

Zirconia-supported phosphotungstic acid as catalyst for alkylation of phenol with benzyl alcohol

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Abstract

The liquid-phase alkylation of phenol with benzyl alcohol was carried out using zirconia-supported phosphotungstic acid (PTA) as catalyst. The catalysts with different PTA loadings (5–20 wt.% calcined at 750 °C) and calcination temperature (15 wt.% calcined from 650 to 850 °C) were prepared and characterized by ³¹P MAS NMR and FT-IR pyridine adsorption spectroscopy. The catalyst with optimum PTA loading (15%) and calcination temperature (750 °C) was prepared in different solvents. ³¹P MAS NMR spectra of the catalysts showed two types of phosphorous species, one is the Keggin unit and the other is the decomposition product of PTA and the relative amount of each depends on PTA loading, calcination temperature and the solvent used for the catalyst preparation. The catalysts with 15% PTA on zirconia calcined at 750 °C showed the highest Brønsted acidity. At 130 °C and phenol/benzyl alcohol molar ratio of 2 (time, 1 h), the most active catalyst, 15% PTA calcined at 750 °C gave 98% benzyl alcohol conversion with 83% benzyl phenol selectivity.
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1. Introduction

Acid catalyzed reactions are among the most important in the chemical industry and alkylation reaction is one class of such reactions. This reaction is usually catalyzed by homogeneous Lewis acids (AlCl₃, BF₃) or strong mineral acids (HF, H₂SO₄), which are highly toxic, generate a substantial amount of waste and cause severe corrosion problems. Considerable efforts are being made to find suitable solid acid catalysts, which can be used successfully to carry out the above type of transformation [1,2]. Heteropoly acids (HPAs) especially Keggin type HPAs are strong Brønsted acid catalysts [3,4]. Phosphotungstic acid (PTA) is the usual catalyst of choice out of various HPAs because of its high acidic strength and rel-

atively high thermal stability. A serious problem associated with the use of this type of materials as heterogeneous catalysts is their low surface area (5–8 m² g⁻¹). The use of HPA in supported form is preferable because of its high surface area compared to the bulk material. Acidic or neutral solids, which interact weakly with HPAs such as silica, active carbon and acidic ion-exchange resin, have been reported to be suitable as HPA supports [5].

Zirconia based solid acids are attracting much attention in recent years. Extensive studies have been carried out on zirconia modified by isopolytungstate (WO_x/ZrO₂), which acts as an efficient solid acid catalyst [6–8]. But, relatively few reports are available on zirconia modified by heteropolytungstates [9–11]. Recently, we had shown that zirconia-supported phosphotungstic acid acts as an efficient catalyst for alkylation and acylation of aromatics and isomerization of *n*-heptane [12–14].

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The alkylation of phenol with different alcohols is industrially important as it is used for the production of a variety of products [15]. Among these, alkylation of phenol with benzyl alcohol has been used for the production of benzyl phenol. Benzyl phenol (hydroxy diphenyl methane) is important, since it is useful as anti-oxidant for organic materials such as plastics, rubbers and petroleum products [16].

The present study deals with the preparation of zirconia-supported PTA catalyst and its characterization by ^{31}P MAS NMR spectroscopy and acidity measurements by FT-IR pyridine adsorption. The catalyst with optimum PTA loading and calcination temperature was prepared in different solvents to study the role of the solvent used for the catalyst preparation in deciding its catalytic activity. These catalysts were used in the liquid-phase alkylation of phenol with benzyl alcohol and the reaction was carried out with the aim to maximize the formation of benzyl phenol.

2. Experimental

2.1. Chemicals

Zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), ammonia (25%), phenol and benzyl alcohol were procured from S.D. Fine Chemicals Ltd., Mumbai. Phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O}$) and tungstic acid (H_2WO_4) were purchased from Aldrich. Methanol was obtained from E. Merck India Ltd., Mumbai. All the chemicals were used as received without further purification.

2.2. Catalyst preparation

The catalysts were prepared by impregnation method using zirconium hydroxide as the support. The support was prepared by the hydrolysis of an aqueous solution of zirconyl chloride with ammonia solution and the precipitate obtained was washed free of chloride and dried at 120°C for 24 h. A series of catalysts with different PTA loadings (5–20 wt.%) were prepared by suspending dried zirconia powder in a methanol solution of PTA. This mixture was stirred for 8–10 h and the excess of methanol evaporated to dryness. The resulting samples were dried at 120°C and calcined in air at 750°C for 4 h. Samples with 15% PTA were calcined between 650 and 850°C to understand the influence of the calcination temperature on the properties and activity of the catalysts. The catalyst with optimum PTA loading (15%) was prepared using different solvents to understand the role of the solvent used for the catalyst preparation. For comparison, a catalyst with 15% PTA was also prepared simply by grinding a mixture of zirconium hydroxide and PTA (neat) for 10 min followed by drying and calcination as mentioned above. The catalysts are represented by x PZ- t , where x represents wt.%, P represents PTA, Z represents zirconia and t denotes the calcination temperature ($^\circ\text{C}$).

For comparison a catalyst with 15% WO_x/ZrO_2 (15 WZ-750) was prepared by wet impregnation of zirconium hydroxide with a solution of tungstic acid dissolved in excess of NH_3 , dried and calcined at 750°C .

2.3. Characterization

^{31}P MAS NMR spectra (Bruker DSX-300) were recorded at 121.5 MHz with high power decoupling using a Bruker 4 mm probe head. The spinning rate was 10 kHz and the delay between two pulses was varied between 1 and 30 s to ensure that a complete relaxation of the ^{31}P nuclei occurred. The chemical shifts are given relative to external 85% H_3PO_4 .

The nature of the acid sites (Brönsted and Lewis) of the catalyst samples was characterized by in situ FT-IR spectroscopy with chemisorbed pyridine. For catalysts with different PTA loading, pyridine adsorption (NICOLET MODEL 60 SXB) studies were performed by heating in situ a self-supporting wafer (20 mg) of the sample from room temperature to 400°C with a heating rate of 5°C min^{-1} under vacuum (10^{-6} mbar). The samples were kept at 400°C for 3 h followed by cooling to 100°C . Pyridine vapor (10 mmHg) was introduced into the cell and allowed to equilibrate for 45 min followed by evacuation at 100°C for 30 min and the IR spectrum was recorded. Then the temperature was slowly increased and IR spectra were recorded at different temperatures up to 400°C .

The FT-IR (Shimadzu SSU 8000) pyridine adsorption studies for the 15 PZ catalyst calcined at different temperatures were carried out in the DRIFT (diffuse reflectance infrared Fourier transform) mode. A calcined powder sample in a sample holder was placed in a specially designed cell. The samples were then heated in situ from room temperature to 400°C at a heating rate of 5°C min^{-1} in a flowing stream (40 ml min^{-1}) of pure N_2 . The samples were kept at 400°C for 3 h and then cooled to 100°C and then pyridine vapor ($20\ \mu\text{l}$) was introduced under N_2 flow and the IR spectra were recorded at different temperatures up to 400°C . A resolution of 4 cm^{-1} was attained after averaging over 500 scans for all the IR spectra reported here.

2.4. Catalytic activity

The liquid-phase alkylation reactions were carried out in a 50 ml glass batch reactor with anhydrous CaCl_2 guard tube. The temperature was maintained by silicon oil bath equipped with a thermostat and magnetic stirrer. The catalyst freshly activated at 500°C was weighed in the reactor and then the reaction mixture was added according to the proportion desired. For example, a typical reaction mixture consists of 4.2 g of phenol, 0.8 g benzyl alcohol together with 0.08 g of catalyst. After a definite time interval, the reaction was stopped and the reaction mixture was diluted with 5 ml methanol and the catalyst was separated. The filtrate was analyzed using a Shimadzu 14B gas chromatograph using SE-52 packed column,

coupled with FID. The product identification was carried out using GC–MS. Conversion was defined as the percentage of benzyl alcohol converted into products.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. ^{31}P MAS NMR

The ^{31}P MAS NMR spectra of the catalysts with 5–20% PTA and 15% catalyst calcined from 650 to 850 °C are shown in Fig. 1. For low loadings, and at calcination temperature of 750 °C a broad signal above –20 ppm is observed. Fig. 2 represents the ^1H – ^{31}P cross-polarization (CP) spectra of the catalyst 15 PZ-750 and this indicates the attenuation of the peak above –20 ppm and hence hydrogen is associated with this phosphorous species. In agreement with literature data, this peak is attributed to phosphorous in the Keggin unit [17,18,12]. For high loadings and at higher calcination temperature, a second signal appears below –20 ppm, which can be attributed to phosphorous oxide resulting from the decomposition of the polyoxometalate [10]. This phosphorous oxide represents 20 and 45% of the total phosphorous for 15 and 20 PZ-750 catalysts and 80% for 15 PZ-850 catalyst, respectively. The ^{31}P MAS NMR spectra of catalysts with different PTA loading and calcination temperatures show that the Keggin unit starts decomposition at a PTA loading of ca. 15% at 750 °C. This result suggests that the catalyst 15 PZ-750 attains a geometric monolayer of PTA on zirconia.

The 15 PZ-750 catalyst was selected to study the role of the solvent used for the catalyst preparation. The NMR spectra of the catalysts prepared in different solvents show two signals, one above –20 ppm and one below –20 ppm (not shown) and the signal intensities depend on the solvent used for the catalyst preparation. We have observed a direct relation between P–OH intensity and the dielectric constant of

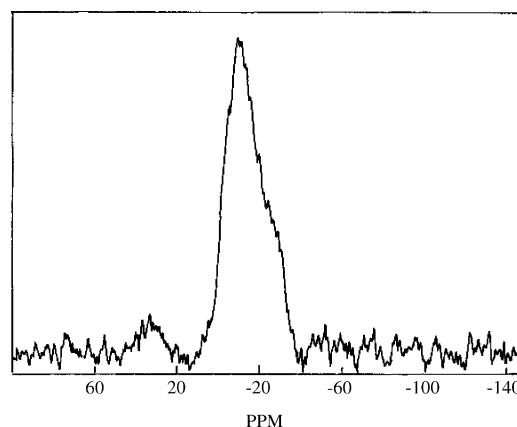


Fig. 2. CP MAS NMR spectra of 15% catalyst.

the solvent [19] used for the catalyst preparation (Table 2). It is evident from Table 2 that the P–OH intensity i.e., the amount PTA in Keggin form, increases with dielectric constant of the solvent with water as an exceptional solvent. In aqueous solution, heteropolyanions are not stable at pH > 1 as reported by McGarvey and Moffat and which is the case observed in this study [20]. The low P–OH intensity of the catalyst prepared in water is attributed to the low stability of PTA in water [21].

The different behaviors of the catalyst prepared in different solvents can also originate from diffusion limitation of PTA in to the pores of the support. Since the HPA anions are very weakly solvated in solvents, the solubility of heteropoly acids depends on the solvation of cations [22]. Thus the effective size of the Keggin unit can vary from solvent to solvent and hence the diffusivity of the polyanion which ultimately results in different dispersion of HPA on the support and hence the amount of intact PTA present in the ZrO₂ surface after calcination. These results are in good agreement with the observations of Fournier et al. who suggest the use of DMF as solvent to achieve good dispersion during the preparation of supported heteropoly acid catalysts [21]. We have used methanol as solvent for the detailed study due to its higher volatility and easiness in handling.

3.1.2. FT-IR pyridine adsorption

The use of IR spectroscopy to detect the adsorbed pyridine enables us to distinguish among different acid sites. The FT-IR pyridine adsorption spectra of catalyst with different PTA loadings and of 15% PZ calcined at different temperatures are shown in Fig. 3. The catalysts showed Brönsted (B) and Lewis (L) acidity at 1536 and 1442 cm⁻¹, respectively, and the B/L ratio calculated from the IR absorbance intensities, are given in Table 1. The B/L ratio shows that the relative Brönsted acidity increases with PTA loading up to 15% and decreased with further loading. For 15% catalyst, the Brönsted character increases up to 750 °C calcination, while above that, an increase in Lewis acidic character is observed (Table 1). The catalyst 15 PZ-750 shows two B/L ratios 1.06 and 1.5 and the different values are due to the

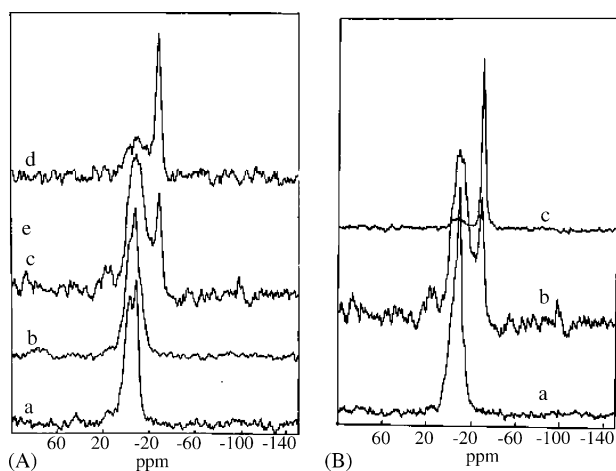


Fig. 1. ^{31}P MAS NMR spectra of (A) catalysts with different PTA loadings: (a) 5%, (b) 10%, (c) 15%, (d) 20%; (B) 15% catalyst calcined at different temperatures: (a) 650 °C, (b) 750 °C, (c) 850 °C.

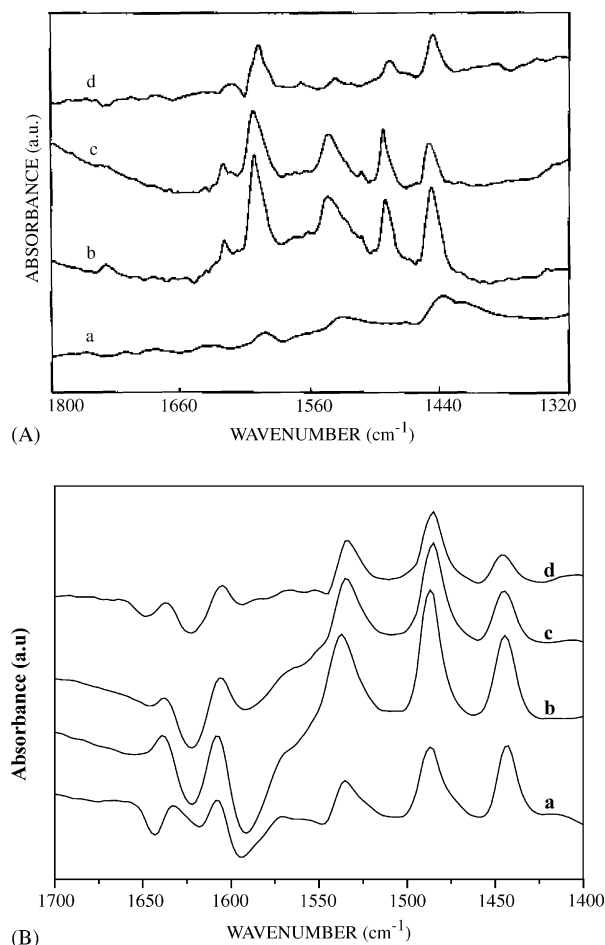


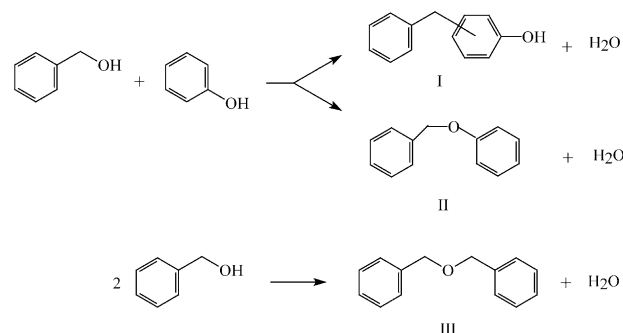
Fig. 3. The IR spectra of pyridine adsorbed on (A) catalysts with different PTA loadings: (a) 5%, (b) 10%, (c) 15%, and (d) 20%; (B) 15% catalyst calcined at different temperatures: (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 800 °C after in situ activation at 300 °C.

difference in the pyridine adsorption analysis. The catalysts with different PTA loadings were done under vacuum using NICOLET MODEL 60 SXB instrument, while the catalyst with different calcination temperatures were done under N₂ flow using Shimadzu SSU 8000 instrument. Thus, the catalyst 15 PZ-750 shows the maximum relative Brønsted acidity and this corresponds to a monolayer of PTA on ZrO₂ [14].

Since Brønsted acidity increases with calcination temperature until monolayer coverage, we propose that during calcination, support dehydroxylates and undergoes crystallization and during this process the interaction of HPA with the support is partially weakens and part of the H⁺ ions which are

Table 1
FT-IR pyridine adsorption data of various catalysts

Effect of PTA loading		Effect of calcination temperature (°C)	
Catalyst	B/L (<i>I</i> ₁₅₃₆ / <i>I</i> ₁₄₄₂)	Catalyst	B/L (<i>I</i> ₁₅₃₆ / <i>I</i> ₁₄₄₂)
5 PZ-750	0.32	15 PZ-650	0.59
10 PZ-750	0.64	15 PZ-700	0.92
15 PZ-750	1.06	15 PZ-750	1.50
20 PZ-750	0.27	15 PZ-800	1.20



Scheme 1.

involved in interaction with the support is getting free and acts as Brønsted acid sites.

Thus, the highest acidity corresponds to ca. one monolayer of polyoxometalate and is also evident from ³¹P MAS NMR spectra. So, we can describe the evolution of the catalysts as follows: until a PTA loading of ca. 15% at 750 °C, or for a 15% catalyst up to a calcination temperature of 750 °C, i.e., up to a monolayer, the heteropolyanion is well dispersed on the zirconia surface and it retains its integrity. When the coverage exceeds monolayer, the polyanions is not stabilized by zirconia and decomposes to its oxides.

3.2. Catalytic activity

The liquid-phase alkylation of phenol with benzyl alcohol (BA) was carried out using zirconia-supported PTA as catalyst. The analysis of the products showed that the reaction resulted in the formation of ring alkylated product, benzyl phenol (BP-I) and *O*-alkylated product, phenyl benzyl ether (PBE-II). In addition benzyl ether (BE-III) also formed as one of the product (Scheme 1).

The influence of PTA loading on BA conversion and product selectivity is shown in Fig. 4. Pure zirconia calcined at 750 °C does not show any activity for this reaction. The catalyst with 5% PTA shows 0.6% conversion and it increases

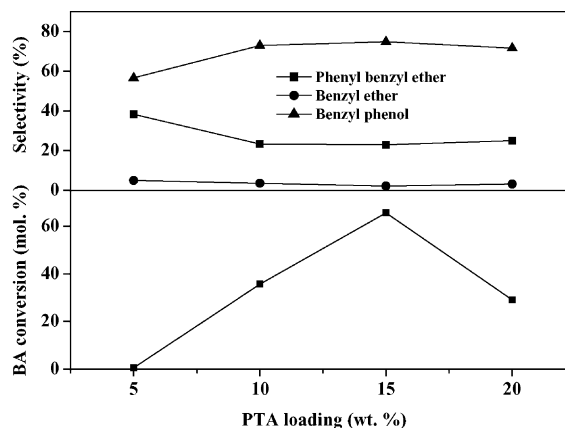


Fig. 4. Influence of PTA loading on benzyl alcohol conversion and product selectivity (conditions: total weight = 5 g; catalyst weight = 0.08 g; temperature = 90 °C; phenol/benzyl alcohol (molar ratio) = 6; time = 1 h).

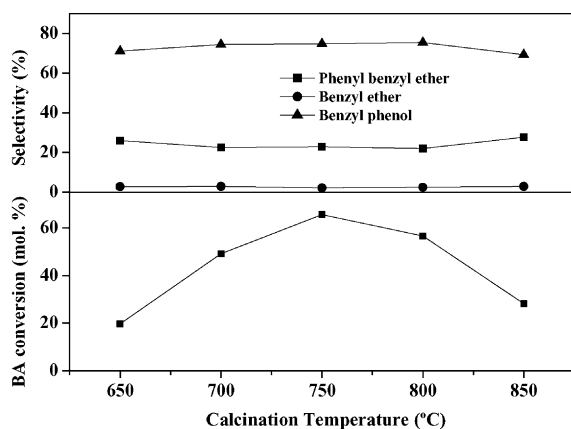


Fig. 5. Influence of calcination temperature on benzyl alcohol conversion and product selectivity (conditions: total weight = 5 g; catalyst weight = 0.08 g; temperature = 90 °C; phenol/benzyl alcohol (molar ratio) = 6; time = 1 h).

to 35% at 10% PTA loading. The catalyst with 15% PTA showed the maximum conversion of 65%. Further increase in PTA loading results in the decrease of conversion. The selectivity to different products is found to depend on PTA loading. The BP selectivity increased from 56 to 75%, while the selectivity to PBE decreased from 38 to 23% as the PTA loading increased from 5 to 15%. The BE selectivity was similar for catalyst with different PTA loadings.

In order to study the influence of calcination temperature, catalysts with 15% PTA calcined between 650 and 850 °C were used in the reaction. The effect of calcination temperature on conversion and selectivity are shown in Fig. 5. The catalyst calcined at 650 °C gave 19% BA conversion and it increased to 65% at 750 °C calcination. The conversion is found to decrease with further increase in calcination temperature. At 650 °C, BP selectivity was 71% and it increased to 74% at 700 °C, while PBE selectivity decreased from 26 to 22%. Not much change in BP selectivity was observed in the calcination temperature range of 700–800 °C. As the calcination temperature increased from 800 to 850 °C, BP selectivity decreased from 75 to 69%, while PBE selectivity increased from 22 to 27%. The BE selectivity was similar in the calcination temperature range studied. The catalyst with 15% PTA calcined at 750 °C shows maximum conversion, which corresponds to the catalyst with the highest B/L ratio i.e., the highest Brönsted acidity (Table 1). Thus the conversion of BA increases until the PTA monolayer, but above which it decreased [14]. However, the catalyst 15 WZ-750 under similar conditions gave 26% BA conversion.

Therefore, the catalyst with optimum PTA loading (15%) and calcination temperature (750 °C) was taken to study the role of the solvent used for catalyst preparation in the alkylation of phenol with BA. The catalyst 15 PZ-750 prepared in different solvents showed that the conversion of BA increases with P–OH intensity (Table 2). The catalyst prepared without solvent showed the lowest benzyl alcohol conversion of 11% while the catalyst prepared in DMF showed the high-

Table 2

P–OH intensity, dielectric constant and benzyl alcohol conversion of 15% catalyst prepared in different solvents (conditions: total weight = 5 g; catalyst weight = 0.08 g; temperature = 90 °C; phenol/benzyl alcohol (molar ratio) = 6; time = 1 h)

Solvent	Dielectric constant	P–OH intensity ^a (%)	Conversion (mol%)
Neat	–	32	11
Ether	2.21	33	16
1,4-Dioxane	4.30	36	28
Acetic acid	6.20	40	31
Ethyl acetate	6.02	44	32
THF	7.60	46	33
Acetone	20.60	52	48
Water	79.70	65	50
Methanol	32.60	80	66
DMF	36.70	82	68

^a Relative amount of PTA in Keggin form.

est conversion of 68%. It has to be noted that there is not much difference in BA conversion for the catalysts prepared in methanol and DMF.

The catalyst 15 PZ-750 (prepared in methanol) was used to study different reaction parameters. The influence of reaction temperature was studied from 70 to 130 °C (Fig. 6). It is found that temperature has a profound effect on the reaction. Increasing the temperature of the reaction increases the BA conversion and affects the product distribution selectivity towards C-alkylated product. At 70 °C, the conversion was only 8% and it increased to 30% at 90 °C. An increase of 59% BA conversion was observed when the temperature was increased from 90 to 110 °C. At 130 °C, BA conversion was found to be 98%. As the temperature increased from 70 to 130 °C, BP selectivity increased from 70 to 83% and PBE selectivity decreased from 22 to 10%. Under similar reaction conditions PBE gave BP and BA gave BE as the products. Thus, the decrease in PBE selectivity is due to the transformation of O- to C-alkylated product with an increase in temperature. It has shown that such rearrangement occurred on heating or by contact with an acid catalyst [23]. Thus BP is a primary

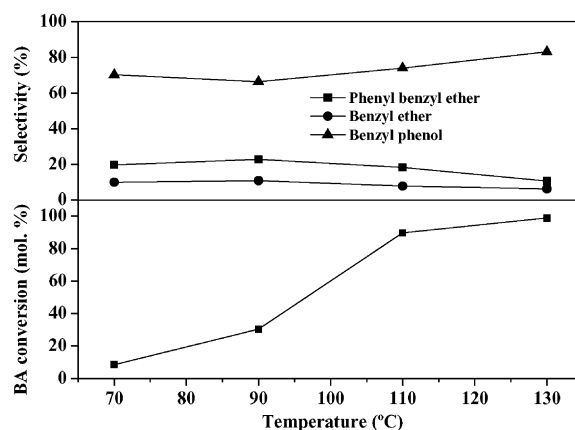


Fig. 6. Influence of reaction temperature on benzyl alcohol conversion and product selectivity (conditions: total weight = 5 g; catalyst weight = 0.18 g; phenol/benzyl alcohol (molar ratio) = 2; time = 1 h).

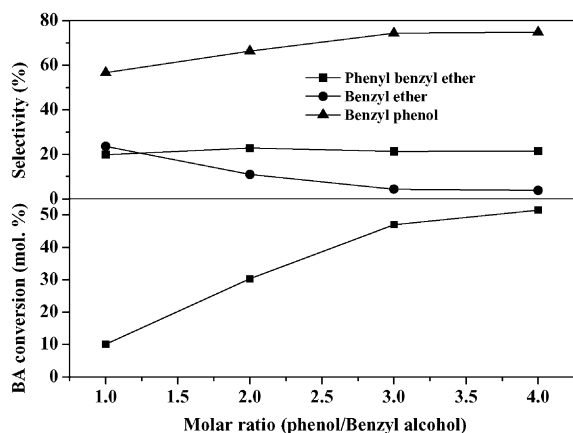


Fig. 7. Influence of molar ratio on benzyl alcohol conversion and product selectivity (conditions: total weight = 5 g; catalyst weight = 0.18 g; temperature = 90 °C; time = 1 h).

product while PBE is a primary and/or a secondary product and it transforms to BP during reaction. With an increase in temperature the BE selectivity was decreased from 10 to 6%.

The effect of phenol/benzyl alcohol molar ratio (1–4) on BA conversion and product selectivity was studied keeping the total weight of the reaction mixture constant (Fig. 7). As the molar ratio increases from 1 to 4, the alcohol conversion increased from 10 to 51%, while the selectivity to BP increased from 56 to 74%. Molar ratio has an important effect on BE selectivity. As the molar ratio increased from 1 to 4, BE selectivity decreased from 23 to 3%. However, there is not much change in the selectivity to PBE was observed in the molar ratio range studied.

The reaction was studied by varying the catalyst amount from 5 to 20 wt.% of BA and it showed that catalyst weight has an appreciable effect on BA conversion (Fig. 8). However an increase in conversion does not result in appreciable change in selectivity.

Finally, the effect of the reaction time is studied at 90 °C and is shown in Fig. 9. When the reaction time increases, the

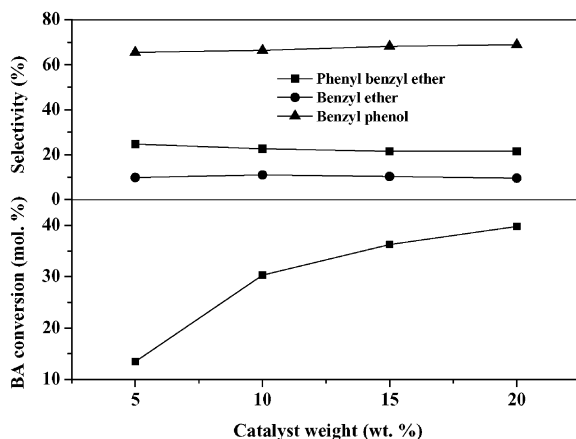


Fig. 8. Influence of catalyst weight on benzyl alcohol conversion and product selectivity (conditions: total weight = 5 g; temperature = 90 °C; phenol/benzyl alcohol (molar ratio) = 2; time = 1 h).

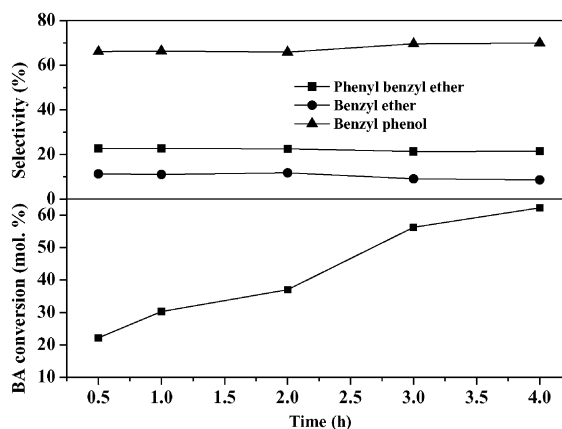


Fig. 9. Influence of time on benzyl alcohol conversion and product selectivity (conditions: total weight = 5 g; catalyst weight = 0.18 g; temperature = 90 °C; phenol/benzyl alcohol (molar ratio) = 2).

conversion increases while selectivity to different products was similar. The results of alkylation of phenol with benzyl alcohol can be summarized as, the lower reaction temperature and phenol/benzyl alcohol molar ratio results in higher selectivities for *O*-alkylated (PBE and BE) products. *C*-alkylated products become major at high temperature and higher molar ratio.

For heterogeneous catalysts, it is also important to study the recycling of the catalyst. The recyclability of 15 PZ-750 catalyst was tested in the alkylation of phenol with benzyl alcohol at 130 °C (10 wt.% catalyst, 2:1 molar reactants ratio). For this purpose, the reaction was stopped when the conversion reached 43% and the catalyst removed by filtration. The filtrate immediately reused in the reaction and it is found that there was no change in conversion and selectivity. In addition, the separated catalyst was reused (after washing with dichloromethane and drying) with fresh reaction mixture and was found that there was no loss in catalytic activity. These data are in agreement with the absence of catalyst leaching and a purely heterogeneous nature of the reaction.

4. Conclusions

Zirconia-supported phosphotungstic acid acts as an efficient catalyst for the alkylation of phenol with benzyl alcohol. The activity of the catalyst found to depend on PTA loading, calcination temperature and solvent used for the catalyst preparation. Under the reaction conditions of 130 °C and phenol/benzyl alcohol molar ratio of 2 (time, 1 h), the most active catalyst, 15% PTA calcined at 750 °C gave 98% benzyl alcohol conversion with 83% benzyl phenol selectivity.

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References

- [1] A. Corma, *Chem. Rev.* 95 (1995) 559.
- [2] A. Corma, H. Garcia, *Chem. Rev.* 103 (2003) 4307.
- [3] C.L. Hill (Ed.), *Chem. Rev.* 98 (1998) 1.
- [4] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [5] Y. Wu, X. Ye, X. Yang, X. Wang, W. Chu, Y. Hu, *Ind. Eng. Chem. Res.* 35 (1996) 2546.
- [6] D.G. Barton, S.L. Soled, E. Iglesia, *Top. Catal.* 6 (1998) 87.
- [7] S. Kuba, P. Lukinskas, R.K. Grasselli, B.C. Gates, H. Knözinger, *J. Catal.* 216 (2003) 353.
- [8] F.D. Gregorio, V. Keller, *J. Catal.* 225 (2004) 45.
- [9] E. Lopez-Salinas, J.G. Hernandez-Cortez, M.A. Cortes-Jacome, J. Navarrete, M.E. Llanos, A. Vazquez, H. Armendariz, T. Lopez, *Appl. Catal. A* 175 (1998) 43.
- [10] E. Lopez-Salinas, J.G. Hernandez-Cortez, I. Schifter, E. Torres-Garcia, J. Navarrete, A. Gutierrez-Carrillo, T. Lopez, P.P. Lottici, D. Bersani, *Appl. Catal. A* 193 (2000) 215.
- [11] S. Patel, N. Purohit, A. Patel, *J. Mol. Catal. A* 192 (2003) 195.
- [12] B.M. Devassy, S.B. Halligudi, S.G. Hegde, A.B. Halgeri, F. Lefebvre, *Chem. Commun.* (10) (2002) 1074.
- [13] B.M. Devassy, S.B. Halligudi, S.P. Elangovan, S. Ernst, M. Hartmann, F. Lefebvre, *J. Mol. Catal. A* 221 (2004) 113.
- [14] B.M. Devassy, F. Lefebvre, S.B. Halligudi, *J. Catal.*, in press.
- [15] H.-W. Voges, in: B. Elvers, S. Hawkins, G. Schulz (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, vol. A19, VHC, Weinheim, Germany, 1991, p. 328.
- [16] T. Matsuura, Y. Ohkatsu, *Polym. Degrad. Stability* 70 (2000) 59.
- [17] M. Misono, *Chem. Commun.* (13) (2001) 1141.
- [18] S. Uchida, K. Inumaru, M. Misono, *J. Phys. Chem. B* 104 (2000) 8108.
- [19] I.M. Smallwood, *Handbook of Organic Solvent Properties*, Arnold, London, 1996.
- [20] G.B. McGarvey, J.B. Moffat, *J. Mol. Catal.* 69 (1991) 137.
- [21] M. Fournier, R. Thouvenot, C. Rocchiccioli-Deltcheff, *J. Chem. Soc., Faraday Trans.* 87 (1991) 349.
- [22] L.C.W. Baker, D. Glick, *Chem. Rev.* 98 (1998) 3.
- [23] J. Weitkamp, S. Ernst, C.Y. Chen, *Stud. Surf. Sci. Catal. B* 49 (1989) 1115.