to test the stability of the HPW on the supported catalyst, HPW31@AC was excessively washed in ethanol overnight. As discussed above, XPS analysis indicated partial washout of HPW from the supported catalyst after this washing process in ethanol. The activity of the washed catalyst was also experimentally measured in the vapor phase etherification reaction of isoamylene with ethanol. The isoamylene fractional conversion result obtained at 363 K with 0.64 g of washed HPW31@AC was 0.081, while the fractional conversion obtained with unwashed HPW31@AC was 0.103 at the same temperature. These results indicated that the activity loss of the supported catalyst after washing in ethanol was quite small. This is a significant result indicating the stability of the supported catalyst.

Finally, the catalytic activity of HPW was compared with the activities of different acidic catalysts, namely Amberlyst-15

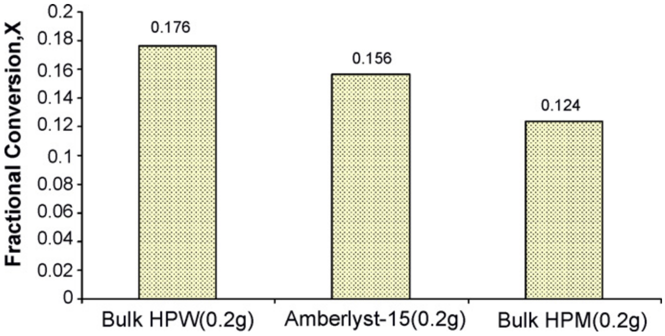

Fig. 11. Activity comparison of different catalysts at $T = 90\,^{\circ}\mathrm{C}$.

and HPMo, which is another heteropoly acid catalyst. Results obtained at 363 K in vapor phase etherification of isoamylene with ethanol are given in Fig. 11. HPW showed higher activity than Amberlyst-15 and also than HPMo. HPW was known to have very high acidity [22,37]. Its acidity is higher than HPMo and also higher than Amberlyst-15. Higher acidity of the catalyst surface is quite advantageous in such etherification reactions. These results showed that HPW is a very good candidate for gas-phase etherification reactions between *iso*-olefins and alcohols. In the case of liquid phase etherifications, supporting and stabilizing of HPW on a supporting material is needed.

4. Conclusions

Basing on the results obtained in this work it was concluded that active carbon supported tungstophosphoric acid catalysts showed very high activity in vapor phase etherification reaction of isoamylene, especially at low temperatures around 353 K. A W/C ratio of 0.026 obtained by XPS in the extensively washed catalyst with ethanol indicated immobilization of significant amount of HPW on the active carbon surface. TGA results also indicated an increase in decomposition temperature of supported HPW than bulk HPW. The catalytic activity of the washed catalyst was about 80% of the unwashed supported catalyst. Active carbon also plays a role as a reservoir for adsorbed reactants and decrease of adsorbed concentration of reactants with an increase in temperature resulted in a decrease of conversion of isoamylene to TAEE. Results of this work also showed that HPW showed higher activity than Amberlyst-15 and HPMo in etherification reaction of isoamylene with ethanol.

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