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## Heteropoly tungstate supported on tin oxide catalysts for liquid phase benzylation of anisole with benzyl alcohol

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#### ABSTRACT

A series of 12-tungstophosphoric acid supported on tin oxide catalysts were prepared and characterized by FT-Infra red, X-ray diffraction, Laser Raman spectroscopy and temperature programmed desorption of ammonia. The characterization results suggest the presence of Keggin ions and the generation of strong acidic sites on the support. The catalysts were evaluated for benzylation of anisole with benzyl alcohol as benzylating agent. The benzylation activity depends on the content of TPA on tin oxide; the catalyst with 15 wt% loading of tungstophosphoric acid showed highest activity. The structural and surface modifications and their influence on benzylation activities were studied by treating the catalysts at different calcination temperatures. The benzylation activity varied with the change in stability of the Keggin ion structure, which depended upon treatment conditions. The alcohol conversion and selectivity were also dependent on the anisole-to-benzyl alcohol ratio, reaction temperature, reaction time and catalyst weight.

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#### 1. Introduction

Usage of solid acid catalysts in organic synthesis has received a lot of interest as these catalysts offer high activity and reusability. Among the different available solid acid catalysts, heteropoly acids have attracted considerable attention in recent times [1,2]. Consequently, acid catalysis and catalytic oxidation are the two major areas of catalysis by HPAs [3,4]. HPAs have been proved to be one of the alternative to traditional acid catalysts due to their strong acidity, as they possess readily available protons in their Keggin structure.

The major disadvantages of HPA as catalyst lie in their low thermal stability and low surface area  $(1-10 \text{ m}^2/\text{g})$ . The acidity of the HPAs can be enhanced by exchanging their protons partially with metal ions such as Cs<sup>+</sup> [5] or by supporting them on acidic supports. Supporting the HPAs on acidic supports not only enhances the acidity but also the thermal stability. Moreover, the HPAs can be made insoluble by supporting on solid support. The support provides an opportunity for HPAs to be dispersed over a large surface area, which results in increased catalytic activity. Various supports like silica [6,7], titania [8,9], active carbon [10], niobia [11,12], zirconia [13,14], alumina [15], MCM-41 [16,17] and acidic ion exchange resins [18] have been used for supporting HPAs. Tin oxide is an important material for various technological applications such as gas sensors and conductive coatings but it has received little attention as a carrier for supported catalysts. In recent times it also received considerable interest in preparation of SnO<sub>2</sub> based solid acid catalysts [19].

The Friedel–Crafts reaction is widely used for the production of alkylated aromatic compounds. Alkylated anisole compounds are constituents of lubricants with improved properties, for example in thermal oxidation and hydrolytic stabilities [20]. In general, acid catalysts such as AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF or H<sub>3</sub>PO<sub>4</sub> have been used for Friedel–Crafts reactions, in spite of their low selectivity and high corrosiveness [21].

The universal tendency to decrease the pollutant effects of industrial processes has stimulated research on heterogeneous catalysis since they are easier to separate from the reaction medium and are more reusable and less corrosive than homogeneous catalysts.

Benzylation of anisole with benzyl chlorides produces HCl, an environmentally undesirable product. Use of benzyl alcohol instead of benzyl chloride is advantageous due to the formation of only water as side product.

Friedel–Crafts reaction using HPAs catalysts has been attracting considerable attention in recent years [22]. Shimizu et al. reported polyvalent-metal salts of heteropolyacids as catalysts for Friedel–Crafts alkylation of aromatics with alcohol [23]. Polymer supported 12-tungstophophoric acid catalysts were studied for benzylation of aromatics [24]. In most of these studies, the role of surface and structural characteristics of HPA are not studied in

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detail. The relations between activity and modification of surface and structural features of HPAs are important. The present study focused on the variation of activity with change in the surface and structural chemistry of supported heteropoly tungstates.

In this work, tin oxide supported heteropoly tungstate catalysts are prepared and evaluated for benzylation of anisole with benzyl alcohol. The prepared catalysts were characterized by different spectroscopy methods and the derived properties are correlated with the observed catalytic activity. The surface and structural features of the catalysts are studied by treating the samples at different temperatures. Reaction parameters such as temperature, molar ratio of the reactants, catalyst weight and effect of catalyst calcination temperature were also evaluated.

#### 2. Experimental

#### 2.1. Catalyst preparation

The chemicals 12-tungstophsphoric acid and tin oxide were obtained from Aldrich Chemicals. A series of catalysts with varying amounts of 12-tungstophsphoric acid supported on tin oxide were prepared by an impregnation method. In a typical procedure, a required amount of TPA was dissolved in water and this solution was added to tin oxide with continuous stirring. The resultant mixture was allowed to stand for 3 h and the excess water was evaporated on a water bath. The dried catalyst masses were kept overnight for further drying in an air oven at 120 °C and finally calcined at 300 °C for 2 h. The catalysts are denoted as x% TPA/SnO<sub>2</sub> where *x* indicates the content of TPA.

#### 2.2. Characterization of catalysts

X-ray powder diffraction patterns were recorded on a Rigaku Miniflex diffractometer using Cu K $\alpha$  radiation (1.5406 Å) at 40 kV and 30 mA and secondary graphite monochromatic. The measurements were obtained in steps of 0.045° with count times of 0.5 s, in the 2 $\theta$  range of 10–80°.

The FT-IR spectra were recorded on a Bio-Rad Excalibur series spectrometer using the KBr disc method.

Temperature programmed desorption of ammonia (TPD) was carried out on a laboratory-built apparatus equipped with a gas chromatograph using a thermal conductivity detector. In a typical experiment, about 0.1 g of the oven dried sample was taken in a quartz tube and treated at 300 °C for 1 h by passing pure helium (99.9%, 50 ml/min). After pretreatment, the sample was saturated with anhydrous ammonia (10% NH<sub>3</sub>–90% He mixture gas) with a flow of 50 ml/min at 100 °C for 1 h and was subsequently flushed with He at the same temperature to remove physisorbed ammonia. The process was continued until a stabilized base line was obtained in the gas chromatograph. Then the TPD analysis was carried out by programming the temperature from 100 to 800 °C at a heating rate of 10 °C/min.

#### 2.3. General alkylation procedure

The alkylation reaction was carried out in a 50 ml three necked round bottom (RB) flask provided with a reflux condenser, a nitrogen gas inlet and a septum for sample removal. In a typical run, 10g of anisole and 3.376g of benzyl alcohol (15:5 molar ratio) were taken in a RB flask and 0.1g catalyst was added. The reaction was carried out at a reaction temperature of 120 °C. The reaction mixture was withdrawn at different intervals and analyzed using a gas chromatograph (VARIAN GC-3800) equipped with a SE-30 column and flame ionization detector. The oven temperature was programmed from 100 to 250 °C at 20 °C/min with N<sub>2</sub> as carrier gas to separate the products.



**Fig. 1.** FT-IR spectra of heteropoly tungstate supported on tin oxide catalysts. (a) SnO<sub>2</sub>, (b) 5% TPA/SnO<sub>2</sub>, (c) 10% TPA/SnO<sub>2</sub>, (d) 15% TPA/SnO<sub>2</sub>, (e) 20% TPA/SnO<sub>2</sub> and (f) 25% TPA/SnO<sub>2</sub>.

The products were identified by GC–MS (SHIMADZU-2010) analysis after the separation of products on a DB-5 column with He as carrier gas.

#### 3. Results and discussion

#### 3.1. Characterization of catalysts

FT-IR patterns of SnO<sub>2</sub>-supported TPA catalysts are shown in Fig. 1. The catalysts showed four bands in the region of 1100–500 cm<sup>-1</sup>; the main bands at 1081, 986, 890, and 800 cm<sup>-1</sup> can be assigned to the stretching vibrations of P–O,  $W=O_t$ ,  $W-O_c-W$ ,  $W-O_e-W$ , respectively, related to Keggin ion [12]. The FT-IR results indicate that the Keggin structure of heteropoly tungstate remained unaltered when supported on SnO<sub>2</sub>.

X-ray diffractograms of the catalysts are shown in Fig. 2. The  $SnO_2$  patterns are predominant in all the catalysts. The diffraction lines suggest the presence of tetragonal cassiterite structure of



**Fig. 2.** XRD patterns of heteropoly tungstate supported on tin oxide catalysts. (a)  $SnO_2$ , (b) 5% TPA/SnO<sub>2</sub>, (c) 10% TPA/SnO<sub>2</sub>, (d) 15% TPA/SnO<sub>2</sub>, (e) 20% TPA/SnO<sub>2</sub> and (f) 25% TPA/SnO<sub>2</sub>.



Fig. 3. Temperature programmed patterns of the catalysts. (a) 5% TPA/SnO<sub>2</sub>, (b) 10% TPA/SnO<sub>2</sub>, (c) 15% TPA/SnO<sub>2</sub>, (d) 20% TPA/SnO<sub>2</sub> and (e) 25% TPA/SnO<sub>2</sub> catalysts.

 $SnO_2$  [25]. The weak peaks related to Keggin ion are visible for the catalysts with TPA content above 15 wt%. The XRD results suggest that TPA is highly dispersed on  $SnO_2$  at low content of TPA.

Ammonia adsorption–desorption technique usually enables one to determine the strength of acid sites present on the catalyst surface together with the total acidity. The TPD of NH<sub>3</sub> profiles of the catalysts are shown in Fig. 3. The distribution of acidity was calculated based on their strengths from TPD profiles and values are shown in Table 1. Three types of desorption peaks in the range of 300–650 °C are present for these catalysts. The peaks observed at low temperature are related to weak acidic sites on the support. The moderate to strong acidic sites in the range 400–500 °C correspond to moderate to strong acidic sites. The peak at 300 °C was predominant in the catalysts with low TPA content. This desorption peak corresponds to the weak acidic sites related to SnO<sub>2</sub>. A desorption peak centered at around 500 °C observed for all the catalysts and its intensity increased with increase in TPA content on SnO<sub>2</sub>. This peak is related to strong acidic sites generated due to the presence

## Table 1 Acid strength distribution of TPA/SpO<sub>2</sub> catalysts

Acid strength distribution of	$IPA/SIIO_2$	catalysts.

Catalyst	Acidity (mmol/g)				
	Weak	Moderate	Strong	Total	
5% TPA/SnO <sub>2</sub> 10% TPA/SnO <sub>2</sub> 15% TPA/SnO <sub>2</sub> 20% TPA/SnO <sub>2</sub> 25% TPA/SnO <sub>2</sub>	0.058 0.009 - -	- 0.048 0.075 0.096 0.089	0.049 0.030 0.056 0.037 0.031	0.107 0.087 0.131 0.133 0.120	

of TPA. Further strong acid sites are observed at 650 °C, which might be related to  $SnO_2$  support. The intensity of these sites decreased with increase in TPA content as seen in the decrease in the amount of strong acidity related to support. The increase in acidity with TPA content related not only to the increase in amount of TPA but also to the high dispersion of TPA on support. The absence of XRD patterns related to Keggin ions for the catalysts with low TPA content suggest the high dispersion of TPA on  $SnO_2$ . The decrease in the intensity of weak and strong acidic sites (peak at 300 and 650 °C) with increase in TPA loading further suggests that these sites are related to  $SnO_2$ .

The catalysts with 15 wt% TPA/SnO<sub>2</sub> showed the presence of moderate and strong acidic sites generated by interaction of TPA with support.

#### 3.2. Catalytic activity

#### 3.2.1. Effect of TPA content

The catalytic activities of TPA/SnO<sub>2</sub> catalysts are presented in Table 2. The support SnO<sub>2</sub> showed very low activity for the benzylation of anisole. The impregnation of TPA on SnO<sub>2</sub> results in the increase of catalytic activity. The alkylation activity increased as a function of active component loading, reached to a maximum for the catalyst with 15 wt% TPA, and remained almost constant with further increase.

The characterization results well support the observed catalytic activity. The catalyst with 15% TPA/SnO<sub>2</sub> showed highly dispersed TPA on SnO<sub>2</sub> as it does not show any diffraction peaks related to TPA. The XRD patterns of TPA that are seen beyond 15 wt% suggest the monolayer coverage of TPA on SnO<sub>2</sub> at this loading. The alkylation activity results can be correlated with the observed acidity of the catalyst. The catalysts, which showed the presence of moderate to strong acidic sites, associated with TPA, exhibited high activity. The 15% TPA/SnO<sub>2</sub> catalyst showed strong acidic sites with high amount of total acidity, as shown in Table 1. The constant activity at high TPA content might be related to the presence of the same amount of total acidity. The results suggest that moderate to strong acidic sites are responsible for benzylation activity.

#### 3.2.2. Effect of catalyst calcination temperature

In order to understand the surface and structural characteristics and their influence on benzylation activity, we subjected the most active 15% TPA/SnO<sub>2</sub> catalyst to calcination at different tempera-

#### Table 2

Effect of TPA loading on tin oxide on the benzylation of anisole.

Catalyst	Conversion of benzyl alcohol (%)	Yield (%)			Selectivity (	Selectivity (%)		
		0-	p-	Ether	0-	p-	Ether	
SnO <sub>2</sub>	1.63	0.53	0.58	0.52	32.59	35.52	31.71	
5%TPA/SnO <sub>2</sub>	14.1	3.78	4.61	5.71	26.83	32.71	40.48	
10% TPA/SnO <sub>2</sub>	85.17	27.56	34.01	23.61	32.36	39.93	27.72	
15% TPA/SnO <sub>2</sub>	95.13	33.98	39.69	21.46	35.72	41.72	22.56	
20% TPA/SnO <sub>2</sub>	89.21	22.92	36.66	22.63	33.53	41.09	25.36	
25% TPA/SnO <sub>2</sub>	95.12	31.93	40.19	22.99	33.56	42.26	24.17	

Reaction conditions: anisole (10g), benzyl alcohol (3.376g), catalyst weight (0.1g), reaction temperature (120°C) and reaction time (1.5h).

o-P-Eth

100

80

60

20

0

800

700

Conversion (%

Fig. 4. Effect of calcination temperature of 15% TPA/SnO<sub>2</sub> catalyst on benzylation activity.

Catalyst calcination temperature (°C)

600

500

tures. The effect of catalyst calcination temperature on benzylation of anisole was studied and the results are shown in Fig. 4. The results suggest that the benzylation activity depends on the calcination temperature of the catalyst. The conversion of benzyl alcohol increased with calcination temperature up to 400 °C and decreased drastically thereafter. The catalyst calcined at 400 °C showed maximum conversion with high selectivity. In order to determine the reasons for variation in activity with catalyst calcination temperature, we rather characterize the catalysts.

# 3.3. Characterization of 15% TPA/SnO<sub>2</sub> catalyst calcined at different temperatures

FT-IR patterns of 15% TPA/SnO<sub>2</sub> catalyst calcined at different temperatures are shown in Fig. 5. The catalysts calcined at 300 and 400 °C showed the bands related to Keggin ions [12]. The characteristic peaks of Keggin ions were absent for the catalyst calcined at higher temperatures. This indicates that the decomposition of TPA into its constituent metal oxides occurred when calcined above 400 °C.



Fig. 5. FT-IR spectra of 15% TPA/SnO<sub>2</sub> catalyst calcined at different temperatures. (a) 300  $^{\circ}$ C, (b) 400  $^{\circ}$ C, (c) 500  $^{\circ}$ C, (d) 600  $^{\circ}$ C and (e) 750  $^{\circ}$ C.



**Fig. 6.** X-ray diffraction patterns of 15% TPA/SnO<sub>2</sub> catalyst calcined at different temperatures. (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C and (e) 750 °C.

X-ray diffractograms of the catalysts obtained at different calcination temperatures are shown in Fig. 6. The samples exhibited the main patterns related to support SnO<sub>2</sub>. However, small patterns corresponding to Keggin ions are clearly seen for the catalyst calcined up to 400 °C. The catalyst calcined beyond 400 °C showed peaks at  $2\theta$  of 23.12, 23.60, 24.38°, which are related to WO<sub>3</sub> phase [26]. The formation of WO<sub>3</sub> is expected as heteropoly tungstate decomposes at high temperature.

Fig. 7 shows the Raman spectra of 15% TPA/SnO<sub>2</sub> catalyst calcined at different temperatures. Raman analysis helps to identify clearly the presence of metal oxide phases when heteropoly Keggin ions are decomposed. The catalysts calcined at 300 and 400 °C showed the peak at 1006 cm<sup>-1</sup> related to asymmetric W = O<sub>t</sub> vibration of Keggin ions. The catalysts calcined at 500–750 °C clearly showed intense peaks at 805, 706 and 273 cm<sup>-1</sup>. The 805 and 706 cm<sup>-1</sup> bands are related to stretching vibrations of W–O–W and the 273 cm<sup>-1</sup> band (not shown) was the characteristic bending mode of WO<sub>3</sub> [27–29]. The Raman spectra clearly suggest the formation of WO<sub>3</sub> due to the decomposition of TPA.



**Fig. 7.** Raman spectra of 15% TPA/SnO<sub>2</sub> catalyst calcined at different temperatures. (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C and (e) 750 °C.

100

80

60

40

20

0

300

400

Selectivity (%)



**Fig. 8.** TPD patterns of 15% TPA/SnO<sub>2</sub> calcined at different temperatures. (a)  $300 \degree C$ , (b)  $400 \degree C$ , (c)  $500 \degree C$ , (d)  $600 \degree C$  and (e)  $750 \degree C$ .

The TPD of NH<sub>3</sub> profiles of 15% TPA/SnO<sub>2</sub> catalyst calcined at 300–750 °C are shown in Fig. 8. The catalyst calcined at low temperatures (300 and 400 °C) showed ammonia desorption peaks related to strong acidic sites of the catalysts. The catalysts calcined at high temperature did not show the presence of so much acidity compared to the low temperature calcined catalysts. The catalysts that contain intact Keggin structure exhibited strong acidity. When the samples were calcined at high temperature the Keggin structure decomposed into its constituents such as WO<sub>3</sub> and the samples did not show high acidity. The characterization studies reveals that the degradation of Keggin ion of heteropoly tungstate occurs when the materials are subjected to high temperature treatment.

The benzylation activity of the catalysts calcined at different temperatures can be directly correlated to the physico-chemical properties of these samples derived from XRD, FT-IR, Laser Raman and TPD measurements of NH<sub>3</sub>. The catalytic activity is related to the presence of acidity, which in turn is related to the existence of intact Keggin ions of heteropoly tungstate on tin oxide.

#### 3.4. Effect of reaction temperature

The reaction parameters are studied to optimize the benzylation activity. The benzylation of anisole was carried out at different temperatures ranging from 80 to 140 °C and the results are presented in Fig. 9. It is observed from the figure that the percentage



Fig. 9. Influence of reaction temperature on the conversion of benzyl alcohol.

yield of benzylated products increased with increase in reaction temperature. The formation of benzylated product increased with temperature and reached a maximum at high temperature. The selectivity towards ether is observed when the reaction is carried out at low temperature.

#### 3.5. Effect of catalyst weight

The effect of catalyst weight on the benzylation reaction was studied and the results are presented in Fig. 10. From the figure one can observe that the yield of benzylated product increased with increase catalyst weight up to 0.1 g and that there is little



Fig. 10. Effect of catalyst weight on the benzylation of anisole.

#### Table 3

Effect of anisole-to-benzyl alcohol molar ratio on benzylation of anisole.

Anisole to benzyl alcohol ratio	Conversion of benzyl alcohol (%)	Selectivity (%)		
		0-	p-	Ether
1.5	21.24	20.96	29.58	49.44
3	72.55	31.19	38.17	30.65
15	99.88	56.86	43.14	-

Reaction conditions: catalyst weight (0.1 g), reaction temperature (120 °C) and reaction time (1 h).

improvement with further increase in catalyst weight. The maximum conversion is reached even with low catalyst amount. The selectivity remained almost identical with variations in catalyst amount.

#### 3.6. Effect of molar ratio of anisole to benzyl alcohol

The effect of the molar ratio of anisole to benzyl alcohol was studied and the results are presented in Table 3. The percentage of dibenzyl ether formation increased with increase in molar ratio of anisole to benzyl alcohol. The increase of ether formation is expected, as the availability of benzyl alcohol is greater. Benzyl alcohol easily undergoes dehydration over acidic sites of the catalyst. It is known that during benzylation, etherification is faster than the alkylation reaction [30]. The formation of dibenzyl ether is expected with high benzyl alcohol concentration due to relatively low rates of benzylation compared to that of dehydration.

#### 4. Conclusions

Tungstophosphoric acid supported on tin oxide catalysts were prepared with retention of Keggin ion structure. Benzylation of anisole with benzyl alcohol activity depends on the content of TPA on tin oxide and also on the calcination temperature of the catalyst. The optimum loading of TPA was 15 wt% and calcination of catalyst up to 400 °C was optimum to obtain high benzylation activity. Benzylation of anisole activity is dependent on the acidity of the catalyst, which depends on the dispersion and retention of Keggin ions of TPA on support. The benzylation activity and selectivity towards benzylated product depend on the reaction temperature and on the anisole-to-benzyl alcohol ratio.

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