

SBA-15 supported HPW: Effective catalytic performance in the alkylation of phenol

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Received 10 February 2006; received in revised form 10 July 2006; accepted 19 July 2006

Available online 28 August 2006

Abstract

SBA-15 was synthesized using non-ionic surfactant as the structure directing agent at 40 °C. It was then impregnated with different loadings (10, 30, 50 and 70%) of phosphotungstic acid. They were characterized by XRD, N₂ adsorption, FT-IR and DRIFT techniques. The physicochemical characterization revealed that SBA-15 could accommodate discrete phosphotungstic acid due to its large pore volume and high surface area. The catalytic activity of these materials was examined in the vapour phase *tert*-butylation of phenol using *tert*-butyl alcohol as the alkylating agent. The influence of reaction parameters such as reaction temperature, reactant feed ratio, WHSV and time on stream was studied, and the results were correlated with physicochemical characteristics of the catalysts. 4-*tert*-Butyl phenol was observed as the major product with high selectivity. Among the catalysts, 30% phosphotungstic acid supported SBA-15 showed high phenol conversion under optimum conditions, which is significantly higher than either phosphotungstic acid loaded mesoporous AIPO or AIMCM-41.

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Keywords: SBA-15; Phosphotungstic acid; PW/SBA-15; Phenol; *tert*-Butylation

1. Introduction

Heteropoly acids (HPA) have witnessed rapid growth in the last decade as solid acid catalyst [1–3]. Polyoxometalates with Keggin structure have been chosen as catalyst because of their easy availability and extreme stability in solution as well as in solid state. 12-Tungstophosphoric acid (PW), in particular, has been the target catalyst among the Keggin series in many earlier reports because of the strongest acidity [4,5]. HPAs have several advantages that make them economically and environmentally attractive. They are good acid catalysts in homogeneous medium. They catalyse a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing compared to conventional mineral acids [6–10]. However, the main disadvantage is their very low surface area (<10 m² g⁻¹) and hence it becomes necessary to disperse HPA on supports that possess large surface area. Although silica, active carbon, acidic ion-exchange resins, etc., are suitable supports, silica is the most often used one since this is relatively

inert towards HPA [11]. Mesoporous MCM-41 have recently attracted attention as support for HPA due to its high surface area coupled with regular hexagonal array of uniform pore size within the mesoporous region [12]. SBA-15 is a newly discovered mesoporous silica molecular sieve with uniform tubular channels whose pore diameter is variable from 50 to 300 Å [13]. It has thicker pore wall and higher hydrothermal stability than MCM-41 [14]. This would make the material a suitable host for acid catalysts such as HPAs. There are a few reports available on the modification of SBA-15 with heteropoly acids and its applications [15,16]. Wang and Zhu [17] have recently reported that PW/SBA-15 exhibits high conversion, selectivity and stability in the alkylation of benzene with 1-dodecene than H-Y zeolite.

Short-chain alkyl phenols are important intermediates for the production of resins, antioxidants, drugs, dyes, polymer additives, agrochemicals and antiseptic substances [18]. The catalytic reaction of phenol with *tert*-butyl alcohol or isobutene or methyl-*tert*-butyl ether is important because C-alkylated products such as 4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol and 2,6-di-*tert*-butylphenol are commercially important. The catalytic reaction of phenol with *tert*-butyl alcohol over mesoporous catalysts in the liquid and gas phase is reported in the literature [19–28]. The present study aims at the synergetic effect of the

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high acidity of HPA and the large surface area of SBA-15 towards *tert*-butylation of phenol using *tert*-butyl alcohol. PW of various loadings supported on SBA-15 were prepared by impregnation method and characterized by powder X-ray diffraction (XRD), N₂ adsorption, FT-IR and DRIFT.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (Merck) was used as the source for silicon. Triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, EO₂₀PO₇₀EO₂₀) was used as the structure directing agent. Phosphotungstic acid was purchased from Lancaster and the other chemicals such as absolute ethyl alcohol (Heymann), phenol (Merck) and *tert*-butyl alcohol (Merck) were used as such without further purification.

2.2. Preparation of catalysts

SBA-15 was synthesized using amphiphilic triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol). The typical synthesis procedure for SBA-15 is as follows: 4 g of amphiphilic triblock copolymer was dispersed in 30 g water. A clear solution was obtained after 3 h of stirring. To the solution 120 g of 2 M HCl was added and stirred for further 2 h. Thereafter, 9 g tetraethylorthosilicate (TEOS) was added to the homogeneous solution under stirring. The resulting mixture was stirred at 40 °C for 24 h and finally heated at 100 °C for 48 h. The solid product was recovered by filtration, washed several times with water and dried over night at 100 °C. Finally, the product was calcined in a flow of air at 540 °C to remove the template.

Supported catalyst was prepared by impregnation of phosphotungstic acid (PW) (H₃PW₁₂O₄₀) on mesoporous SBA-15 by adopting the reported procedure [29]. PW loadings of 10, 30, 50 and 70 wt% supported on SBA-15 were prepared and used in the catalytic studies.

2.3. Characterization

The powder X-ray diffraction patterns of the synthesized materials were collected on a PANalytical X'pert PRO diffractometer using Cu K α ($\lambda = 0.154$ nm) radiation. The diffractograms were recorded in the 2θ range 0.8–30° with a scan rate of 1.2° min⁻¹. Surface area and pore volume were measured by nitrogen adsorption at -196 °C using SMARTSORB 92/93 from Smart instruments company, India. The sample was degassed at 200 °C for 2 h under nitrogen atmosphere prior to analysis. The specific surface area was calculated using BET method. The pore diameter of the materials was obtained from the absorption branch of the nitrogen isotherm using the corrected form of the Kelvin equation by means of Barrett–Joyner–Halenda method as proposed by Kruk et al. [30]. FT-IR spectra of the materials were recorded on a Nicolet (Avatar 360) FT-IR spectrophotometer using KBr pellet technique. About 15 mg of the

sample was pressed (under a pressure of 2 tonnes/cm²) into a self-supported wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range 4000–400 cm⁻¹. The in situ DRIFT spectra were recorded in a Nicolet (Avatar 360) FT-IR spectrophotometer equipped with a high temperature vacuum chamber. About 15 mg of powdered catalyst sample was dehydrated under vacuum (10⁻⁵ mbar) at 250 °C and then cooled to room temperature. Pyridine was adsorbed at the same temperature and allowed to equilibrate. The catalyst was then evacuated under vacuum (10⁻⁵ mbar) at 150 °C for 30 min. The sample was then cooled to room temperature and the spectrum was recorded.

2.4. Catalytic studies

tert-Butylation of phenol was carried out in a fixed-bed, flow-type reactor made up of Borosil glass tube of length 40 cm and internal diameter 2 cm. About 0.5 g of catalyst placed in the reactor tube was heated to the reaction temperature with the help of a tubular furnace controlled by a digital temperature controller. Reactants were fed into the reactor using a syringe infusion pump that could be operated at different flow rates. The bottom of the reactor tube was connected to a coiled condenser and a receiver to collect the products. The liquid products were analysed with a Shimadzu GC-17A gas chromatograph using DB-5 capillary column equipped with flame ionization detector. Further the products were identified using a GC-MS Perkin-Elmer Auto System XL gas chromatograph equipped with a mass spectrometer (Model: Turbo) with helium as the carrier gas.

3. Results and discussion

3.1. Characterization

XRD patterns of SBA-15, PW and PW/SBA-15 of various loading are shown in Fig. 1. The XRD patterns of parent SBA-15 show three well resolved peaks at 0.89°, 1.50° and 1.72° which are indexed to (1 0 0), (1 1 0) and (2 0 0) reflections of ordered hexagonal mesophase as reported earlier [13]. It is interesting to note that, with increase in PW loadings, the intensity of peaks corresponding to (1 1 0) and (2 0 0) planes decreases. It is observed that up to 30%PW loading, the XRD pattern is not affected significantly and also there are no characteristic peaks of bulk PW crystals. Further, the comparison of the XRD patterns of SBA-15 and 30%PW/SBA-15 reveals that the mesoporous structure is rather intact even after the loading of PW. This implies high dispersion of PW on the support. However 50%PW alters the intensity of peaks corresponding to (1 1 0) and (2 0 0) planes apart from giving rise to additional peaks at 9.2° and 25° which are characteristics of bulk PW crystals which are more pronounced with 70%PW loading. Unlike other supports, SBA-15 could accommodate more discrete PW because of its large pore volume and high surface area. The bulk PW peaks could be observed in the amorphous silica and mesoporous AlPO even with PW loading of 25 and 20%, respectively [31,32]. The textural properties of SBA-15 and PW/SBA-15 catalysts are given in Table 1. SBA-15 exhibits high surface area, and as expected,

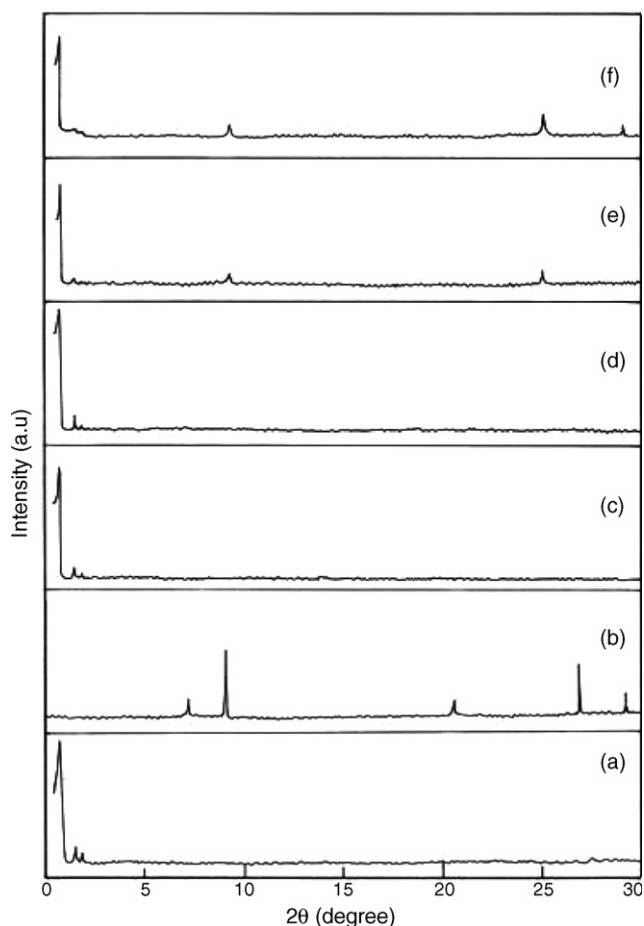


Fig. 1. XRD patterns of (a) SBA-15, (b) PW, (c) 10%PW/SBA-15, (d) 30%PW/SBA-15, (e) 50%PW/SBA-15 and (f) 70%PW/SBA-15.

surface area and pore volume of PW/SBA-15 decrease with the increase in PW loading. It is suggested that most of the PW crystallizes inside the pores of the support. The d_{100} spacing derived from XRD and surface area and pore volume derived by the BET method for SBA-15 and PW/SBA-15 catalysts are presented in Table 1. This observation reveals pore size contraction as a consequence of lining of mesoporous channel by a PW film [32]. Therefore, it is presumed to be present as a uniform film or as a monolayer coverage. The presence of such a type of layer was also already discussed by Liu et al. [33]. It is observed that $480 \text{ m}^2/\text{g}$ of surface area is achieved for 30%PW loading and further loading of 50 and 70%, surface area decreases considerably. This may be attributed to the formation of bulk PW crystals in the pores of SBA-15.

Table 1
Physicochemical characteristics of SBA-15 and PW/SBA-15 materials

Catalyst	A_0 (Å)	d_{100} spacing (Å)	Surface area (m^2/g)	Pore volume (cm^3/g)
SBA-15	114.4	99.1	712	1.05
10%PW/SBA-15	113.6	98.0	560	0.90
30%PW/SBA-15	113.6	98.0	480	0.68
50%PW/SBA-15	111.8	96.9	384	0.46
70%PW/SBA-15	110.7	95.9	297	0.38

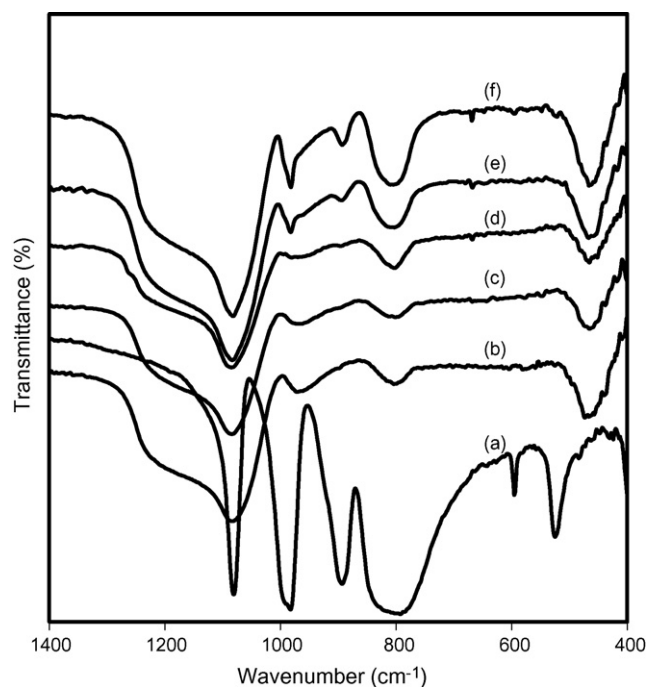


Fig. 2. FT-IR spectra of (a) PW, (b) SBA-15, (c) 10%PW/SBA-15, (d) 30%PW/SBA-15, (e) 50%PW/SBA-15 and (f) 70%PW/SBA-15.

The expulsion of template after calcination was established by FT-IR analysis [34]. Fig. 2 illustrates FT-IR spectra of SBA-15, pure PW and PW/SBA-15 with different loadings. Pure PW shows IR bands approximately at 1081 (P–O in the central tetrahedron), 989 (terminal W=O) and 898 and 806 (W–O–W) cm^{-1} corresponding to asymmetric vibration associated with Keggin ion [35]. The IR bands at approximately 989, 898 and 806 cm^{-1} are clearly observed for all the loaded catalysts and further they are intensified significantly when the PW loading increases from 10 to 70%. This indicates that the primary structure of heteropoly acid is preserved even after supporting on SBA-15.

The in situ DRIFT spectra of pyridine-adsorbed catalysts are shown in Fig. 3. The characteristic skeletal vibrations of

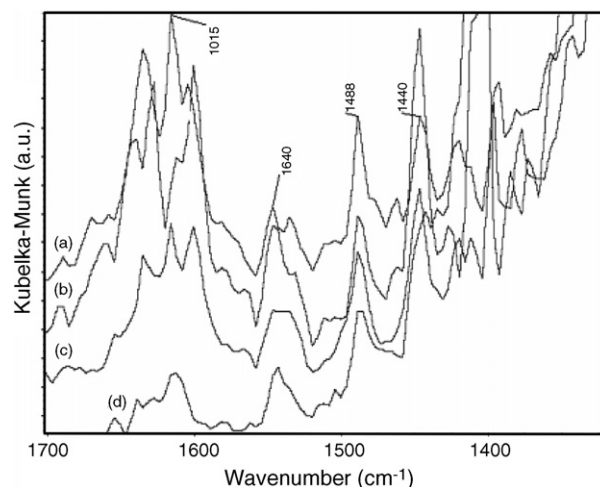


Fig. 3. DRIFT spectra of pyridine adsorption over (a) 70%PW/SBA-15, (b) 50%PW/SBA-15, (c) 30%PW/SBA-15 and (d) 10%PW/SBA-15.

Table 2
Bronsted and Lewis acidity values for PW/SBA-15

Catalyst	Bronsted (B) acid site (mmol/g)	Lewis (L) acid site (mmol/g)	B/L acid site ratio
10%PW/SBA-15	0.13	0.24	0.54
30%PW/SBA-15	0.25	0.31	0.81
50%PW/SBA-15	0.18	0.23	0.78
70%PW/SBA-15	0.15	0.20	0.75

Desorption temperature = 200 °C.

pyridine adsorbed on Lewis acid sites (1446 cm^{-1}), Bronsted acid sites (1548 cm^{-1}) and both Bronsted and Lewis acid sites (1488 cm^{-1}) are clearly evident in all the spectra [36]. The peak at 1615 cm^{-1} is assigned to pyridine associated with strong Lewis acid sites [37] and the peak at 1636 cm^{-1} is assigned to pyridinium ion ring vibration due to pyridine bound-Bronsted acid sites [38]. Further the acidity of the catalyst is calculated using extinction co-efficient of the bands of Bronsted and Lewis acid sites adsorbed pyridine [39] and the acidity values are presented in Table 2. The data in the table indicate high amount of Bronsted and Lewis acid sites in 30%PW/SBA-15. 10%PW/SBA-15 shows lower intensity for Bronsted acid adsorbed pyridine than 30%PW/SBA-15 illustrating absence of sufficient amount of Keggin units. 30%PW/SBA-15 exhibits more intense peak at 1548 cm^{-1} than 50 and 70%PW/SBA-15. Although Keggin structure is evident in all the three catalysts, the relatively low intense peak for higher loading might be due to diffusional constraint. This illustrates a prominent increase in the Bronsted acid sites in 30%PW/SBA-15 as observed from the values in Table 2. The PW forms a fine monolayer dispersion in 30%PW/SBA-15 whereas it aggregates on the pore walls and also block the pore size for 50 and 70%PW/SBA-15, thus leading to poor adsorption and diffusion of reactants and products.

3.2. Catalytic studies

tert-Butylation of phenol was carried out over 10, 30, 50 and 70%PW loaded SBA-15 catalysts in the vapour phase at 175, 190, 200, 225, 250 and 275 °C with a feed ratio 1:3 (phenol:*tert*-butyl alcohol) and WHSV 5.13 h^{-1} . The results are presented in Table 3. The conversion increases with increase in PW loading up to 30% and further increase of PW loading decreases the conversion (Fig. 4). When the PW loading is enhanced from 10 to 30%, the acid sites of the catalyst increase but further increase in loading (50 and 70%) does not result increase of conversion due to aggregation of PW particles on the pore walls and blocking of pores. It is evident from the data in Table 3 that increase of temperature shows pronounced effect on both conversion and products selectivity. As the reaction temperature increases from 175 to 275 °C, the conversion increases slowly, reaches a maximum at 190 °C and decreases thereafter. The predominance of oligomerization of isobutene at high temperatures decreases the conversion.

Among the three products, 4-*tert*-butyl phenol (4-TBP) is obtained with high selectivity over all the catalysts (Table 3). Its selectivity increases significantly with temperature and attains

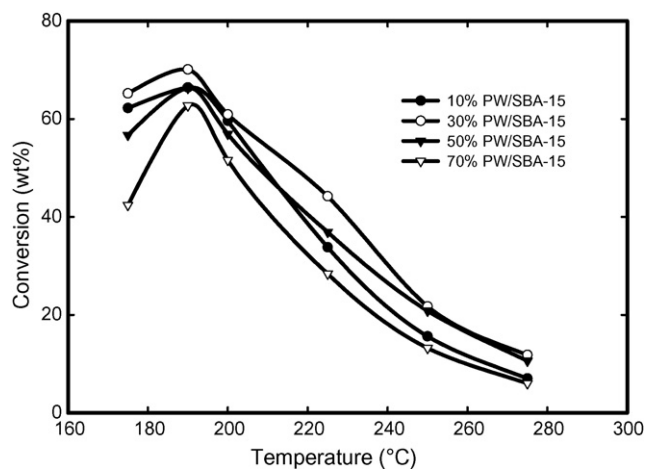


Fig. 4. Conversion of phenol over PW/SBA-15 loaded catalysts as a function of temperature with WHSV = 5.13 h^{-1} and feed ratio = 1:3 (phenol:*tert*-butyl alcohol).

89% at 275 °C over 30%PW/SBA-15. However, the conversion is only 11% at that temperature. The observed high para-selectivity with low phenol conversion has also been reported over other catalysts [40,41]. The selectivity of 2-*tert*-butyl phenol (2-TBP) is low over all PW loaded catalysts since Bronsted acid sites of the loaded catalysts will facilitate adsorption of phenol on the acid sites thus reducing the selectivity of 2-TBP. The selectivity of 2,4-di-*tert*-butyl phenol (2,4-DTBP) is high at low temperature and decreases with increase in temperature. This is due to high stability and availability of *tert*-butyl cation at low temperature which readily reacts with 2-TBP yielding 2,4-DTBP [41]. Among the supported catalysts, 30%PW/SBA-15 is found to exhibit high conversion of phenol which is very well in agreement with acidity measurement data (Table 2). Hence further study was carried out over 30%PW/SBA-15 catalyst.

The effect of feed ratio, viz., 1:1, 1:2, 1:3 and 1:4 on phenol conversion and products selectivity was studied over 30%PW/SBA-15 at 190 °C with WHSV 5.13 h^{-1} . The results are depicted in Fig. 5. The phenol conversion increases with increase in the *tert*-butyl alcohol content in the feed, but the increase is not linear. The increase in conversion is not appre-

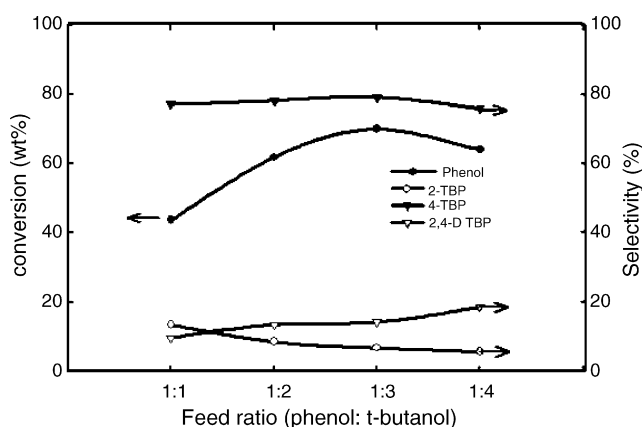


Fig. 5. Effect of feed ratio on phenol conversion and products selectivity over 30%PW/SBA-15 catalyst at 190 °C.

Table 3

Catalytic activity of PW/SBA-15 catalysts in the *tert*-butylation of phenol WHSV = 5.13 h⁻¹; feed ratio = 1:3 (phenol:*tert*-butyl alcohol)

Catalyst	Temperature (°C)	Phenol conversion (%)	Product selectivity (%)		
			2-TBP	4-TBP	2,4-DTBP
10%PW/SBA-15	175	62.2	6.6	77.3	16.1
	190	66.4	7.1	80.6	12.3
	200	59.6	7.7	82.2	10.1
	225	33.8	9.8	83.7	6.5
	250	15.6	10.3	89.7	–
	275	7.0	10.0	90.0	–
30%PW/SBA-15	175	65.2	6.4	78.2	15.4
	190	70.1	6.6	79.2	14.2
	200	60.9	7.2	81.4	11.4
	225	44.2	9.5	81.4	9.1
	250	21.7	9.7	87.6	2.7
	275	11.8	11.0	89.0	–
50%PW/SBA-15	175	56.7	6.0	80.2	13.8
	190	66.3	7.2	80.8	12.0
	200	56.9	7.2	84.2	8.6
	225	36.9	9.5	84.6	5.9
	250	20.8	9.7	88.5	1.8
	275	10.6	9.4	90.6	–
70%PW/SBA-15	175	42.4	6.6	82.1	11.3
	190	62.7	7.5	83.6	8.9
	200	51.6	7.8	84.7	7.5
	225	28.4	9.5	87.0	3.5
	250	13.2	10.6	89.4	–
	275	6.0	–	100.0	–

ciable at 1:3 feed ratio and falls away from the expected value. The increase of feed ratio from 1:1 to 1:3 certainly increases the formation of *tert*-butyl cation on the Keggin surface of PW. Hence even at the feed ratio 1:3 there must be enough number of free acid sites to chemisorb *tert*-butyl alcohol in order to give enhanced conversion. However at 1:4 feed ratio there may be excess unadsorbed *tert*-butyl alcohol which can dilute phenol and partly prevent from reacting with *tert*-butyl cation. The selectivity to 4-TBP remains nearly the same for all the feed ratios, although there is a slight decrease in the selectivity at 1:4 feed ratio. The selectivity to 2-TBP decreases when feed ratio change from 1:1 to 1:4, but the selectivity to 2,4-DTBP increases from 1:1 to 1:4. The decrease in the selectivity of 2-TBP and increase in the selectivity of 2,4-DTBP for different feed ratios appear to be nearly equal in magnitude, suggesting that 2-TBP may be the main precursor for 2,4-DTBP.

The important observation in the effect of feed ratio and of temperature studies is the higher selectivity to 4-TBP than 2-TBP. Since phenol adsorption mainly occurs through its OH group on the surface of Keggin phase, it can be suggested that such adsorption may be prevalent only when the *tert*-butyl cations are not close to the ortho positions of phenol whereas the para position of adsorbed phenol can very well be brought to electrophilic reaction with any alkyl cation chemisorbed close to it. This observation therefore predicts that the electrophilic reaction of phenol with *tert*-butyl alcohol occurs through chemisorption of phenol on the Keggin phase surface through its OH group. Even the main precursor, namely, 2-TBP for the formation of 2,4-DTBP should also require steric free adsorption of phenolic OH

on the Keggin phase surface. This again warrants substitution at the fourth position of 2-TBP, which is already chemisorbed through its OH group.

The effect of WHSV on phenol conversion and products selectivity over 30%PW/SBA-15 was studied at 190 °C with a feed ratio 1:3. The results obtained for different WHSVs are illustrated in Fig. 6. The phenol conversion increases nearly linearly from the initial WHSV of 1.71–5.13 h⁻¹. This increase of phenol conversion suggests clustering of phenol at lower WHSVs which suppress alkylation whereas at higher WHSVs the dispersal of phenol facilitates high conversion. But above 5.13 h⁻¹ the conversion decreases due to rapid diffusion of phe-

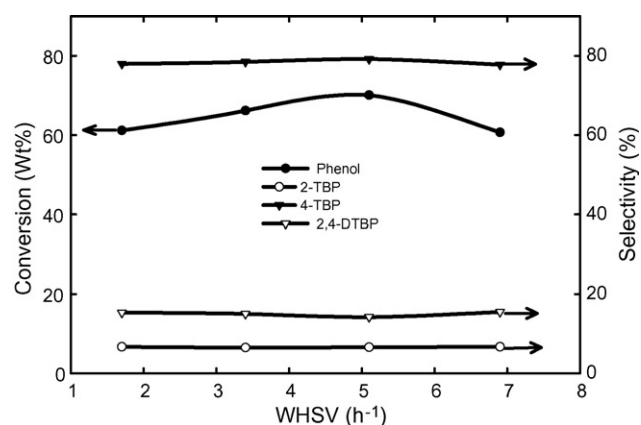


Fig. 6. Effect of WHSV on phenol conversion and products selectivity over 30%PW/SBA-15 at 190 °C with the feed ratio 1:3 (phenol:*tert*-butyl alcohol).

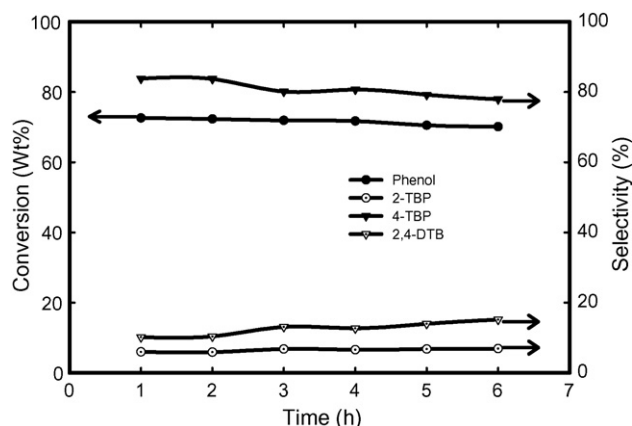


Fig. 7. Effect of time-on-stream on phenol conversion and product selectivity over 30%PW/SBA-15 at 190 °C, WHSV 5.13 h⁻¹ and feed ratio 1:3 (phenol:*tert*-butyl alcohol).

nol from the pores which may be the cause for reduced reaction. Thus the negative effect of WHSVs is clearly observed only above 5.13 h⁻¹. The selectivity to 4-TBP and 2-TBP remains nearly the same with increase in WHSV. This observation illustrates that mesopore structure of the catalyst may be convenient to maintain selectivity of the products over a range of WHSVs. The selectivity of 2,4-DTBP also remains invariant for different WHSVs. Although the consecutive alkylation of 2- or 4-TBP to 2,4-DTBP is a time dependent reaction, the steady value of selectivity illustrates that even WHSV 6.85 h⁻¹ is not sufficiently high to show any variation. Such behavior in these materials may be due to randomly distributed PW Keggin phase that offer constraint for this free diffusion by which the probability both mono- and bi-alkylation can be increased and leveled. As the reactants and products are diffused through the pores very close to PW Keggin phase, there must be certainly more probability for adsorption giving nearly the same product selectivities. Although there is a slight decrease in conversion above 5.13 h⁻¹, the decrease is not very remarkable even for nearly 2 unit increment in WHSVs.

The effect of time on stream on *tert*-butylation of phenol over 30%PW/SBA-15 was carried out with a feed ratio 1:3 and WHSV 5.13 h⁻¹ at 190 °C and the results are depicted in Fig. 7. The phenol conversion remains almost steady with time

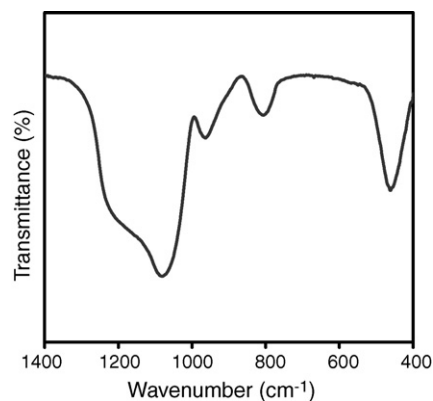


Fig. 8. FT-IR spectrum of 30%PW/SBA-15 spent catalyst after activating at 400 °C for 8 h.

on stream. Hence deactivation of the catalyst by coke deposition or formation of polybutenes is not so important in this study. As a consequence the selectivity of 4-TBP also remains almost steady. Slight decrease in conversion or selectivity does not appear to be important. The selectivity to 2,4-DTBP shows a slight increase with increase in time on stream as a result of slight decrease in the selectivity of 4-TBP. 2-TBP may not be a significant contributing factor to the selectivity of 2,4-DTBP as it does not show decrease in selectivity with time on stream. From these observations it is concluded that adsorption of 4-TBP or 2-TBP is largely prevented in comparison to phenol and hence both 2 and 4-TBP remaining in the vapour phase react with *tert*-butyl cation.

The recyclability of the catalyst was checked by activating the spent catalyst (30%PW/SBA-15) for 8 h in the presence of air at 400 °C and studied its catalytic activity. Fig. 8 shows the FT-IR spectrum of the spent activated catalyst. The three finger print peaks at 975, 898 and 806 cm⁻¹ of Keggin anion of PW clearly indicate that the Keggin structure of PW dispersed on the support is thermally stable at 400 °C [7]. The reaction was then carried out at 190 °C with a feed ratio 1:3 and WHSV 5.13 h⁻¹. The observed conversion of 66.2% over the spent activated catalyst is comparable with that of fresh catalyst where the conversion is found to be 70.1%.

The data in Table 4 compare the results of *tert*-butylation of phenol with *tert*-butyl alcohol over AIMCM-41 (56),

Table 4

Comparison of phenol conversion and product selectivity over 30%PW/SBA-15 with other catalysts under comparable reaction conditions

	30%PW/SBA-15 (this work)	30%PW/SBA-15 (this work)	AIMCM-41 (56) [21]	FeAIMCM-41 (20) [26]	20%PW/AIPO [25]
Phenol: <i>tert</i> -butyl alcohol	1:3	1:3	1:2	1:3	1:3
WHSV (h ⁻¹)	5.13	5.13	4.8	5.12	5.25
Reaction temperature (°C)	175	190	175	200	200
Phenol conversion (%)	65.2	70.1	35.9	70.1	55.5
Selectivity (%)					
TBPE	–	–	–	–	16.3
2-TBP	6.4	6.6	8.1	10.4	8.5
3-TBP	–	–	4.7	–	–
4-TBP	78.2	79.2	83.4	75.2	74.7
2,4-TBP	15.4	14.2	3.9	14.4	–

Reaction time = 1 h.

FeAlMCM-41 (20), 20%PW/AlPO and 30%PW/SBA-15. The data clearly reveal that the performance of 30%PW/SBA-15 in the phenol conversion is significantly higher than AlMCM-41 (56), 20%PW/AlPO and comparable with FeAlMCM-41 (20) catalysts. It is known that MCM-41 and mesoporous AlPO possess unidimensional cylindrical channels without interconnecting pores whereas SBA-15 possess two-dimensional hexagonal mesopores with pore size is much larger than MCM-41 and mesoporous AlPO, which is the advantage of SBA-15 as support.

4. Conclusion

The present investigation reveals that Keggin structure of phosphotungstic acid is retained even at higher loadings in SBA-15. The 30%PW/SBA-15 material is found to possess high Bronsted acidity as evidenced from the pyridine adsorption studies. The catalytic activity of PW/SBA-15 samples in the *tert*-butylation of phenol illustrates that 30%PW/SBA-15 is the most active catalyst. The phenol conversion of 70% over this catalyst is significantly higher than 20%PW supported mesoporous AlPO under the same condition. Although 50 and 70%PW/SBA-15 contain higher number of Keggin units than 30%PW/SBA-15, they exhibit less activity due to partial blocking of pores. The retainment of almost the same activity for 6 h of stream by 30%PW/SBA-15 is an important observation. The recyclability of the spent catalyst is yet another interesting aspect of PW/SBA-15.

Acknowledgements

The authors gratefully acknowledge the financial support from the Department of Science and Technology (DST) (Sanction No. SR/S1/PC-24/2003), Government of India, New Delhi, for this research work. One of the authors (G. Satish Kumar) is grateful to DST for the research fellowship. The authors acknowledge the powder XRD facility created in the Department out of the liberal funding from DST under FIST program.

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