



Liquid phase Friedel–Crafts benzylation of aromatics on a polymer-supported 12-tungstophosphoric acid catalyst

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ABSTRACT

12-Tungstophosphoric acid (TPA) impregnated on polyaniline, zirconia and silica were chosen for the Friedel–Crafts benzylation of aromatics with benzyl alcohol as benzylating agent. TPA supported on polyaniline (PANI) was found to be selective towards monobenzylation and no dibenzylation was observed. This increased catalytic activity and selectivity can be attributed to the dispersion of TPA in the polyaniline matrix. The TPA supported on polyaniline was characterized by XRD, FTIR, BET and elemental analysis. The catalyst was found to be reusable for five cycles without appreciable loss in activity.

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1. Introduction

Diphenylmethane and substituted diphenylmethanes are industrially important compounds used as pharmaceutical intermediates [1] and fine chemicals [2,3]. Liquid phase Friedel–Crafts alkylation is usually carried out for their synthesis under homogeneous conditions using alkyl halides as alkylating agents and Lewis acids such as AlCl_3 or Bronsted acids such as H_2SO_4 as catalysts [4]. Also there are reports on rare earth metal triflates [5]. However, these homogeneous catalysts suffer from the inherent problems of corrosiveness, non-reusability and waste management. To overcome these problems efforts have been made towards the development of environmentally benign and easy to handle solid acid catalysts. Metal triflates supported on MCM-41 [6], modified zeolites [7], clays [8,9] are some of the heterogeneous catalysts commonly used for the benzylation reaction. Most of these catalysts are not reusable and in many cases benzylating agent used is benzyl chloride which leads to the formation of HCl and hence the process is not ecofriendly. The increased tendency of alkylated products towards further alkylation and isomerisation, coupled with the long contact of the reactant with the catalyst, result in a complex mixture of products. Polyalkylation, isomerization, transalkylation, dealkylation and polymerization all occur under ambient conditions. Therefore, there is substantial interest to carry out alkylation reaction with efficient solid acid catalysts with minimum side reactions and maximum selectivity towards monoalkylation.

Heteropolyacids (HPAs) are strong Bronsted acid catalysts and more acidic than conventional solid acids like zeolites and mixed oxides. The supported form of HPA is preferable because of its high surface area compared with the bulk material and better accessibility of reactants to the active sites. Acidic or neutral solids such as silica, active carbon, and acidic ion-exchange resin which interact weakly with HPAs, polymers [10,11] such as polyacetylene [12], polypyrrole [13] and polythiophene [14] can be used as supports. The Keggin units entrapped in conjugated polymers exhibits different catalytic selectivity it may be due to the chemical interactions with polyaniline matrix [14,15]. 12-Tungstosilicic acid and 12-molybdophosphoric acid supported on polyaniline have been found to be effective catalysts for hydrocarbon cracking [16], MTBE synthesis [17] and oxidation reactions [18].

In the present investigation, we have prepared several catalysts by supporting 12-tungstophosphoric acid (TPA) on polyaniline (PANI), zirconia and silica. Among these catalysts TPA supported on polyaniline was found to be selective towards monobenzylation. This increased catalytic activity and selectivity can be attributed to the dispersion of TPA in the polyaniline matrix.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of TPA supported on polyaniline

In the first step, polyemeraldine base was prepared. 10 mL (109.5 mM) of freshly distilled aniline was dissolved in 125 mL of 1.5 M HCl. To the pre cooled aniline solution (0 °C), 100 mL of

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54.8 mM ammonium persulfate oxidant was added drop wise. After the addition of the oxidant, the reaction mixture was kept under constant stirring for 4 h. The polyaniline hydrochloride precipitate was separated by centrifugation and washed consecutively with water, methanol and diethyl ether in order to remove the oligomers and side products of the reaction. The polymer was vacuum dried until constant mass. Deprotonation of polyaniline hydrochloride was achieved in 3 wt% aqueous ammonia solution. Deprotonated polymer was again washed with water and methanol and dried in vacuum to obtain the polyemeraldine base.

In the second step, protonation of polyemeraldine base was carried out in an acetonitrile solution of 12-tungstophosphoric acid (TPA). Different levels of protonation can be obtained by varying the TPA/polyemeraldine base ratio.

TPA supported on zirconia and silica were prepared and characterized as per reported procedures [19–22].

2.2. Catalyst characterization

The elemental composition of W and P in the catalysts was determined by ICP-AES spectrometry. Surface area measurements were carried out by nitrogen adsorption on a Micromeritics ASAP 2010 instrument at an adsorption temperature of 77 K. XRD studies were performed with a conventional powder diffractometer (Philips 1050) using graphite monochromatised $\text{CuK}\alpha$ radiation. The FTIR spectra were recorded on a Perkin-Elmer (Spectra 100) spectrometer.

2.3. Representative procedure for the benzylation reaction

Benzyl alcohol (0.05 mol) was treated with arene (0.3 mol) using TPA supported on polyaniline (0.16 g) at 80 °C for 4 h. Stoichiometric excess of the arene was taken to avoid dibenylation. Course of the reaction was monitored by TLC and GC. The reaction mixture was diluted with hexane and the solution was filtered to separate the catalyst. The reaction mixture was cooled, the catalyst was filtered and the product was analyzed by gas chromatography (GC) [Chemito 2000 instrument equipped with an SGE BP 10 capillary column (30 m × 0.3 mm i.d.) and a flame ionization detector]. The products were also identified by GC–mass spectrometry (Shimadzu GC-MS with RTX wax capillary column (30 m × 0.32 mm i.d.)). The sensitivity of the reactant and products in GC was calibrated by comparison with standard compounds purchased commercially. The conversion of benzyl alcohol and the selectivity for the products were calculated by the molar basis of the amount of introduced and consumed benzyl alcohol.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Elemental analysis and BET surface area measurements

The elemental composition of W and P in the catalysts was determined and results are depicted in Table 1. Surface areas of

Table 1
Percentage composition of P and W in different catalysts

Catalyst	% Composition		Surface area (m^2/g)
	P	W	
TPA	–	–	6
TPA/PANI (fresh)	0.59	41.89	80
TPA/PANI (spent)	0.57	40.47	79
TPA/ ZrO_2	0.45	31.95	130
TPA/silica	0.38	26.98	147

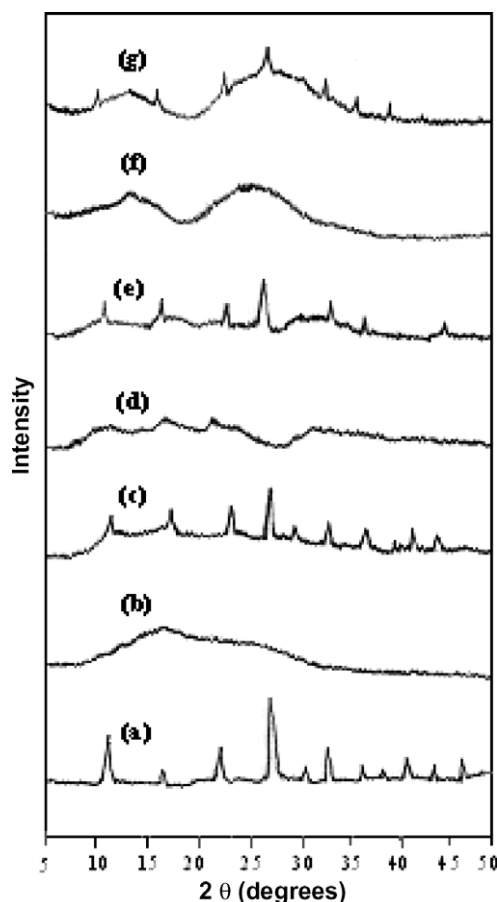


Fig. 1. XRD patterns of (a) TPA; (b) polyemeraldine base; (c) TPA-PANI; (d) ZrO_2 ; (e) TPA- ZrO_2 ; (f) silica and (g) TPA-silica.

the catalysts were measured by BET surface area technique. Surface areas of various catalysts prepared are mentioned in Table 1.

3.1.2. X-ray diffraction studies

XRD patterns of different samples are as shown in Fig. 1. The degree of crystallinity is retained in the polyaniline matrix. Undoped polyemeraldine base is amorphous in nature, but incorporation of TPA results in an increase in crystallinity. XRD spectrum of unsupported TPA exhibits characteristic peaks ($2\theta = 10^\circ$ and 28°). In case of all the supported catalysts these peaks were found to retain.

3.1.3. IR spectral analysis

The stability of the Keggin structure was confirmed by FTIR spectral analysis (Fig. 2). Keggin structure remains intact on various supports. TPA exhibits typically three major bands at 1070, 981 and 890 cm^{-1} which are assigned to stretching absorption modes of oxygen atom bonded to tungsten and phosphorous (W=O), (P–O) and (W–O–W) respectively of the Keggin ion $[\text{PW}_{12}\text{O}_{40}]^{3-}$. These bands are slightly shifted due to the interaction of metal ion with the support.

3.2. Catalytic activity

3.2.1. Optimization of the reaction parameters

As a model reaction, we have chosen toluene as the substrate and benzyl alcohol as the benzylation agent. To avoid acid catalyzed polymerization and intermolecular alkylation of benzyl alcohol, toluene was taken in excess as compared to benzyl alcohol. 12-Tungstophosphoric acid (TPA) shows 80% conversion of the alcohol

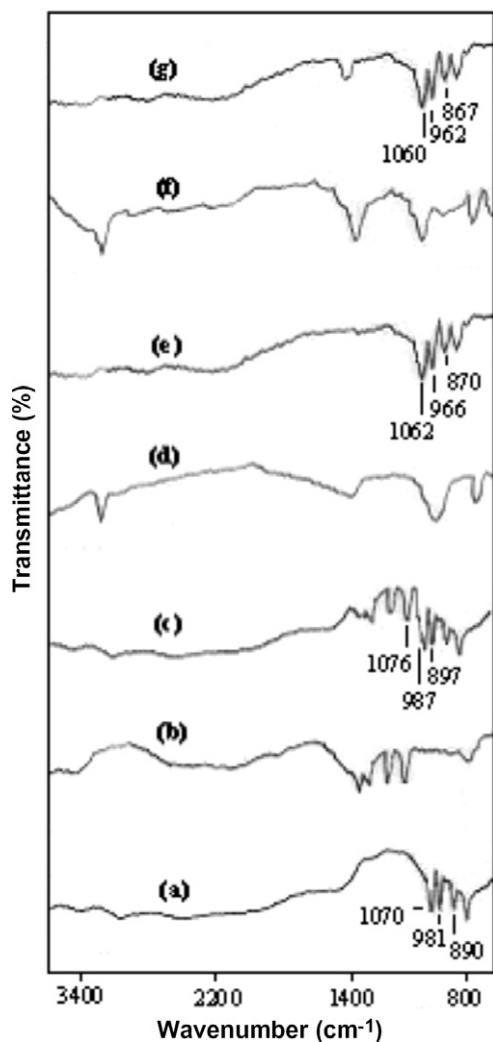


Fig. 2. FTIR spectra of (a) TPA; (b) polyemeraldine base; (c) TPA-PANI; (d) ZrO₂; (e) TPA-ZrO₂; (f) silica and (g) TPA-silica.

with 60% selectivity towards monobenylation and 40% for dibenzyl ether at 80 °C in 2 h. But when we used TPA supported on polyaniline as a catalyst, the selectivity towards monobenylation increased to 100% and only 4-benzyl toluene was formed after 4 h. No dibenzyl ether was observed at the end of the reaction. We have noticed that as the reaction progressed, dibenzyl ether formation rapidly increased as a result of intermolecular dehydration of benzyl alcohol, while the benzylation product formed slowly

Table 2
Benzylation of benzene in the presence of benzyl alcohol

Catalyst	Conversion of benzyl alcohol (%)	Selectivity (%)		
		Monobenylation	Dibenzyl ether	Dibenylation
TPA	80 ^a	60	40	–
TPA-PANI	96	100	–	–
TPA-ZrO ₂	62	90	10	–
TPA-silica gel	40	90	10	–
PANI	No reaction	–	–	–
ZrO ₂	No reaction	–	–	–
Silica	No reaction	–	–	–

Benzyl alcohol (0.05 mol), toluene (0.3 mol), catalyst amount (0.16 g) at 80 °C for 4 h.

^a Reaction was run for 2 h.

[23]. This catalyst possesses sufficient Bronsted acidity to form benzyl cation from the reaction between dibenzyl ether and water formed in the reaction through dehydration of benzyl alcohol. Hence, we did not find dibenzyl ether at the end of the reaction.

In order to support these observations, we have performed separate experiments. Dibenzyl ether (0.025 mol) and water (0.05 mol) were reacted with toluene in the presence of TPA supported on PANI. Water and toluene were used in excess to avoid polyalkylation. In this case 4-benzyl toluene was the only product obtained with 94% yield in 4 h. Also, when benzyl alcohol was reacted with TPA supported on PANI 74% dibenzyl ether was obtained in 3 h. These experiments clearly show that, with our catalytic system dibenzyl ether undergoes reversible hydrolysis to give benzyl alcohol which further reacts with toluene to give selectively monobenzylated product.

When benzyl alcohol was reacted with arenes with the other catalysts under the same conditions different product distribution was observed. In case of TPA supported on zirconia, conversion of benzyl alcohol was 62% with 90% selectivity for monobenylation and 10% selectivity for dibenzyl ether. In case of TPA supported on silica, the conversion of benzyl alcohol was 40% with 90%

Table 3
Benzylation of arenes using benzyl alcohol, in the presence of 12-tungstophosphoric acid supported on PANI using benzyl alcohol as benzylation agent in 4 h at 80 °C^a

Entry	Substrate	Conversion ^b (%)	Monobenylation selectivity (%)	
			o-	p-
1		96	–	–
2		98	–	100
3		98	100	0
4		98	100	0
5		97	32.0	68.0
6		97	26.4	75.6
7		97	25.3	74.7
8		98	24.6	76.4
9		93	30.2	69.8
10		91	30.5	69.5
11		86	32.4	67.6
12		92	22.4	77.6

^a Benzyl alcohol (0.05 mol), treated with aromatic substrate (0.3 mol) with PANI supported TPA (0.16 g) at 80 °C for 4 h.

^b Conversion with respect to benzyl alcohol.

Table 4

Comparison of the catalytic performance of other reported solid acids with 12-tungstophosphoric acid supported on polyaniline for the benzylation of benzene

No.	Catalyst	Conversion (%)	Selectivity (%)			Refs.
			DPM	BzOBz	Others	
1	TPA	80 ^a	62	38	5	–
2	TPA–PANI	96 ^b	100	0	0	–
3	TPA–ZrO ₂	62 ^b	90	10	0	–
4	TPA–silica gel	40 ^b	90	10	0	–
5	Sc(OTf) ₃ /MCM-41	100 ^c	91	1.7	7.3	[6]
6	H β (Si/Al = 15)	100 ^d	92	8	0	[7]
7	H–Mordenite	89 ^d	96	4	0	[7]
8	K10–FeAA120	84.5 ^e	27.2	72.8	0	[9]
9	K10–SbAA120	100 ^f	90.6	0	9.4	[23]
10	HPW/MCM-41	100 ^g	80	3.8	16	[24]

DPM: diphenyl methane, BzOBz: dibenzyl ether, others: dibenzylated products.

^a Benzyl alcohol (50 mmol), benzene (300 mmol), catalyst amount (160 mg) at 80 °C for 2 h.

^b Benzyl alcohol (50 mmol), benzene (300 mmol), catalyst amount (160 mg) at 80 °C for 4 h.

^c Benzyl alcohol (2 mmol), benzene (112 mmol), catalyst amount (40 mg) at 80 °C for 2 h.

^d Benzyl alcohol (2 mmol), benzene (112 mmol), catalyst amount (100 mg) at 80 °C for 1 h.

^e Benzyl alcohol (6.25 mmol), benzene (112 mmol), catalyst amount (100 mg) at 80 °C for 7 h.

^f Benzyl alcohol (6.25 mmol), benzene (112 mmol), catalyst amount (100 mg) at 80 °C for 1 h.

^g Benzyl alcohol (9.24 mmol), benzene (192 mmol), catalyst amount (50 mg) at 90 °C for 4 h.

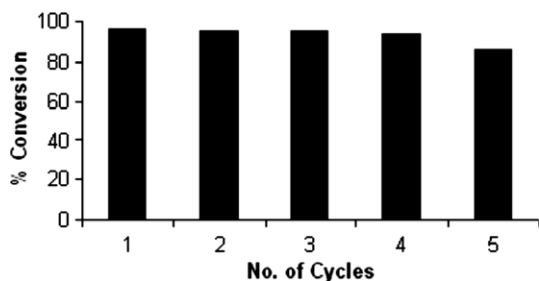


Fig. 3. Reusability study of TPA–PANI for benzylation of benzene.

selectivity for monobenzylation and 10% selectivity for dibenzyl ether (Table 2). This difference in the catalytic selectivity might be due to the considerable reduction in the Bronsted acidity and the formation of Lewis acidic sites due to the coordination of TPA with Zr⁴⁺ and Si⁴⁺. To explore the further synthetic viability of the catalyst we have studied various electron-donating as well as electron-withdrawing substrates (Table 3).

3.2.2. Comparison of the catalytic performance of TPA–PANI with reported catalysts

We have compared the catalytic performance of TPA–PANI with reported catalysts for the benzylation of benzene using benzyl alcohol as benzylating agent. The results are shown in Table 4. TPA–PANI was found to possess 100% selectivity for monobenzylation.

3.2.3. Reusability study of the catalyst

In order to find the reusability of TPA supported on PANI, it was separated from the reaction mixture, washed with hexane and acetone. The catalyst was dried in vacuum and reused for fresh lot of toluene (0.3 mol) with benzyl alcohol (0.05 mol). The catalyst was found to be reusable for five cycles without significant loss in activity. The reusability results revealed that the activity of the spent and fresh catalyst was almost the same clearly demonstrating the efficiency of the catalyst (Fig. 3).

4. Conclusion

We have designed an efficient, reusable catalyst for the monobenzylation reaction. Moreover use of benzyl alcohol as benzylating agent makes the process environmentally friendly as water is the byproduct of the reaction. Also reactant itself functions as the solvent, unreacted reactants can be recovered and reused. Hence the present protocol is suitable for industrial applications.

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