



Tin exchanged heteropoly tungstate: An efficient catalyst for benzylation of arenes with benzyl alcohol

Ch. Ramesh Kumar, K.T. Venkateswara Rao, P.S. Sai Prasad, N. Lingaiah*

Catalysis Laboratory, Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad, AP 500 607, India

ARTICLE INFO

Article history:

Received 22 November 2010
Received in revised form 4 January 2011
Accepted 6 January 2011
Available online 16 January 2011

Keywords:

Arene
Benzyl alcohol
Benzylation
Tungstophosphoric acid
Tin

ABSTRACT

The partial exchange of tin with the protons of 12-tungstophosphoric acid (TPA) results in a highly active heterogeneous catalyst for benzylation of arenes with benzyl alcohol as benzylating agent. The catalysts were characterized by X-ray diffraction, Laser-Raman and FT-IR of pyridine adsorption. The catalytic activity depends significantly on the extent of tin exchanged with the protons of heteropoly tungstate. The characterization results suggest the presence of Lewis acidic sites by the exchange of tin. The catalyst with partial exchange of Sn showed high benzylation activity, which in turn related to variation in acidity of the catalysts. The catalyst is highly active for benzylation reaction irrespective of the nature of substituted arenes and benzyl alcohols. These catalysts are highly active compared to other acid catalysts used for benzylation of different arenes. The catalyst is easy to separate from reaction mixture and exhibit consistent activity upon reuse. The plausible reaction mechanism based on the role of both Lewis and Bronsted acid sites of the catalyst was discussed.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Benzylation of arenes is an important reaction in the synthesis of diarylmethane derivatives, which are useful intermediates in organic and polymer synthesis [1]. Diphenylmethane and substituted diphenylmethanes are industrially important compounds used as pharmaceutical intermediates and fine chemicals [2]. These diarylmethane derivatives have interesting biological and physiological properties. Benzylnaphthalenes are useful as intermediates for organic synthesis in the field of additives for lubricants, dyes and anti oxidants [3]. The common synthetic method for diarylmethane derivatives has been the Friedel–Crafts type alkylation of arenes with benzyl halides using Lewis acid or Bronsted acids as catalysts.

In recent times, a switch from alkyl halide to alcohol, ester or olefins as alkylating agent using late d-block and f-block metal catalysts have been reported [4]. Rare earth metal triflates, Ir/Sn bimetallic complexes [4], are reported for the Friedel–Crafts alkylation. These homogeneous catalysts are not desirable as they are required in stoichiometric quantities, generate waste and involve multi step procedure for their preparation.

There exist few studies where heterogeneous catalysts are used for Friedel–Crafts alkylation [5–10]. However, in most of the cases the benzylating agents are benzyl chlorides. Heterogeneous cat-

alysts such as supported metal triflates [5,6], zeolites [7,8], clay materials [9,10] and mesoporous solid acid catalysts [3,11] are reported. Many of these catalysts are not selective and require longer reaction times to obtain reasonable yields.

Heteropoly acids (HPAs) are promising catalysts with strong acidity used as catalysts for various types of reactions, particularly in selective oxidation and acid-catalyzed reactions [12–14]. The major disadvantage of HPAs as catalysts lies in their low thermal stability, low surface area (1–10 m²/g) and solubility in polar media. The advantage of HPAs is that they can be made as heterogeneous acid catalysts with high thermal stability by supporting them on suitable supports and/or by exchanging the protons present in HPAs with metal ions [15].

In this paper, tin exchanged 12-tungstophosphoric acid (Sn_xTPA) catalysts with varying Sn content were prepared and evaluated for benzylation of arenes with benzyl alcohols. The catalyst activities were correlated to the extent of Sn exchanged, which results in the variation of Lewis and Bronsted acidity. Benzylation of different arenes with benzyl alcohol, substituted benzyl alcohols and secondary benzyl alcohols were carried to reiterate the scope of the catalysts.

2. Experimental

2.1. Catalyst preparation

A series of tin-exchanged 12-tungstophosphoric acid (Sn_xTPA) catalysts were prepared with varying tin content. In a typical

* Corresponding author. Tel.: +91 40 27193163; fax: +91 40 27160921.
E-mail address: nakkalingaiah@iict.res.in (N. Lingaiah).

method required amount of TPA was dissolved in distilled water and to this solution calculated amount of SnCl_2 was added with continuous stirring. The resultant mixture was stirred for 3 h and the excess water was evaporated on a water bath at 100°C . The dried catalyst masses were kept for further drying in an air oven and finally calcined at 300°C for 2 h. The catalysts are denoted as Sn_xTPA , where x indicates number of Sn atoms in $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns of the catalysts were recorded on Rigaku Miniflex diffractometer using $\text{Cu K}\alpha$ radiation (1.5406 \AA) at 40 kV and 30 mA. The measurements were obtained in steps of 0.045° with account time of 0.5 s and in the 2θ range of $10\text{--}80^\circ$.

The Fourier Transform Infrared (FT-IR) spectra were recorded on a Bio-rad Excalibur series spectrometer using KBr disc method. The nature of the acid sites (Bronsted and Lewis) of the catalyst samples was determined by FT-IR spectroscopy with chemisorbed pyridine. The pyridine adsorption studies were carried out in the diffuse reflectance infrared Fourier transform (DRIFT) mode. The ratio of Bronsted and Lewis acidities was estimated from the IR peak intensity corresponding to these acid sites.

The total acidity of the catalysts was measured by temperature programmed desorption of ammonia (TPD- NH_3). In a typical experiment, 0.1 g of catalyst was loaded and pretreated in He gas at 300°C for 2 h and cooled to room temperature. The adsorption of NH_3 is carried out by passing a mixture of 5% NH_3 balanced He gas over the catalyst for 1 h at 100°C . The catalyst surface was flushed in He gas at 100°C for 2 h to flush off the physisorbed NH_3 . The TPD of the catalysts was carried in a He gas flow at a flow rate of 30 ml/min with a temperature ramp of $10^\circ\text{C}/\text{min}$. The NH_3 desorption was monitored using thermal conductivity detector (TCD) of a gas chromatograph.

Confocal Micro-Raman spectra have been recorded at room temperature in the range of $100\text{--}4000\text{ cm}^{-1}$ using a Horiba Jobin-Yvon LabRam HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source of excitation wavelength 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were usually loosely spread onto a glass slide below the confocal microscope for Raman measurements.

2.3. General alkylation reaction procedure

The alkylation reaction was carried-out in a 50 ml two-necked round bottom flask provided with a reflux condenser. In a typical run, 10 g of anisole and 3.37 g of benzyl alcohol (15:5 molar ratios) along with 0.1 g catalyst were taken in flask. The reaction was carried out at a reaction temperature of 120°C . The reaction mixture was withdrawn at different intervals and analyzed by a gas chromatography (VARIAN GC-3800) equipped with a SE-30 column and flame ionization detector. The identification of products was made from GC-MS (SHIMADZU-2010) analysis.

3. Results and discussion

3.1. Characterization

FT-IR patterns of Sn_xTPA are shown in Fig. 1. The catalysts showed four characteristic bands in the region of $1100\text{--}500\text{ cm}^{-1}$. The main peaks observed at 1081, 981, 888, and 800 cm^{-1} , were related to the asymmetric stretching vibrations of P-O , W=O_t , $\text{W-O}_c\text{-W}$, and $\text{W-O}_e\text{-W}$ respectively of characteristic Keggin ion [16]. This indicates that the Keggin structure remained unaltered during the exchange of TPA protons with tin.

Fig. 2 shows the X-ray diffractograms of the catalysts. The XRD pattern suggests the presence cubic structure of highly crystalline

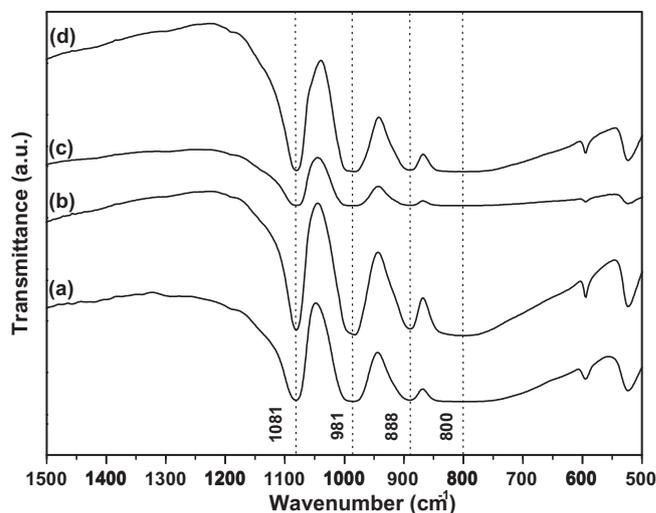


Fig. 1. FT-IR spectra of (a) TPA, (b) $\text{Sn}_{0.5}\text{TPA}$, (c) Sn_1TPA , and (d) $\text{Sn}_{1.5}\text{TPA}$ catalysts.

heteropoly tungstate. There was no change in the patterns with variation in tin content suggests the existing of Keggin ion structure of tin containing heteropoly tungstate. The XRD results are in support of the observations made from FT-IR.

Raman spectra of Sn_xTPA catalysts are presented in Fig. 3. Heteropoly tungstate shows characteristic Raman bands at 1006 , 992 and 905 cm^{-1} related to Keggin ion of TPA [17,18]. The present catalyst showed the symmetric vibration of W=O_t band at 1006 cm^{-1} with a shoulder at 992 cm^{-1} [19]. The Raman results endorse the XRD and FT-IR results, which suggest the presence of intact heteropoly tungstate Keggin ion structure even after exchange of tin.

Pyridine adsorption on the surface of solid acid allows one to distinguish different acid sites. FT-IR pyridine adsorption spectra of Sn_xTPA catalysts are shown in Fig. 4. The spectra showed pyridine adsorption bands at 1635 , 1607 , 1536 , 1442 , and 1421 cm^{-1} . The band at 1635 , and 1536 cm^{-1} were related to Bronsted acid sites [20–22]. Pyridine molecules bonded to Lewis acid sites showed the vibrations at 1607 , 1442 , and 1421 cm^{-1} [20,21]. The band at 1486 cm^{-1} is a combined band originating from pyridine bonded to both Bronsted and Lewis acid sites [20]. The pyridine adsorption FT-IR spectra suggest the presence of both Lewis and Bronsted acidity.

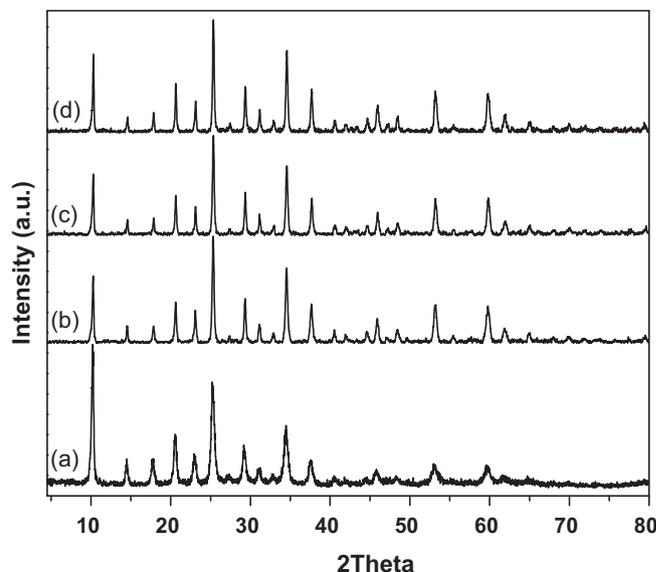


Fig. 2. XRD pattern of (a) TPA, (b) $\text{Sn}_{0.5}\text{TPA}$, (c) Sn_1TPA , and (d) $\text{Sn}_{1.5}\text{TPA}$ catalysts.

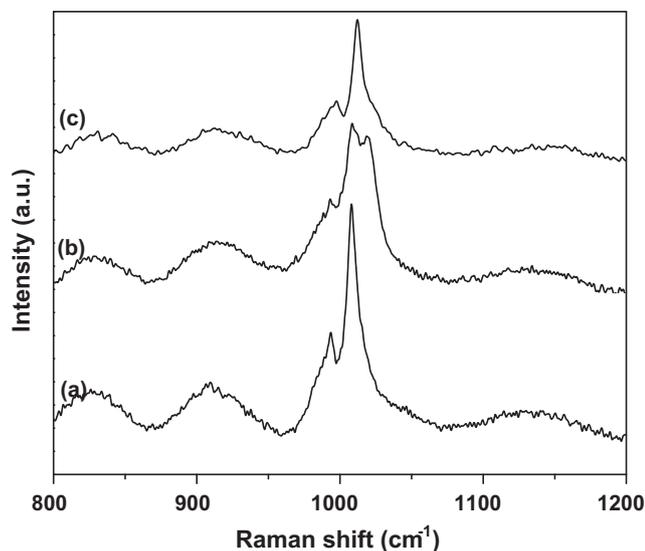


Fig. 3. Raman spectra of (a) $\text{Sn}_{0.5}\text{TPA}$, (b) Sn_1TPA , and (c) $\text{Sn}_{1.5}\text{TPA}$ catalysts.

The ratio of Bronsted and Lewis acid sites was calculated from the intensities of absorbance at 1536 and 1442 cm^{-1} and presented in Table 1. Bronsted acidity is well known for heteropoly acids due to the presence of protons. The Lewis acidity arises with the exchange of TPA protons by tin. Lewis acidity is associated to the coordinately unsaturated Sn^{+2} species in the catalyst. The B/L acidity ratio varied with the content of Sn exchanged. Partially exchanged catalysts showed high Bronsted acidity compared to fully exchanged catalyst. The mobility of residual protons for the partially substituted HPAs is high and results in increased Bronsted acidity along with Lewis acidity [23].

The ammonia TPD results are shown in Fig. 5. The patterns showed a strong desorption peak around $550\text{--}600^\circ\text{C}$ and a small hump in between 200 and 250°C . The high temperature desorption

Table 1
Variation in Bronsted to Lewis acidity of Sn_xTPA catalysts.

S.no.	Catalyst	B/L ratio (I_{1536}/I_{1442})
1.	$\text{Sn}_{0.5}\text{TPA}$	1.10
2.	Sn_1TPA	1.27
3.	$\text{Sn}_{1.5}\text{TPA}$	1.10

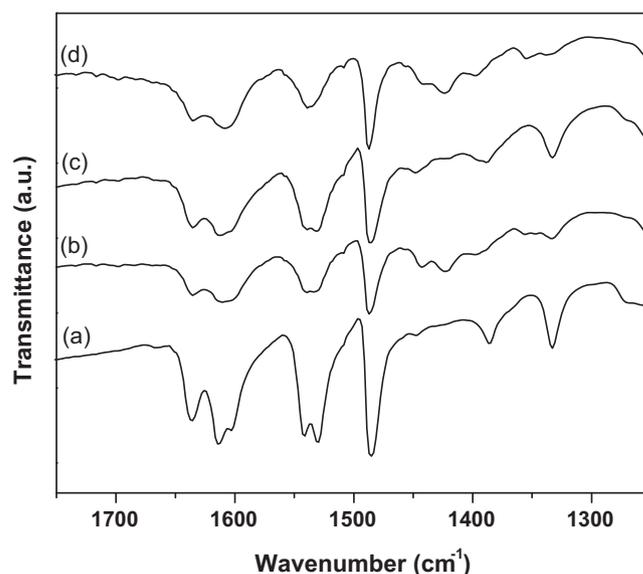


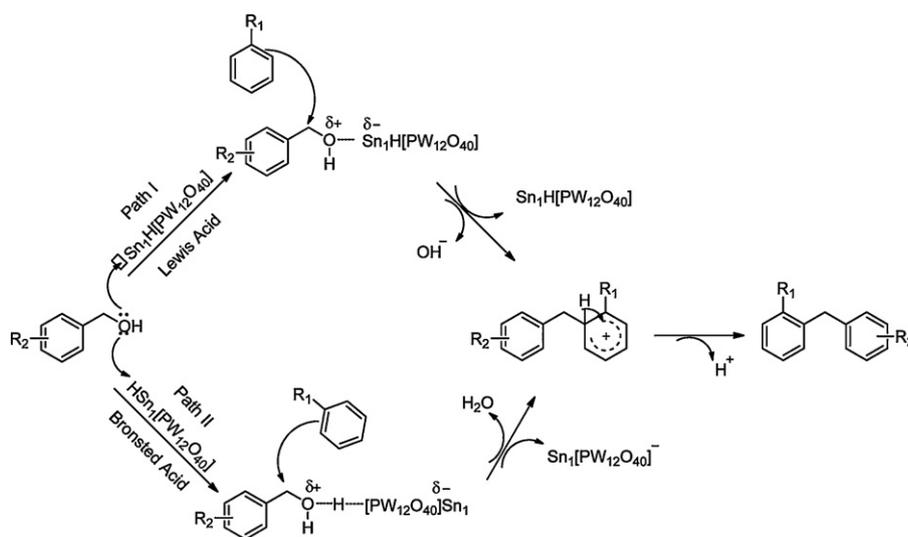
Fig. 4. FT-IR spectra of pyridine adsorbed on (a) TPA, (b) $\text{Sn}_{0.5}\text{TPA}$, (c) Sn_1TPA , and (d) $\text{Sn}_{1.5}\text{TPA}$ catalysts.

peak related to the strong acidic sites of the catalysts. The amount of strong acid sites is relatively more for $\text{Sn}_1\text{HPW}_{12}\text{O}_{40}$ (Sn_1TPA) catalyst. The high temperature desorption peak is shifted towards lower temperature with increase in the exchangeable Sn. The fully exchanged catalyst $\text{Sn}_{1.5}\text{PW}_{12}\text{O}_{40}$ ($\text{Sn}_{1.5}\text{TPA}$) showed desorption peak which is shifted marginally to lower temperature with less intensity due to absence of residual protons. The heteropoly acids exchanged partially with metal ions generally exhibit more acidity due to the mobility of residual protons [21].

3.2. Catalytic activity for benzylation

Initially, Sn_xTPA catalysts were tested for their activity for the benzylation of anisole with benzyl alcohol and the results are shown in Table 2. This model reaction carried to optimize the reaction conditions, catalyst loading and reaction temperature.

The activity results suggest that Sn_1TPA catalyst showed near complete conversion of benzyl alcohol with high selectivity to alkylated products. The high activity resulted with the exchange of Sn



Scheme 1. Plausible reaction mechanism for benzylation of arene with benzyl alcohol over Sn_1HTPA catalyst.

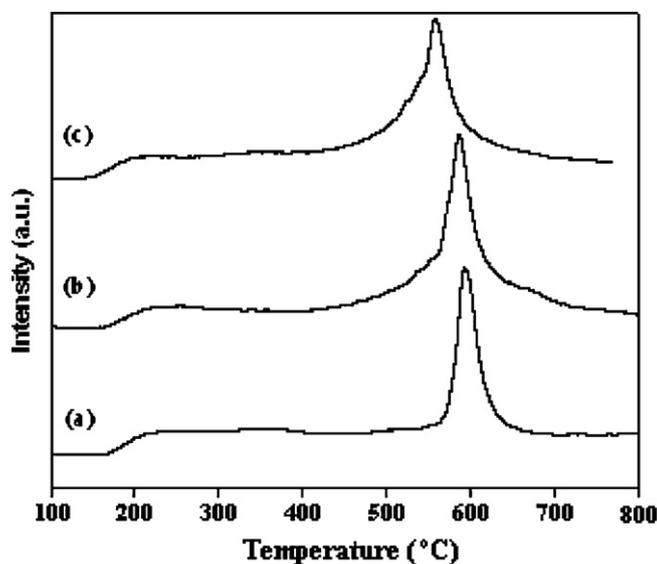


Fig. 5. Ammonia TPD profiles of (a) $\text{Sn}_{0.5}\text{TPA}$, (b) Sn_1TPA , and (c) $\text{Sn}_{1.5}\text{TPA}$ catalysts.

with the protons of TPA. The catalytic activities of the Sn_xTPA catalysts are related to their physico-chemical properties. Among all the catalysts Sn_1TPA showed highest activity. This catalyst exhibited higher acidity with more B/L ratio. The partial exchange of Sn

Table 2
Benzylation of anisole with benzyl alcohol over Sn_xTPA catalysts.

S.no.	Catalyst	Reaction time (min)	Conversion ^a (%)	Yield (%)		
				o-	p-	Ether
1.	TPA	45	93	36.61	42.43	14.12
2.	$\text{Sn}_{0.5}\text{TPA}$	30	94	34.46	40.09	19.28
3.	Sn_1TPA	30	100	45.05	54.08	–
4.	$\text{Sn}_{1.5}\text{TPA}$	30	89	32.59	35.46	21.11

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

^a Conversion with respect to benzyl alcohol.

results in high mobility of residual protons, leading to increased Bronsted acidity. The intact Keggin structure even after exchange of protons with tin allows in generating Lewis acid sites along with their Bronsted acidic sites. The presence of both Bronsted and Lewis acidity might be responsible for high catalytic activity even at short reaction times. The FT-IR, XRD, Raman and acidity measurements support the reasons mentioned for the high benzylation activity of the catalysts.

The plausible reaction mechanism is presented in Scheme 1. The participation of both Lewis and Bronsted acid sites of the catalysts was elucidated for the benzylation of arenes with benzyl alcohol. The plausible mechanism and the catalyst characteristics supports the high activity of the catalysts due to the generation of new Lewis acidic sites with the presence of tin and Bronsted acidity because of the mobile nature of residual protons of heteropoly tungstate.

The scope of the present catalyst system was evaluated for the benzylation of different arene with variety of benzyl alcohols and the results are presented in Table 3. Benzylation of electron rich arenes such as anisole, toluene, xylenes, cresols and mesitylene with benzyl alcohol are presented. In all the cases benzyl alcohol conversion is near 100% with quantitative yield to the corresponding benzyl arene within short reaction times. The di-substituted arenes underwent benzylation relatively at longer reaction times. The alkylation products are predominantly ortho/para substituted ones. The para selectivity is relatively more in most of the cases.

In Table 4, benzylation of variety anisoles with benzyl alcohol and substituted benzyl alcohols are presented. Both electron-rich (4-methyl benzyl alcohol and 4-methoxy benzyl alcohol) and electron-poor benzyl alcohol could react with anisole and gave corresponding diarylmethanes in high yields. When benzyl alcohol reacted with substituted anisoles such as 4-methyl anisole, 4-fluoro anisole, and 4-bromo anisole the product is ortho benzylation one, with complete conversion of benzyl alcohol. The reaction of substituted benzyl alcohols such as 4-methyl benzyl alcohol, 4-methoxy benzyl alcohol and 2-bromo benzyl alcohol with anisole forms corresponding benzylation products with para isomer as major product in an hour.

The reaction of substituted anisoles (4-methyl anisole and 4-bromo anisole) with substituted benzyl alcohols (4-methyl

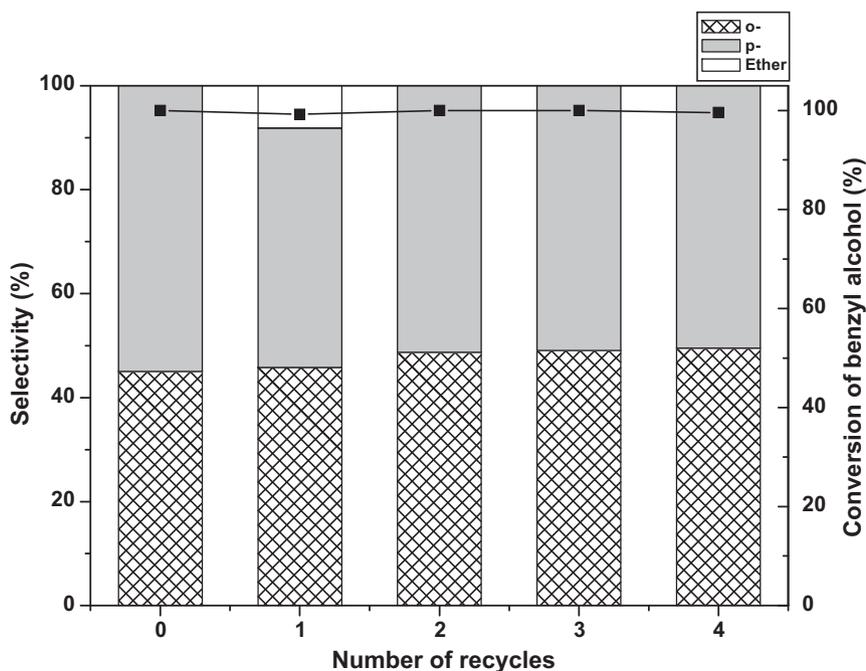
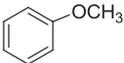
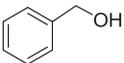
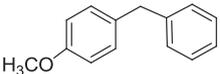
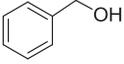
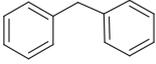
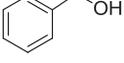
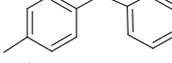
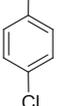
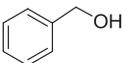
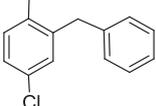
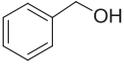
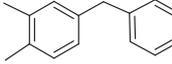
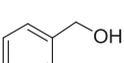
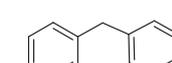
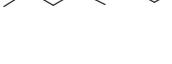
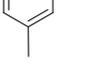
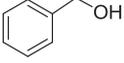
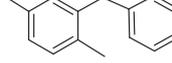
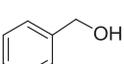
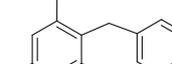
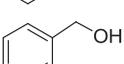
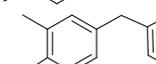
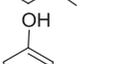
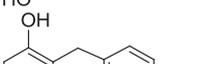


Fig. 6. Reusability data of Sn_1TPA catalyst for benzylation of anisole.

Table 3
Benzylation of different substituted arenes over Sn₁TPA catalyst.

S.no.	Arene	Alcohol	Time (min)	Product	Selectivity (o:-p:-)
1.			30		45:55
2.			30		–
3.			60		–
4.			60		31:69 ^a
5.			75		–
6.			60		31:69 ^b
7.			60		–
8.			45		–
9.			60		45:54 ^c
10.			75		24:76 ^d
11.			30		29:71 ^e

Reaction conditions: Benzyl alcohol (3.376 g), arene (10 g), catalyst weight (0.1 g), and reaction temperature 120 °C.

^a 3-benzyl-4-chloro-1-methylbenzene:2-benzyl-4-chloro-1-methylbenzene.

^b 2-benzyl-1,3-dimethylbenzene:1-benzyl-2,4-dimethylbenzene.

^c 2-benzyl-6-methyl phenol:4-benzyl-2-methyl phenol.

^d 3-benzyl-4-methyl phenol:2-benzyl-4-methyl phenol.

^e 1-benzyl-2,3-dimethoxybenzene:4-benzyl-1,2-dimethoxybenzene.

benzyl alcohol, 4-methoxy benzyl alcohol, and 2-bromo benzyl alcohol) produced the corresponding benzylated products in good yields with complete conversion of benzyl alcohol within 60 min of reaction time irrespective of substitution in benzyl alcohol.

Benylation of anisole and substituted anisole with secondary alcohols are presented in Table 5. It is noteworthy to mention that the present catalytic system is highly effective even when secondary benzyl alcohols were used as benzylating agents. Anisole reacted smoothly with 1-phenylethanol and diphenylmethanol yielding corresponding ortho and para products with high para selectivity. Where as, substituted anisoles (4-fluoro and 4-methyl anisole) gave selectively only one isomer (ortho) within short reaction time.

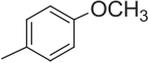
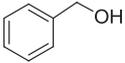
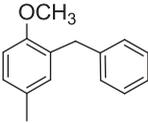
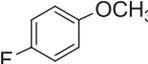
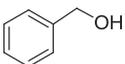
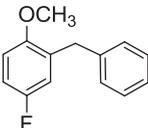
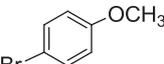
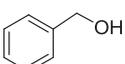
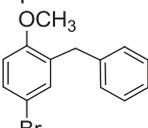
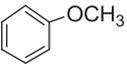
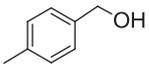
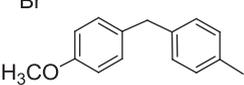
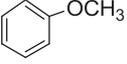
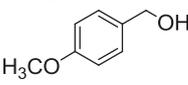
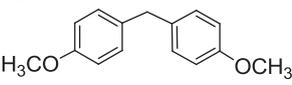
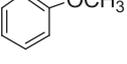
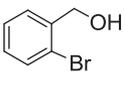
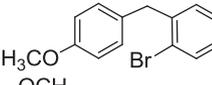
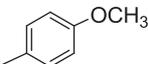
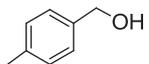
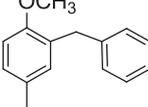
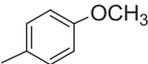
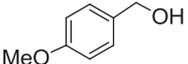
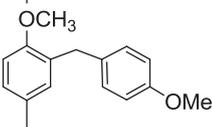
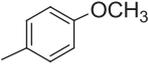
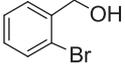
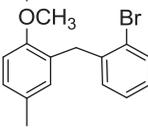
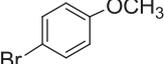
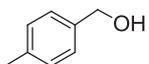
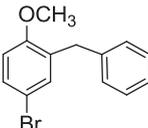
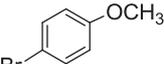
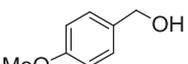
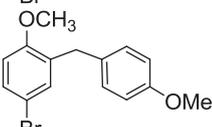
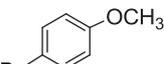
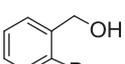
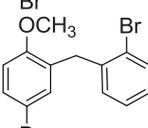
Benylation of naphthalene with different benzyl alcohols and secondary alcohols are studied and the results are summarized in Table 6. Benylation of naphthalene is very important and carried by complex catalytic systems such as AlCl₃-CH₃NO₂ and AlCl₃-

PhNO₂ [24,25]. There are no details of solid acid catalysts used for benylation of naphthalene with benzyl alcohol and secondary benzyl alcohols. The results suggest that benylation of naphthalene with different substituted alcohols underwent smoothly with high conversion of alcohol with good selectivity towards the corresponding benzylated naphthalenes.

3.3. Comparison of the catalytic activity of Sn₁TPA with reported catalysts

The present catalyst Sn₁TPA was compared with the reported catalysts for the benylation of anisole with benzyl alcohol. The comparative results are shown in Table 7. When compared to other catalysts, present catalyst showed complete conversion of benzyl alcohol within 30 min with selectivity towards p- and o-isomers. Where as the other reported solid acid catalysts took about 90–540 min to get a similar conversion. The reported H₃PO₄-WO₃-Nb₂O₅ heteropoly acid catalysts showed good activ-

Table 4
Benzylation of substituted anisoles with variety of benzyl alcohols over Sn₁TPA catalyst.

S.no.	Arene	Alcohol	Time (min)	Major product	Rigio isomer (o:-p:-)
1.			30		-
2.			150		-
3.			45		-
4.			60		38:62
5.			30		20:80
6.			30		43:57
7.			60		-
8.			60		-
9.			60		-
10.			30		-
11.			30		-
12.			30		-

Reaction conditions: Benzyl alcohol (3.376 g), arene (10 g), catalyst weight (0.1 g), and reaction temperature 120 °C.

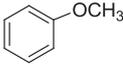
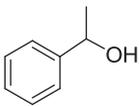
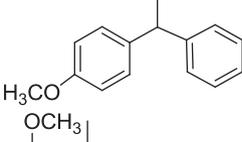
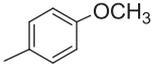
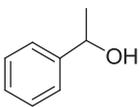
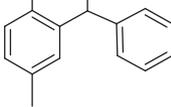
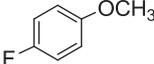
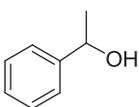
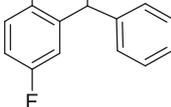
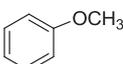
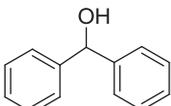
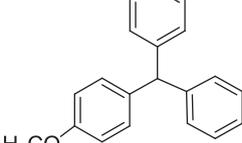
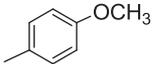
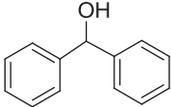
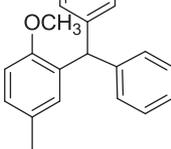
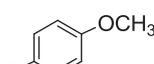
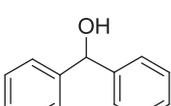
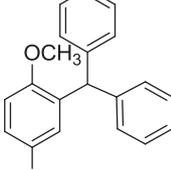
ity only when the heteropoly acid is decomposed to its intermediate species. These results reiterate the high activity and selectivity of SnHPW₁₂O₄₀ catalyst for benzylation reactions.

3.4. Reusability of the catalyst

In order to find the reusability of SnHPW₁₂O₄₀ catalyst, after the reaction the catalyst was separated from the reaction mixture by simple filtration and washed with ethyl acetate. The catalyst

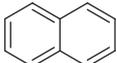
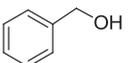
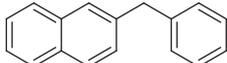
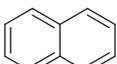
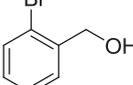
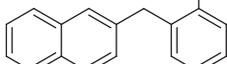
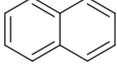
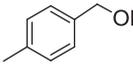
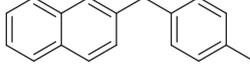
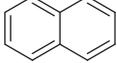
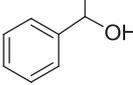
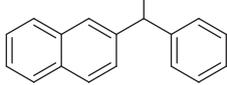
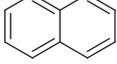
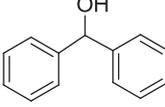
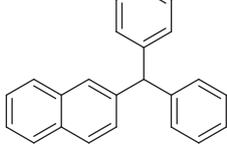
was dried in oven at 120 °C for 1 h and reused for benzylation of anisole with benzyl alcohol. The catalyst recycles activity data was shown in Fig. 6. From the figure it was found that conversion of benzyl alcohol almost same without any significant loss in activity even after fourth cycle. The catalyst exhibited consistent selectivity towards benzylation product barring a marginal selectivity towards ether in the first cycle. The reusability results clearly demonstrated the efficiency of the catalyst.

Table 5
Benzylation of anisole and substitution anisole with secondary alcohols over Sn₁TPA catalyst.

S.no.	Arene	Alcohol	Time (min)	Major product	Rigio isomer (o:-p-)
1.			15		30:70
2.			15		-
3.			15		-
4.			15		13:87
5.			15		-
6.			15		-

Reaction conditions: Benzyl alcohol (3.376 g), arene (10 g), catalyst weight (0.1 g), and reaction temperature 120 °C.

Table 6
Benzylation of naphthalene with variety of benzyl alcohols and secondary alcohols over Sn₁TPA catalyst.

S.no.	Arene	Alcohol	Time (min)	Major product	Rigio isomer (1:-2-)
1.			15		22:78
2.			15		39:61
3.			15		18:82
4.			15		20:80
5.			15		17:83

Reaction conditions: Benzyl alcohol (3.376 g), naphthalene (11.85 g), catalyst weight (0.1 g), and reaction temperature 120 °C.

Table 7
Comparison of the catalytic activity of Sn₁TPA with other reported solid acids catalysts.

Catalyst	Reaction temp. (°C)	Time (min.)	Conversion ^a (%)	Selectivity (%)				Ref.
				o-	p-	Ether	Other	
Sn1TPA	120	30	100	45	54	–	–	Present work
Nb ₂ O ₅ + H ₃ PO ₄	Reflux	540	99.2	85.2 ^b	–	12.8	2.0	[26]
SiO ₂ –Si–SCF ₃	Reflux	180	–	100 ^b	–	–	–	[27]
H ₃ PO ₄ –WO ₃ –Nb ₂ O ₅	80	180	100	93.4 ^b	–	0.3	–	[28]
Niobiumphosphate	160	<360	100	34.3	53.1	5.2	7.4	[29]
Nb ₂ O ₅ /Al ₂ O ₃	160	90	100	29.2	44.9	20.3	6.3	[30]
TPA-PANI	80	240	98	24.6	76.4	–	–	[2]

^a Conversion with respect to benzyl alcohol.

^b Benzylated product yield.

4. Conclusions

In summary, tin exchanged TPA catalysts are prepared with retention of Keggin ion structure. The Sn_xTPA catalysts showed high benzylation activity and their activity depends on the extent of tin content. The presence of Sn generated Lewis acidity, which affected the overall catalytic activity. The catalyst with partial exchange of tin Sn₁TPA showed highest activity due to the presence of more number of both Lewis and Bronsted acidic sites. The role of both Lewis and Bronsted acidic sites of the catalysts for benzylation are explained by the plausible reaction mechanism. The catalysts showed excellent benzylation activity within short reaction times with high selectivity compared to other reported catalysts. The catalyst is easy to recover and exhibits consistent activity and selectivity for benzylation reaction. The reported catalyst is active for the benzylation reaction irrespective of the nature of substituted arene and benzyl alcohols.

Acknowledgement

The authors RK and KTVR thank Council of Scientific and Industrial Research (CSIR), India for the award of Junior and Senior Research Fellowships respectively.

References

- [1] H.B. Sun, B. Li, S. Chen, J. Li, R. Hua, *Tetrahedron* 63 (2007) 10185–10188.
- [2] J.R. Satam, R.V. Jayaram, *Catal. Commun.* 9 (2008) 1937–1940.
- [3] G.D. Yadav, S.A. Purandare, *J. Mol. Catal. A: Chem.* 263 (2007) 26–31.
- [4] P. Susmita, Sujit Roy, *Tetrahedron* 63 (2007) 9146–9152.
- [5] F. Duris, D.B. Baudry, A. Dormond, J.R. Desmurs, J.M. Bernard, *J. Mol. Catal. A: Chem.* 188 (2002) 97–104.
- [6] K. Mantri, K. Komura, Y. Kubota, Y. Sugi, *J. Mol. Catal. A: Chem.* 236 (2005) 168–175.
- [7] V.R. Choudhary, S.K. Jana, N.S. Patil, S.K. Bhargava, *Micropor. Mesopor. Mater.* 57 (2003) 21–35.
- [8] E. Diaz, S. Ordonez, A. Vega, A. Auroux, J. Coca, *Appl. Catal. A: Gen.* 295 (2005) 106–115.
- [9] A. Phukan, J.N. Ganguli, D.K. Dutta, *J. Mol. Catal. A: Chem.* 202 (2003) 279–287.
- [10] D.U. Singh, S.D. Samant, *J. Mol. Catal. A: Chem.* 223 (2004) 111–116.
- [11] V.R. Choudhary, R. Jha, *Appl. Catal. A: Gen.* 333 (2007) 42–48.
- [12] M. Misono, *Catal. Rev. Sci. Eng.* 29 (1987) 269–321.
- [13] I.V. Kozhevnikov, *Appl. Catal. A: Gen.* 256 (2003) 3–18.
- [14] M.N. Timofeeva, *Appl. Catal. A: Gen.* 256 (2003) 19–35.
- [15] K. Shimizu, K. Niimi, A. Satsuma, *Appl. Catal. A: Gen.* 349 (2008) 1–5.
- [16] Ch. Ramesh Kumar, P.S. Sai Prasad, N. Lingaiah, *Appl. Catal. A: Gen.* 384 (2010) 101–106.
- [17] C. Rocchiccioli-deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* 22 (1983) 207–216.
- [18] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113–252.
- [19] G. Ranga Rao, T. Rajkumar, *J. Colloid Interface Sci.* 324 (2008) 134–141.
- [20] G. Busca, *Catal. Today* 41 (1998) 191–206.
- [21] E.P. Parry, *J. Catal.* 2 (1963) 371–379.
- [22] X.K. Yang, L.F. Chen, J.A. Wang, L.E. Norena, O. Novaro, *Catal. Today* 148 (1) (2009) 160–168.
- [23] M. Misono, *Chem. Commun.* 13 (2001) 1141–1152.
- [24] A.A. Khalaf, M.S.I.T. Makki, R.A. Kabil, R. Mansoura, *Sci. A: Bull. Chem.* 21 (1) (1994) (Chem. Abstr., 123, 285451).
- [25] H.A. Albar, S.A. Basaif, A.A. Khalaf, *Indian J. Chem: Sect.: Org. Chem. Med. Chem.* 35B (2) (1996) 161–166.
- [26] M. Morais, E.F. Torres, L.M.P.M. Carmo, N.M.R. Pastura, W.A. Gonzalez, A.C.B. Santos, E.R. Lachter, *Catal. Today* 28 (1996) 17–21.
- [27] D.Q. Zhou, J.H. Yang, G.M. Dong, M.Y. Huang, Y.Y. Jiang, *J. Mol. Catal. A: Chem.* 159 (2000) 85–87.
- [28] K. Okumura, K. Yamashita, M. Hirano, M. Niwa, *J. Catal.* 234 (2005) 300–307.
- [29] M.H.C. Cruz, J.F.C. Silva, E.R. Lachter, *Catal. Today* 118 (2006) 379–384.
- [30] M.H.C. Cruz, M.A. Abdel-Rehim, A.S. Rocha, J.F.C. Silva, A.C. Faro Jr., E.R. Lachter, *Catal. Commun.* 8 (2007) 1650–1654.