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Short Communication

Nitration of phenol over silica supported $H_4PW_{11}VO_{40}$ catalyst

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ABSTRACT

Vanadium incorporated tungstophosphoric acid ($TPAV_1$) supported on silica was synthesized and characterized by BET-surface area, Fourier transform infrared spectroscopy, X-ray diffraction and Laser Raman techniques. Nitration of phenol was studied at room temperature (25 °C) using HNO_3 in the presence of 0–20 wt.% $TPAV_1/SiO_2$ catalysts taking 1, 2-dichloroethane as solvent. The effects of various parameters such as phenol/HNO_3 mole ratio, reaction time, catalyst weight, and stirring speed on the catalyst activity were studied. 8 wt.% $TPAV_1/SiO_2$ has shown the best activity, regioselectivity and reusability in the nitration of phenol, with a conversion of 92.6% and o-nitrophenol selectivity of 97.9%.

1. Introduction

Nitration of phenol to ortho nitrophenol (ONP) is an industrially important process for which a corrosive mixture of nitric acid and sulfuric acid is used. However, over nitration and oxidation of by-products result in poor selectivity and generating huge amount of waste. The ortho/para ratio of products also remains as 1:2 [1,2]. Alternate technologies carrying the nitration with N_2O_4 [3], $NaNO_3$ [4], ceric ammonium nitrate [5], metal nitrates [6], nitronium tetrafluoroborate [7] and zirconyl nitrate [8] were partially successful. For the nitration of phenol solid acid catalysts are found to be good alternatives for sulfuric acid. The catalysts include Claycop (copper (II) nitrate supported on K10-Montmorillonite) [9], zeolites-based solid acids [10], ionic liquids [11], sulfated titania [12] and TBAB as transfer catalyst [13]. Recently, the application of nano sized tungsten oxide supported on sulfated SnO_2 [14] has also been reported. However there is a necessity for the development of new class of catalysts that could operate at room temperature (RT).

Heteropolyacids (HPAs) with Keggin structure have been used as catalysts for various acid-catalyzed reactions [15,16]. Bulk HPAs have low thermal stability, low surface area ($2\ m^2/g$) and solubility in polar solvents. However, in some supported systems, like phosphotungstic acid supported on silica, the surface area, thermal stability and water resistance can be enhanced. Parida et al. [17] and Heravi et al. [18] have carried out this reaction on silicotungstic acid supported on zirconia and vanadium incorporated molybdophosphoric acid, respectively. Among the Keggin-based super acids phosphotungstic acid ($H_3PW_{12}O_{40}$; TPA) is the most preferred one based on its thermal stability [15] and acidity [19].

In the present communication, we disclose an efficient environmentally benign, reusable $TPAV_1/SiO_2$ catalyst for phenol nitration at RT. The advantage of the present catalyst is that its preparation is simple, inexpensive and the catalyst offers high product yield within reasonable reaction time.

2. Experimental

$H_4PW_{11}VO_{40}$ ($TPAV_1$) was prepared using $NaVO_3$, Na_3PO_4, and $Na_2WO_4 \cdot 2H_2O$ (Loba Chemie, India). The preparation procedure reported by Tsigdinos et al. [20] for vanadium incorporated molybdophosphoric acid was adopted for the synthesis of $H_4PW_{11}VO_{40}$. $NaVO_3$ (7.33 mmol) dissolved in 15 ml of deionized water at 80 °C was mixed with aqueous Na_2HPO_4 (7.3 mmol in 20 ml of water) and cooled to room temperature. Concentrated H_2SO_4 (5 ml) was then added to give a red solution. Aqueous $Na_2WO_4 \cdot 2H_2O$ (79.32 mmol dissolved in 50 ml of water) was then added to the above solution drop-wise with vigorous stirring followed by slow addition of concentrated H_2SO_4. $TPAV_1$ was obtained with ether extraction followed by evaporation and recrystallization. The catalyst mass was kept for further drying in an air oven at 120 °C for 12 h and finally calcined at 300 °C for 2 h.

For the preparation of supported catalysts, calculated amounts of $TPAV_1$ (0–20 wt.%) were dissolved in deionized water and added to appropriate amounts of silica support adopting the wet impregnation method. The excess water was evaporated on a water bath, the masses were air dried at 120 °C for 8 h and then calcined at 300 °C for 4 h.

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The reactor consisted of a mechanically agitated flat-bottom glass vessel of 100 ml capacity. The assembly was kept in an isothermal oil bath at 25 °C. The typical reaction mixture consisted of 10 mmol of phenol and 10 mmol of nitric acid with 0.05 g of the catalyst, and 30 ml of 1, 2-dichloroethane (DCE) taken as solvent. The reaction was carried out at a stirring speed of 800 rpm. The product mixture was filtered, an aqueous mixture of ethyl acetate and sodium bicarbonate was then added to the filtrate, the two immiscible layers separated and the organic layer concentrated by evaporation. Isolation of the product was carried out with the reaction mixture obtained after 3 h of reaction. The products were analyzed in a GC-MS, (Shimadzu, Model QP 2010 S) using a 5 wt.% SE-30 on Chromosorb WHP capillary column.

BET surface areas of the catalysts were determined on a Micromeritics (Auto Sorb-2910) instrument with nitrogen physisorption at −196 °C. XRD patterns of the catalysts were obtained with a Rigaku Miniflex (Rigaku Corporation, Japan) using Ni filtered Cu Kα radiation ($\lambda = 1.5406$ Å). The FT-IR spectra were recorded on a DIGILAB (USA) spectrometer, with a resolution of 1 cm^{-1} using KBr disk method.

Raman spectra of the samples were collected on a UV–vis Raman spectrometer system (Horiba-Jobin Yvon LabRam-HR) equipped with a confocal microscope, 2400/900 grooves/mm gratings, and a notch filter. The UV laser excitation at 325 nm was supplied by a Yag doubled-diode pumped laser (20 mW).

3. Results and discussions

The FTIR spectra of SiO_2, $TPAV_1$ and $TPAV_1/SiO_2$ catalysts are shown in Fig. 1. The Keggin structure was intact after the incorporation of V in the tungsten matrix of TPA, as shown in the inset of Fig. 1. However, such clarity could not be obtained from the spectra of the supported catalysts. With the substitution of a V atom for W in the primary structure of the oxoanion ($TPAV_1$ catalyst), the P–O and W═O bands shifted toward lower wave numbers due to a reduced structural symmetry [14]. A new peak also appeared at 1056.8 cm^{-1} (Fig. 1) confirming the vanadium incorporation. Pure silica support exhibited three main bands at 1100 cm^{-1} (broad and very strong), 800 cm^{-1} (medium) and 470 cm^{-1} (strong), which partly overlapped with the characteristic bands of the Keggin unit [21]. This is an important observation compared with pure TPA. It should be emphasized that some bands had overlapped with those of the support. The weak absorption band at 1640 cm^{-1} (H_2O bending) indicates the presence of moisture. In the present case, the strong bands of silica masked the band at 1056.8 cm^{-1} in supported $TPAV_1$ catalysts. However, information can still be obtained from the less affected regions. The bands placed at 980 and 800 cm^{-1} can be ascribed to Keggin ion. These small non-overlapped bands also confirm the presence of the Keggin ion on the support.

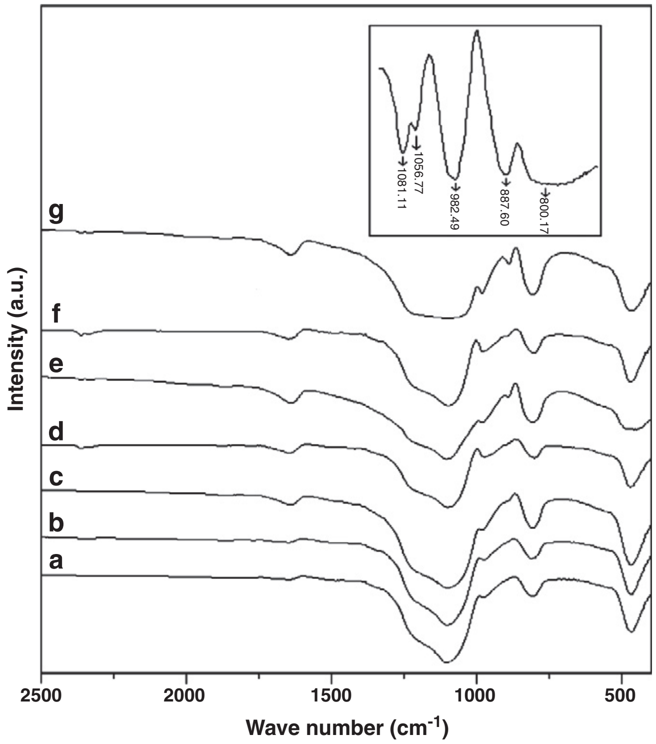

Fig. 1. FT-IR spectra of SiO_2, $TPAV_1$ and $TPAV_1/SiO_2$ catalysts. (a) SiO_2 (b) 5 wt.% $TPAV_1/SiO_2$ (c) 8 wt.% $TPAV_1/SiO_2$ (d) 10 wt.% $TPAV_1/SiO_2$ (e) 12 wt.% $TPAV_1/SiO_2$ (f) 15 wt.% $TPAV_1/SiO_2$ (g) 20 wt.% $TPAV_1/SiO_2$.

The Laser-Raman spectra of $TPAV_1/SiO_2$ catalysts are shown in Fig. 2. TPA/SiO_2 exhibited bands around 1009, 992 cm^{-1} and a broad peak around 905 cm^{-1} [22]. The Raman spectrum (Fig. 2) of $TPAV_1/SiO_2$ showed an extremely strong W═O stretching band with its maximum at 1000 cm^{-1} and other components at 981, 903 cm^{-1} at higher loadings, i.e. 12 and 20 wt.%. The peaks in the bands of $TPAV_1/SiO_2$ shifted toward lower wave numbers compared to TPA/SiO_2 [22] due to vanadium incorporation. The bands at 1000 and 981 cm^{-1} can be assigned to the terminal $W-O_t$ (O_t-terminal oxygen atom) symmetric and asymmetric stretching modes, respectively [23]. The band at 903 cm^{-1} is the characteristic band for the asymmetric stretching vibration of bridging $W-O_b-W$ (O_b-corner-sharing bridging oxygen atom). Thus, the Raman spectra also confirm the incorporation of V in TPA.

The X-ray diffractograms of the samples are shown in Fig. 3. The patterns reveal the amorphous nature of the catalysts at lower loadings due to high dispersion of the acid on silica. At higher loadings (>10 wt.% $TPAV_1$) the Keggin peaks were clearly observable. This might be due to the increase in crystallinity of $TPAV_1$ beyond 10 wt.% $TPAV_1/SiO_2$. With increasing loading of $TPAV_1$ there may be a chance for agglomeration of $TPAV_1$ particles on the surface of the support. The appearance of peaks at $2\theta = 10.24$, 20.50, 23.26 and 25.47° strongly suggests that the Keggin structure was intact in the catalysts [24].

HPAs by themselves have very low surface area. When impregnated on silica (490 m^2/g) they can be distributed on the surface of the support. The surface area (Table 1) showed a decreasing trend with increase in the amount of $TPAV_1$. It may be expected that plugging of

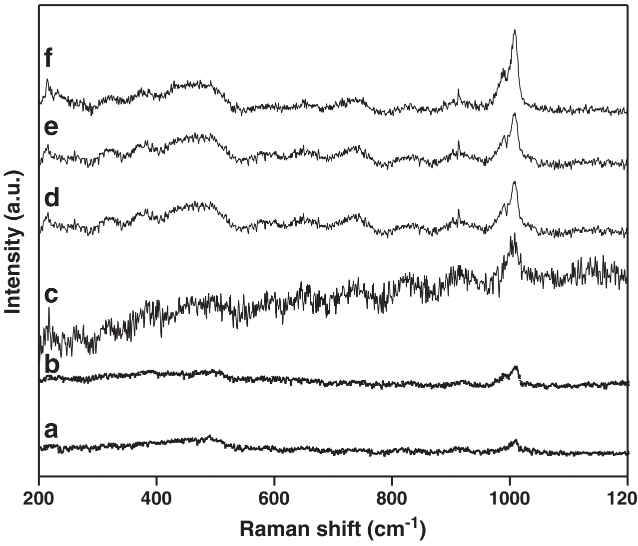

Fig. 2. Laser-Raman spectra of $TPAV_1/SiO_2$ catalysts. (a) 5 wt.% $TPAV_1/SiO_2$ (b) 8 wt.% $TPAV_1/SiO_2$ (c) 10 wt.% $TPAV_1/SiO_2$ (d) 12 wt.% $TPAV_1/SiO_2$ (e) 15 wt.% $TPAV_1/SiO_2$ (f) 20 wt.% $TPAV_1/SiO_2$.

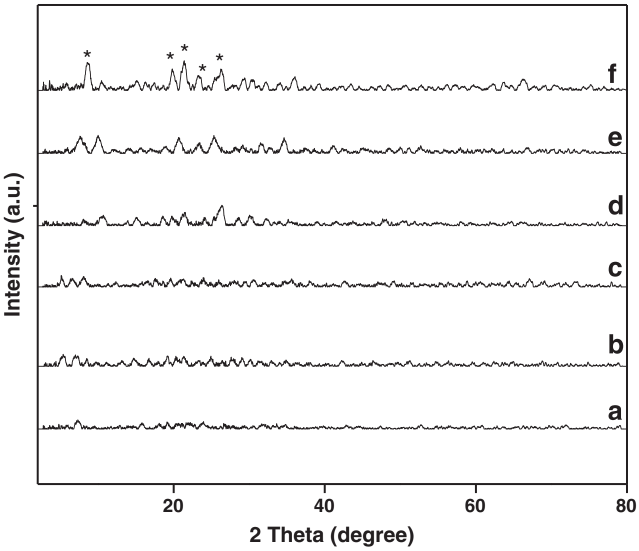

Fig. 3. XRD patterns of silica supported $TPAV_1$ catalysts. (a) 5 wt.% $TPAV_1/SiO_2$ (b) 8 wt.% $TPAV_1/SiO_2$ (c) 10 wt.% $TPAV_1/SiO_2$ (d) 12 wt.% $TPAV_1/SiO_2$ (e) 15 wt.% $TPAV_1/SiO_2$ (f) 20 wt.% $TPAV_1/SiO_2$; $TPAV_1$ (*).

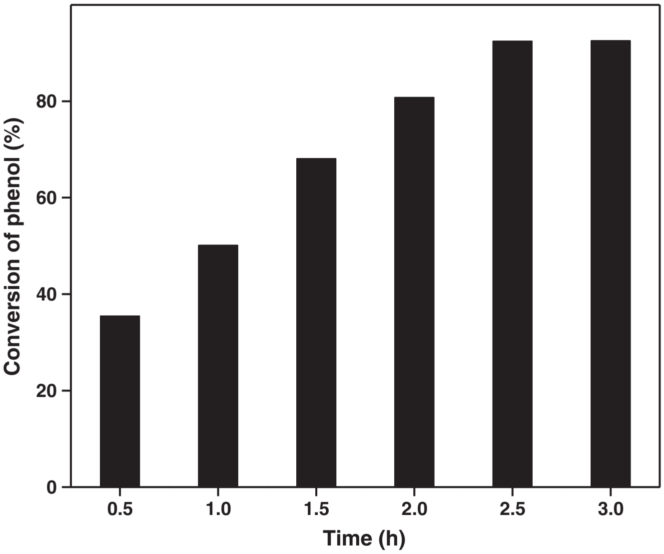

Fig. 4. Effect of reaction time on conversion of phenol.

active component in the pores of the support decreased the surface area, at least in the case of highly loaded catalysts. The significant decrease in surface area beyond 15 wt.% $TPAV_1$ can be considered as due to bulk $TPAV_1$ formation on the support surface.

The effect of the speed of agitation on activity was studied from 600 to 1200 rpm. It was observed that the conversion of phenol and the selectivity to ONP were practically the same in all the cases above 800 rpm. Hence, all further reactions were carried out at 800 rpm.

Nitration of phenol carried out on $TPAV_1/SiO_2$ catalysts at 25 °C showed excellent catalytic behavior in DCE solvent (Table 1). 8 wt.% $TPAV_1/SiO_2$ catalyzed the formation of ONP efficiently giving a total yield of 90.6% in DCE. Higher activity as well as selectivity of the catalyst may be due to high surface area and the well dispersed nature of $TPAV_1$ on silica. The activity test was also carried out on unsupported TPAV1 and TPA catalysts. The conversion (30–40%) and ONP selectivity (55–65%) were less than that of the supported system. The values obtained on TPA/SiO_2, not containing vanadium, were insignificant. The main advantage with 8 wt.% $TPAV_1/SiO_2$ is the higher ONP/PNP ratio (46.6) obtained at RT. Parida et al. [15] have reported good yield (≈86%) at room temperature but the ONP/PNP ratio was low. Heravi et al. [18] have carried out phenol nitration on unsupported vanadium (V)-substituted polyoxomolybdates, $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 1$–3), at 78 °C. The yield on WO_3 supported on sulfated SnO_2 was a maximum of 92.1% at 60 °C. Besides there was over nitration to di and trinitrophenol [25]. Our catalyst compares well with that of Sungajadevi et al. [12] in terms of environmentally benign nature of the catalyst; Jiang et al. [4] in terms of usage of less number of reactants and solvents; Dagade et al. [26] in terms of usage of lower catalyst concentration and Esakkidurai et al. [10] in terms of obtaining higher yield of ONP.

Table 1
Surface area values, conversion and selectivity data on (0–20 wt.%) $TPAV_1/SiO_2$ catalysts during nitration of phenol.

Sample	BET (m^2/g)	Phenol conversion (%)	Selectivity (%)		ONP/PNP
			ONP	PNP	
Without catalyst	–	9.5	49.3	51.7	0.9
$5TPAV_1/SiO_2$	410	60.4	87.5	12.5	7.0
$8TPAV_1/SiO_2$	380	92.6	97.9	2.1	46.6
$10TPAV_1/SiO_2$	340	80.3	93.8	6.2	15.1
$12TPAV_1/SiO_2$	318	64.0	81.9	18.1	4.5
$15TPAV_1/SiO_2$	278	55.0	59.7	40.3	1.5
$20TPAV_1/SiO_2$	190	43.4	53.7	46.3	1.1

(ONP — Ortho nitrophenol, PNP — Para nitrophenol).

Fig. 4 shows the effect of reaction time on phenol conversion at 25 °C taking DCE as solvent and 8 wt.% $TPAV_1/SiO_2$. Increase in reaction time increased the conversion giving 90.6% yield of ONP between 2.5 h and 3 h and the conversion remaining constant thereafter.

The effect of nitric acid/substrate molar ratio on conversion is shown in Table 2. With increase in molar ratio the conversion increased reaching 100% at a ratio of 1.25, with over-nitration beyond a ratio of 1.25.

The stability of 8 wt.% $TPAV_1/SiO_2$ was studied to establish its reuse. The catalyst collected by filtration after each use was washed with distilled water and dried at 120 °C. Only a marginal decrease of 3% in the activity was found after four reuses (Fig. 5), which might be due to the loss of catalyst during handling.

4. Conclusions

Regioselective nitration of phenol can be productively carried out using $TPAV_1/SiO_2$. Phenol can be selectively nitrated to ONP with nitric acid in DCE solvent. 8 wt.% $TPAV_1/SiO_2$ is found to be the optimum loading on silica. The reaction can be effectively carried out at 25 °C with high yields. The catalyst is reusable with consistent activity.

Acknowledgments

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Table 2
Effect of nitric acid/phenol mole ratio on the activity of 8 wt.% $TPAV_1/SiO_2$ at 25 °C.

Nitric acid/phenol (mole ratio)	Phenol conversion (%)
0.50	47.5
0.75	70.0
1.00	92.0
1.25	100

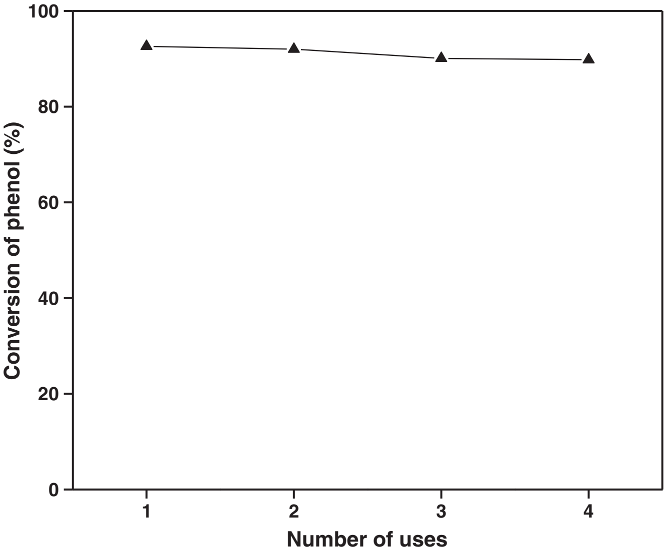

Fig. 5. Reusability of 8 wt.% $TPAV_1/SiO_2$ catalyst.

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