Liquid phase bromination of phenol
III. Over heteropoly acid (HPA)-impregnated titanium phosphate (TiP)

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Abstract

Heteropoly acid (HPA)-impregnated titanium phosphate (TiP) was prepared by an incipient wetness impregnation method by varying the weight percent of HPAs like phosphotungstic acid (PWA), phosphomolybdic acid (PMoA), silicotungstic acid (SiWA) and silicomolybdic acid (SiMoA). All the samples were characterized by XRD, FTIR, acid sites, pore size distribution, and TG-DTA. The catalytic activities of all the samples were evaluated by carrying out the liquid phase bromination of phenol using KBr and hydrogen peroxide. The reaction products were analysed by GC through a capillary column. From the product analysis it was found that PWA/TiP, dried at 110 °C shows the highest conversion (98%). Even so SiWA/TiP dried at 110 °C shows the highest *para*-selectivity (30%), higher than any other HPA/TiP. The selectivity increases with an increase in the activation temperature up to 400 °C and thereafter it remains constant. The reaction proceeds through the formation of Br⁺ (bromonium ion) which attacks the phenol ring, forming different brominated products.
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Keywords: Heteropoly acid-impregnated titanium phosphate; Bromination; Potassium bromide; Hydrogen peroxide; *para*-selectivity

1. Introduction

Halogenated organic compounds form an important class of intermediates as they can be converted efficiently into other functionality by simple chemical transformations. Halogenated arenes and alkanes are precursors to organometallic reagents [1] useful in synthetic organic chemistry. Introduction of bromine into organic molecules is an important and fundamental reaction in organic chemistry, owing to the considerable commercial importance of such compounds. They can be used as potent, antitumor, antibacterial, antifungal, antineoplastic, antiviral and antioxidising agents and also as industrial intermediates in the manufacture of pharmaceuticals, agrochemicals and other speciality products, for instance, flame-retardants [2–6]. The traditional bromination involves the use of nonselective hazardous acidic reagents such as mineral acids and metal halides, which can lead to separation difficulties and unacceptable levels of toxic, corrosive and waste materials. The classical direct bromination of aromatic compounds suffers from being wasteful in bromine employed, one half ends up as hydrogen bromide. In large-scale operations this is an environmental as well as an economic problem. Oxybromination [7–10] using HBr as a bromine source, H_2O_2 as an oxidant which was thought to be possible solution to overcome this said difficulties met with partial success, since HBr is highly toxic and corrosive as harmful as molecular bromine to the environment. The replacement of such reagents by nontoxic and more selective reagents is very desirable and represents an important goal in the context of clean synthesis.

Heteropoly acids and their acidic salts having the Keggin structure are known to be excellent acid catalysts [11–14]. Heteropoly acids are polyoxometalates made up of heteropolyanions having metal-oxygen octahedral as the basic structural unit [15]. They can be represented by the general formula: $[XM_{12}O_{40}]^{x-8}$ where X is the central heteroatom (Si⁺⁴, P⁺⁵, etc.), x is its oxidation state, and M is the metal ion (W⁺⁶, Mo⁺⁶, V⁺⁵, etc.). The negative charge can be compensated by

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hydrogen ions or a wide variety of cations (e.g. HPA salts). One of the main drawbacks of the Keggin-type HPA is their low specific surface area (1–10 m^2/g) [16,17] that limits their applications in gas–solid phase reactions. The catalytic activity of supported HPA depends on the HPA loading, the pretreatment conditions and the type of the support material. Acidic or neutral substances such as: SiO$_2$ [18,19], active carbon [20,21], acidic ion-exchange resin [22], TiO$_2$ [23,24] are suitable as supports. Also the thermal stability of HPA is influenced by the support [25,26]. Oxidative bromination of a range of aromatics with HBr in presence of oxygen catalysed by heteropoly acid [27] and regioselective oxybromination of phenols with HBr gas catalysed by H$_5$PMo$_{10}$V$_2$O$_{40}$ (HPA-2) are also reported [10].

In the present work, we have used heteropoly acid (HPA)-impregnated TiP as catalyst for the liquid phase bromination of phenol taking easily available KBr as the brominating source and H$_2$O$_2$ as the oxidant.

2. Experimental

2.1. Material preparation

The heteropoly acids (HPAs) such as phosphotungstic acid (PWA), phosphomolybdic acid (PMoA), silicotungstic acid (SiWA) and silicomolybdic acid (SiMoA) were prepared by the method described in the literatures [28,29]. HPA-impregnated TiP was prepared by an incipient wetness impregnation method. Appropriate quantity of HPA in weight percent was taken in 1 g of neat TiP in aqueous solution in a beaker. It was heated to 70 °C with continuous stirring till complete dryness. Then it was kept in the air oven at 110 °C overnight and activated at various temperatures for further study.

2.2. Physico-chemical characterization

The XRD patterns were taken on a Philips PW 1710 diffractometer with automatic control. The patterns were run with monochromatic Cu K$_\alpha$ radiation with a scan rate of 2° min^{-1}.

The FTIR spectra were taken using a Nicolet Instruments Corporation instrument (Model: Magna 550) in a KBr matrix in the range of 400–4000 cm^{-1}.

The strong and Bronsted acid sites of all the samples were determined by the spectrophotometric method [30] by irreversible adsorption of pyridine (PY) and 2, 6-dimethyl pyridine (DMPY).

Average pore volume, average pore radius and pore size distribution were determined by N$_2$ adsorption–desorption method at liquid nitrogen temperature (−196 °C) using SORPTOMATIC 1990 SERIES instrument. Prior to adsorption–desorption measurements all the samples were degassed at 110 °C in vacuum for 5 h.

TG-DTA analyses of samples dried at 110 °C were carried out using a Thermal Analyzer (Perkin-Elmer (TG/DTA), Model: Diamond). The thermogravimetry (TG) and differential thermal analysis (DTA) experiments were performed in N$_2$ using 4–5 mg samples at a heating rate of 10 °C/min.

2.3. Procedure for liquid phase bromination of phenol

Two hundred milligrams HPA/TiP (catalyst), substrate (phenol = 2 mmol) and KBr (2.2 mmol) in acetic acid (4 ml) were taken in a 100 ml two-necked round-bottomed flask. 30% H$_2$O$_2$ (2.2 mmol) was then added drop-wise to the reaction mixture and the contents were allowed to stir at room temperature [31]. After 5 h of the reaction, the catalyst was filtered and washed with ether, followed by the washing with sodium bicarbonate. The organic layer was extracted with ether and dried over anhydrous sodium sulfate. The products were analysed with a Shimadzu GC (GC-17A) through a capillary column.

3. Results and discussion

3.1. Physico-chemical characterization

Figs. 1 and 2 show the XRD pattern of 15 wt.% of HPAs (PWA, PMoA, SiWA and SiMoA) impregnated TiP dried at
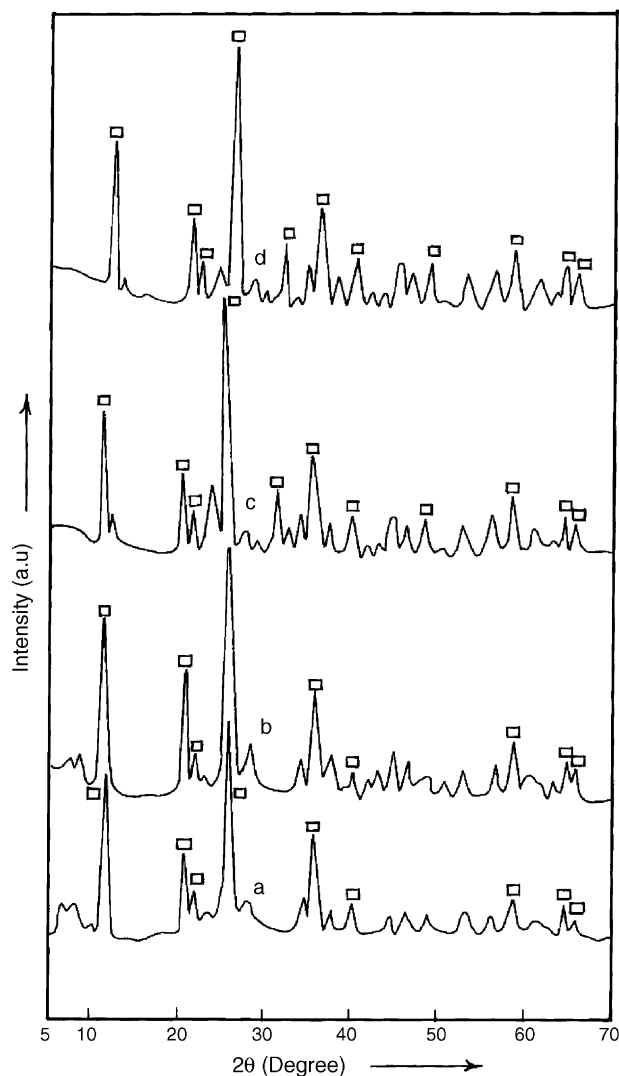

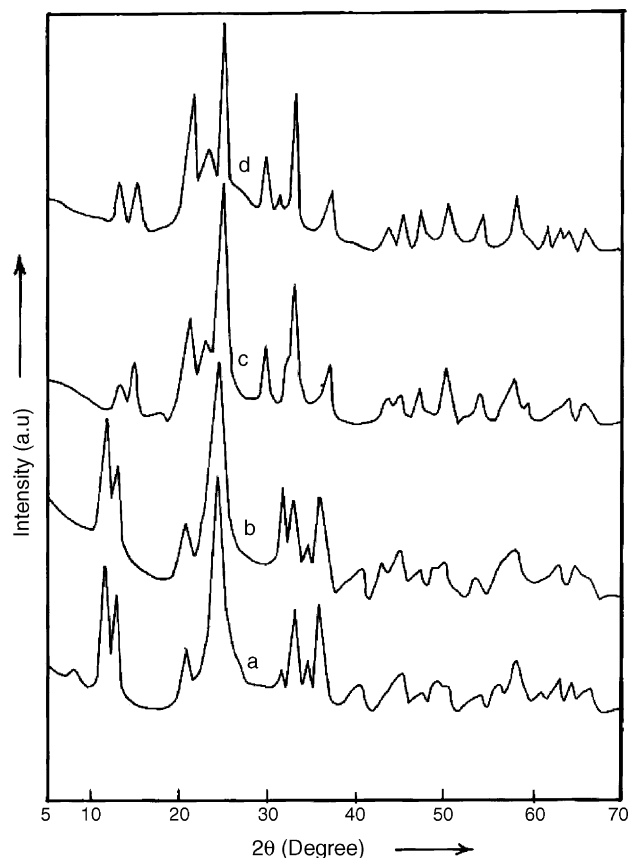Fig. 1. XRD patterns of 15 wt.% samples of (a) PWA/TiP (b) PMoA/TiP (c) SiWA/TiP (d) SiMoA/TiP, dried at 110 °C.

Fig. 2. XRD pattern of 15 wt.% SiWA/TiP activated at (a) 200 °C (b) 300 °C (c) 400 °C (d) 500 °C.

Fig. 3. FTIR spectra of (a) 5 (b) 10 (c) 15 (d) 20 wt.% PWA/TiP, dried at 110 °C.

Fig. 4. FTIR spectra of (a) 5 (b) 10 (c) 15 (d) 20 wt.% PMoA/TiP, dried at 110 °C.

110 °C and calcined form of SiWA impregnated TiP (15 wt.%), respectively. Fig. 1 shows that all the impregnated products are well crystalline. The blank squares indicate the peaks due to TiP. The other peaks are coming from Keggin molecules. Some peaks of HPA also overlapped with that for TiP. This may possibly be due to the interaction of HPA with that of TiP as support. Similar observations were reported by Chimienti et al. [32]. Fig. 2 shows that with increase in the calcination temperature the crystallinity increases for 15 wt.% SiWA loaded TiP. This may be due to the well dispersion of species on the surface of the support at higher temperature. It was also observed that, with increase in the temperature, the Keggin molecule breaks up to form a WO_3 species which is stable at higher temperature.

Figs. 3-6 show the FTIR spectra of different weight percent of PWA, PMoA, SiWA and SiMoA-impregnated TiP. It was observed that for 110 °C dried samples, the Keggin bands are found at 1021.2, 613.9 and 522 cm^{-1} for PWA/TiP (Fig. 3). Similarly at 1031.4, 1011, 619 and 542.6 cm^{-1} for PMoA/TiP (Fig. 4), at 1031.4, 614 and 522 cm^{-1} for SiWA/TiP (Fig. 5) and at 1128, 619, 547 and 410 cm^{-1} for SiMoA/TiP (Fig. 6) are observed. With increase in the loading of HPA intense bands are observed. The band observed at 1622–1627 cm^{-1} for 110 °C dried HPA-impregnated TiP may be due to the bending vibrations of –OH of water associated with PO_4^{3-} which supports the presence of water of crystallisation in the lamellar solids. In all cases an adsorption band was observed in between 3600
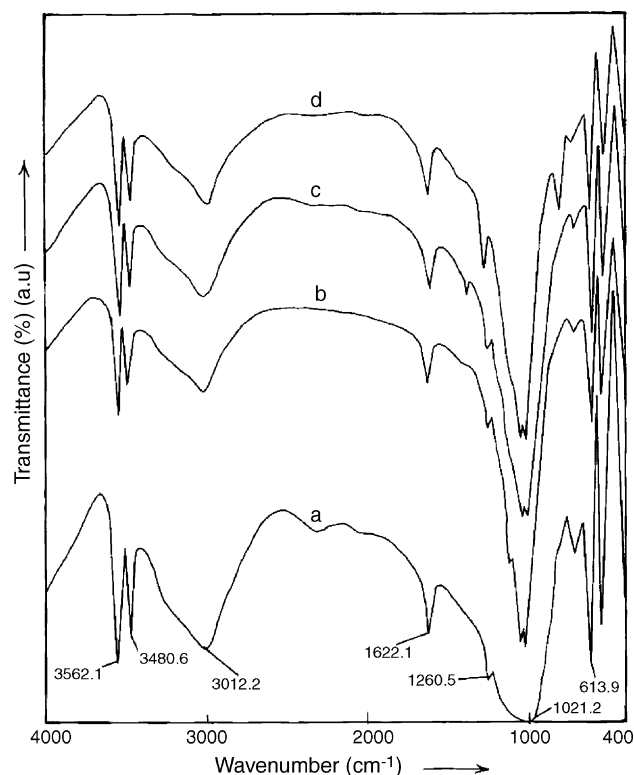
Fig. 5. FTIR spectra of (a) 5 (b) 10 (c) 15 (d) 20 wt.% SiWA/TiP, dried at 110 °C.
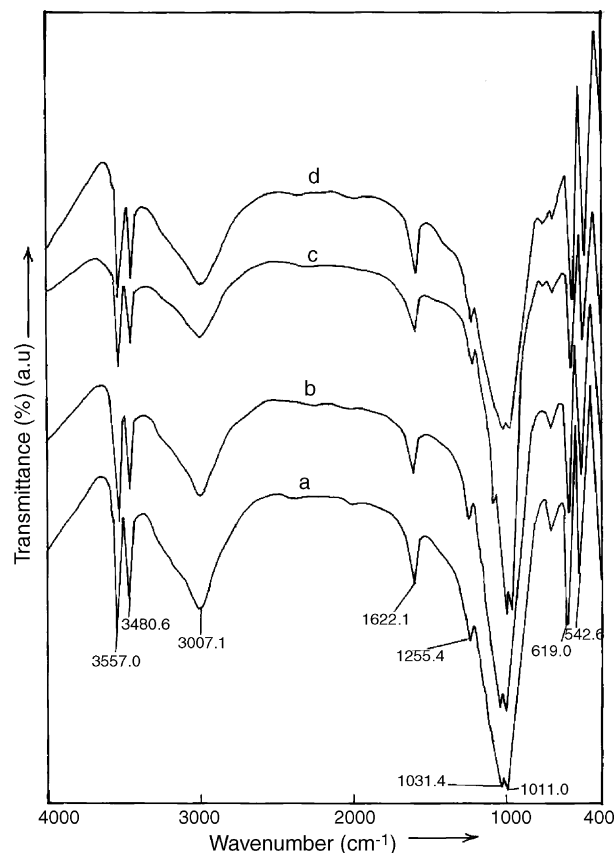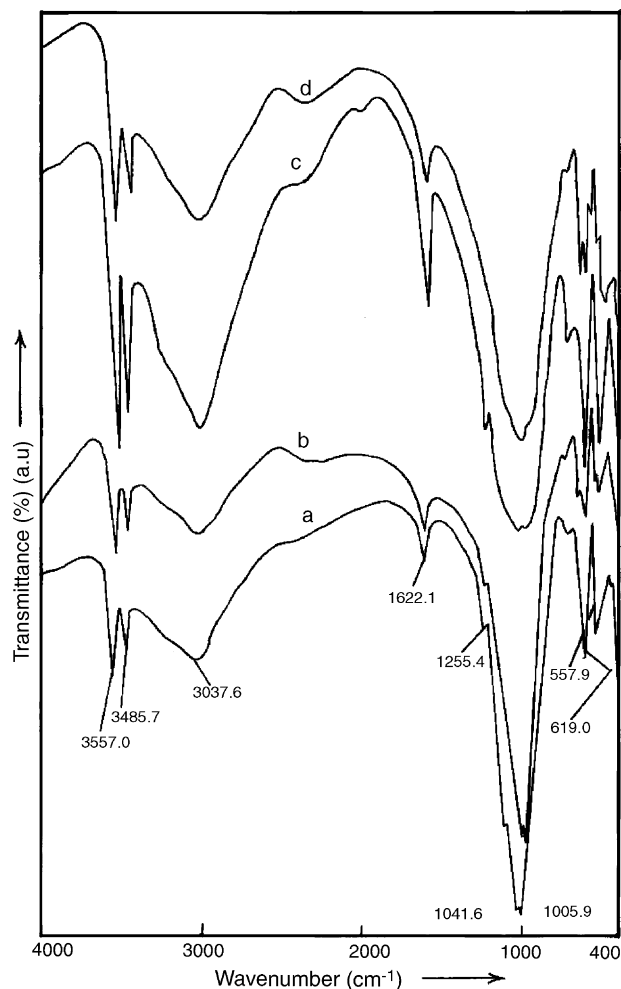

Fig. 6. FTIR spectra of (a) 5 (b) 10 (c) 15 (d) 20 wt.% SiMoA/TiP, dried at 110 °C.
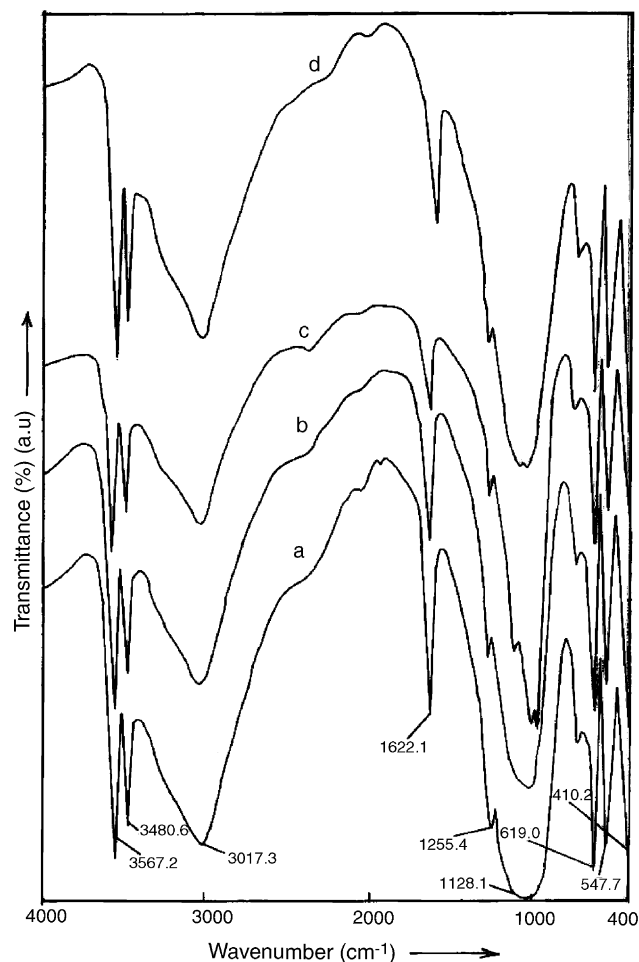
and 3000 cm^{-1} which is probably due to stretching vibration of –OH group and of physically adsorbed water and the broadness of the peak is mainly due to the existence of hydrogen bond [33–35]. One can see the respective peak is absent in case of calcined 15 wt.% SiWA/TiP (Fig. 7) due to loss of –OH groups, this could be the main reason for decrease of the acid sites at higher temperature which is also proved by acid sites determination (Table 1). The broad peak in the region of 3600–3400 cm^{-1} in calcined and uncalcined samples was observed which is mainly due to the stretching vibration of P–OH and Ti–OH. In Fig. 7, a Lacunary [W$_{11}$SiO$_{39}$]$^{-8}$ Keggin anions, i.e. a defect Keggin structure lacking one WO$_3$ unit in the region of 995 cm^{-1} was observed in the 500 °C calcined SiWA/TiP along with the disappearance of the band at 1627 cm^{-1}. This is in agreement with the observation reported by Lopez-Salinas et al. [36] for 12-tungstophosphoric acid supported on zirconia.

From Table 1, it was observed that the 15 wt.% PWA/TiP has the highest value of Bronsted acid sites (82.52 μmol/g) as well as the strong acid sites (130.3 μmol/g). On the other hand by varying the weight percent of different HPAs the strong as well as the Bronsted acid sites go on increasing as these acids are considered to be superacids or Bronsted acid rich acids [37]. But above 15 wt.%, the acid sites remains almost constant. The acid
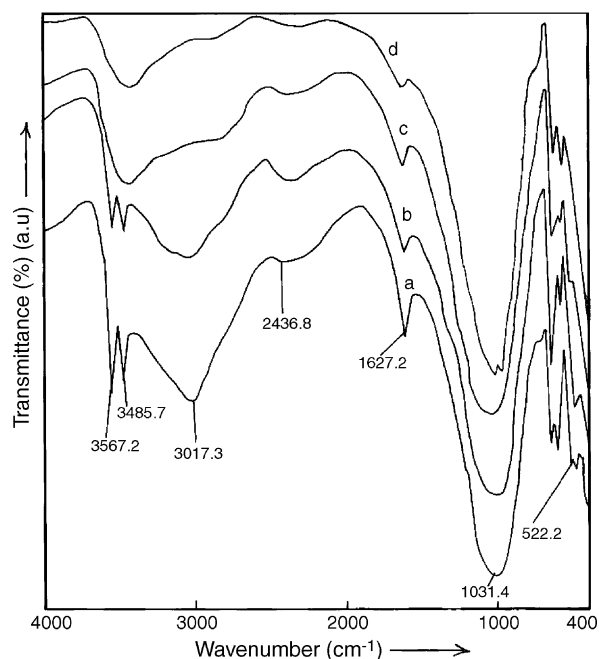

Fig. 7. FTIR spectra of 15 wt.% SiWA/TiP activated at (a) 200 °C (b) 300 °C (c) 400 °C (d) 500 °C.

Table 1
Strong and Bronsted acid sites of various HPA-impregnated TiP

Sample code	Strong acid sites (μmol/g)	Bronsted acid sites (μmol/g)
5 wt.% PWA/TiP[a]	112.2	72.93
10 wt.% PWA/TiP	120.9	77.32
15 wt.% PWA/TiP	130.3	82.52
20 wt.% PWA/TiP	131	84
5 wt.% PMoA/TiP[b]	99.2	49.2
10 wt.% PMoA/TiP	104.39	52.19
15 wt.% PMoA/TiP	108.56	54.92
20 wt.% PMoA/TiP	109	55.5
5 wt.% SiWA/TiP[c]	110.32	60.49
10 wt.% SiWA/TiP	117.53	63.9
15 wt.% SiWA/TiP	127.49	70.53
20 wt.% SiWA/TiP	128	71.2
5 wt.% SiMoA/TiP[d]	80.9	26.93
10 wt.% SiMoA/TiP	84.52	28.25
15 wt.% SiMoA/TiP	88.93	30.23
20 wt.% SiMoA/TiP	89.2	31
15 wt.% SiWA/TiP 200 °C	121.59	60
15 wt.% SiWA/TiP 300 °C	113.9	49.2
15 wt.% SiWA/TiP 400 °C	111.32	46.12
15 wt.% SiWA/TiP 500 °C	110	45

  [a] Phosphotungstic acid (PWA)-impregnated titanium phosphate.
  [b] Phosphomolybdic acid (PMoA)-impregnated titanium phosphate.
  [c] Silicotungstic acid (SiWA)-impregnated titanium phosphate.
  [d] Silicomolybdic acid (SiMoA)-impregnated titanium phosphate.

sites of PWA/TiP is the highest, even so the SiWA/TiP showed the highest *para*-selectivity (Table 2). The acid activity of the catalysts based on HPA/TiP depends on the preparation technique and different operative variables, since both determine the nature of HPA species present on the surface, their concentration, their dispersion and interaction with the support. During the impregnation there is a strong interaction between HPA and

Table 2
Liquid phase bromination of phenol[a] using different HPA-impregnated TiP

Catalysts[b]	Conversion (%)	Selectivity (%)[c]		
		2-BP	4-BP	di-BP
5 wt.% PWA/TiP	88	74	26	0
10 wt.% PWA/TiP	94	81	18	1
15 wt.% PWA/TiP	98	91	9	0
20 wt.% PWA/TiP	98.5	92	6	2
5 wt.% PMoA/TiP	74	57	25	15
10 wt.% PMoA/TiP	78	61	15	24
15 wt.% PMoA/TiP	83	70	10	20
20 wt.% PMoA/TiP	84	73	8	19
5 wt.% SiWA/TiP	86	70	30	0
10 wt.% SiWA/TiP	91	74	25	1
15 wt.% SiWA/TiP	97	79	21	0
20 wt.% SiWA/TiP	98	82	15	3
5 wt.% SiMoA/TiP	65	54	24	22
10 wt.% SiMoA/TiP	69	59	21	20
15 wt.% SiMoA/TiP	72	62	19	19
20 wt.% SiMoA/TiP	73	64	15	21

  [a] Phenol (2 mmol), KBr (2.2 mmol), H_2O_2 (2.2 mmol), Catalyst (200 mg) and acetic acid (4 ml).
  [b] HPA-impregnated TiP dried at 110 °C.
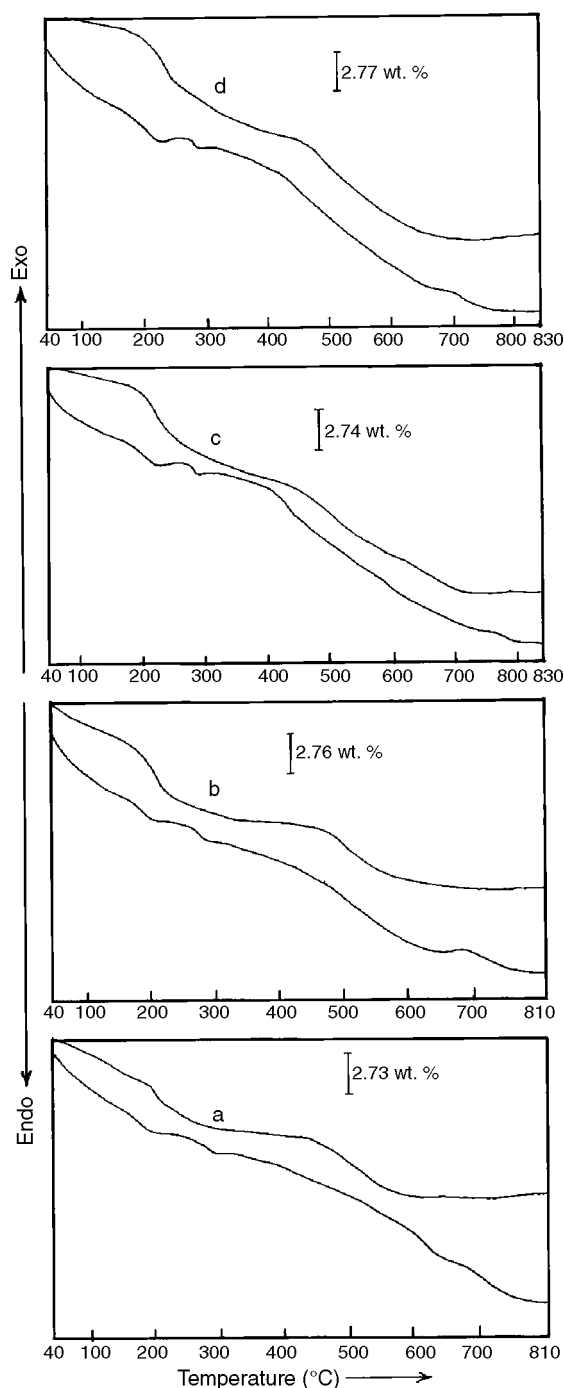 [c] The products were identified and quantified by GC.

Fig. 8. TG-DTA of 15 wt.% samples of (a) PWA/TiP (b) PMoA/TiP (c) SiWA/TiP (d) SiMoA/TiP, dried at 110 °C.

TiP is assumed to of electrostatic type due to transfer of proton to TiP.

Fig. 8 shows the thermal analysis report of 15 wt.% HPA/TiP (HPA, different heteropoly acids). The DTA of HPA/TiP shows that in all cases there are two endothermic peaks at around 190–205 and 280–290 °C associated with the loss of water molecules. An broad weak exothermic peak was observed in the range 300–650 °C, which could possibly be due to the combined effect of Keggin ion transformation and slow phase transition from layered TiP to titanium pyrophosphate (TiP is not com-
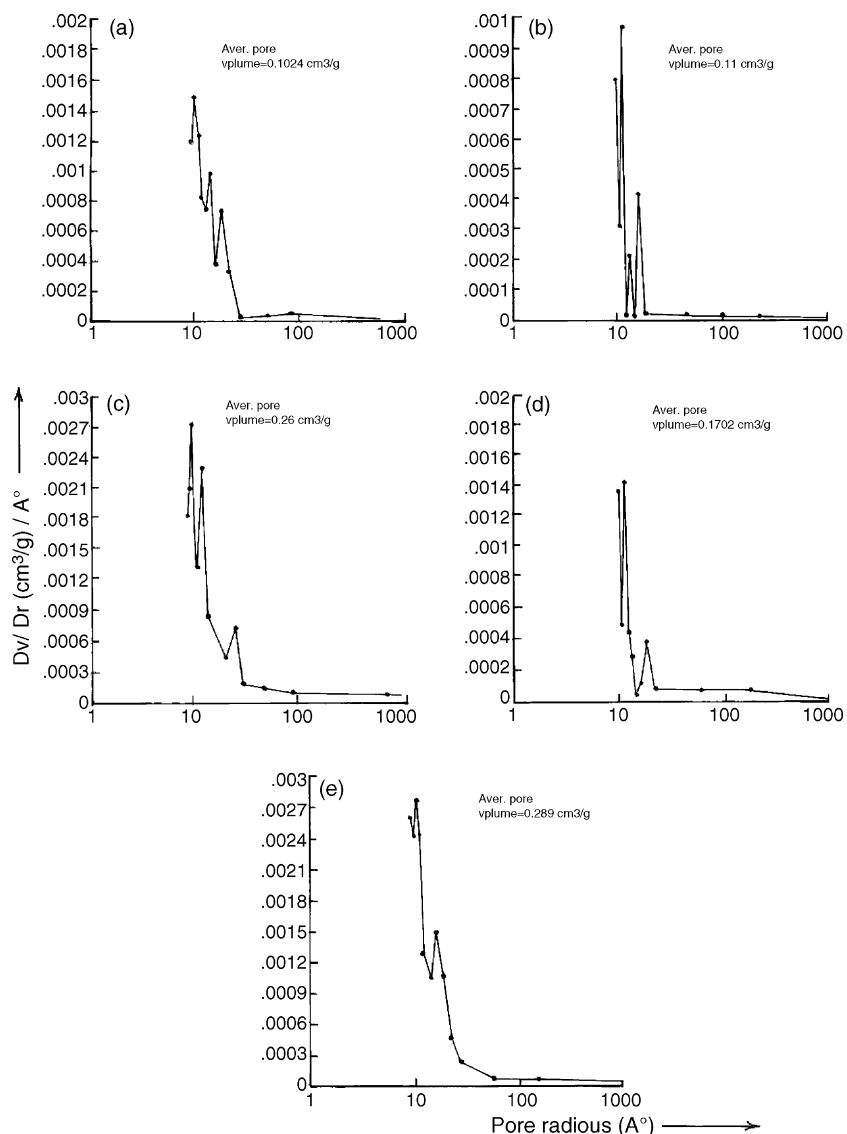
Fig. 9. Pore size distribution of 15 wt.% samples of (a) PWA/TiP (b) PMoA/TiP (c) SiWA/TiP (d) SiMoA/TiP, dried at 110 °C (e) SiWA/TiP, calcined at 400 °C.

pletely converted to TiP$_2$O$_7$). This observation was also reported earlier by Parida et al. [38]. The Keggin ion decomposition of HPA in different HPA/TiP was observed as a exothermic peak in the range of 680–700 °C.

Fig. 9(a)–(e) represent the pore size distribution of 15 wt.% HPA-impregnated TiP and 400 °C calcined 15 wt.% SiWA-impregnated TiP. It was observed that all most all samples are found to be mesoporous. The average pore volume was found to be in the range of 0.1–0.3 cm^3/g. One can see the pore volume of 15 wt.% SiWA-impregnated TiP, calcined at 400 °C was found to be much higher than that of other HPA-impregnated TiP (0.289 cm^3/g).

3.2. Catalytic activity

We have investigated the use of different weight percent concentrations of HPA-impregnated titanium phosphate, as catalyst in the bromination reaction of phenol with KBr and hydrogen

peroxide at room temperature in acetic acid. The results (Table 2) show that all the catalysts dried at 110 °C are active for catalyzing the reaction. The selectivity values (%) of 4-BP, 2-BP and di-BP obtained are shown in Table 2.

From Table 2, it was found that 15 wt.% PWA/TiP, dried 110 °C showed the highest conversion (%), i.e. 98%. In the similar way, the 15 wt.% SiWA/TiP, dried at 110 °C was also showing almost the same conversion (97%). But one can clearly notice that the 4-BP formation is found to be more in the case of 15 wt.% SiWA/TiP than in that of PWA/TiP. Except PWA/TiP and SiWA/TiP, all other cases along with 4-BP and 2-BP, significant amount of di-BP was also formed. So the variations of different reaction parameters were studied on 15 wt.% SiWA/TiP.

3.2.1. Effect of activation temperature

To study the effect of activation temperature, the catalyst 15 wt.% SiWA/TiP was activated at the temperature ranging from 110 to 500 °C. Fig. 10 shows the rate of phenol conversion
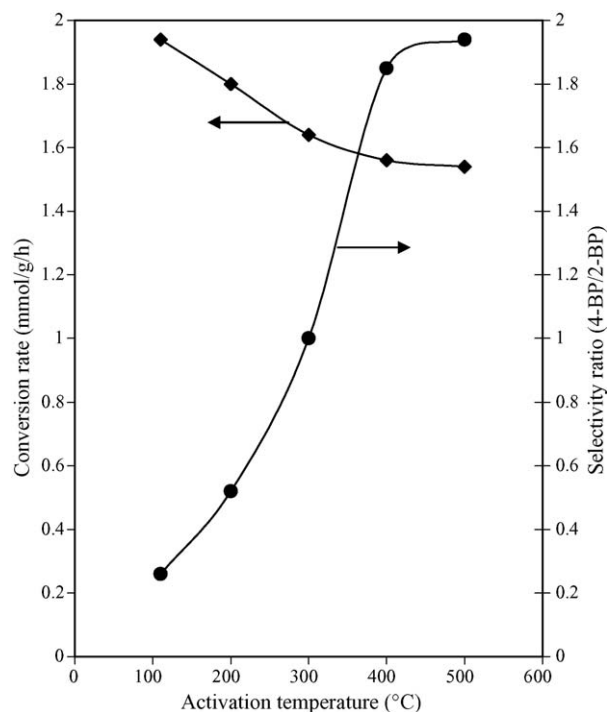
Fig. 10. Effect of activation temperature on the rate of conversion of phenol and selectivity ratio (4-BP/2-BP). Phenol = 2 mmol; KBr = 2.2 mmol; 30%H_2O_2 = 2.2 mmol; catalyst = 200 mg; acetic acid = 4 ml and reaction time = 5 h.

Fig. 11. Effect of reaction time (h) on conversion (%) and selectivity ratio (4-BP/2-BP). Phenol = 2 mmol; KBr = 2.2 mmol; 30%H_2O_2 = 2.2 mmol; catalyst = 200 mg and acetic acid = 4 ml.

(mmol/g/h) and selectivity (4-BP/2-BP) as a function of activation temperature. With activation temperature the rate of phenol conversion decreases from 1.94 to 1.54 mmol/g/h, but there is a noticeable increase in the selectivity (4-BP/2-BP). Narender et al. [31] reported that Bronsted acid sites are responsible for the formation of brominated products. So we can say due to loss of Bronsted acid sites (Table 1) at higher activation temperature, the rate of phenol conversion decreases. With increase in the activation temperature, the selectivity ratio increases from 0.26 to 1.85. This is probably due to presence of Lewis acid sites which is in agreement with Choudary et al. [39]. After 400 °C the selectivity ratio as well as conversion rate remain almost constant. This may be due to formation of Lacunary species at 500 °C which was confirmed from FTIR (Fig. 7). Again the pore volume results (Fig. 9) also support the above observations. The pore volume of 400 °C calcined SiWA/TiP was found to be 0.289 cm^3/g which is higher than any other HPA-impregnated TiP dried at 110 °C.

3.2.2. Effect of reaction time

Fig. 11 explains the effect of variation of reaction time on percentage of conversion and product selectivity (4-BP/2-BP), the rest of the conditions remaining constant. With increase in the reaction time from 0.5 to 6 h, the percentage of conversion and selectivity ratio increase from 23.29% to 78% and from 1.05 to 1.85, respectively up to 5 h, thereafter the values remain almost constant. Definite trend was not observed in the formation of 2-BP and di-BP. In all cases 4-BP is the major product.
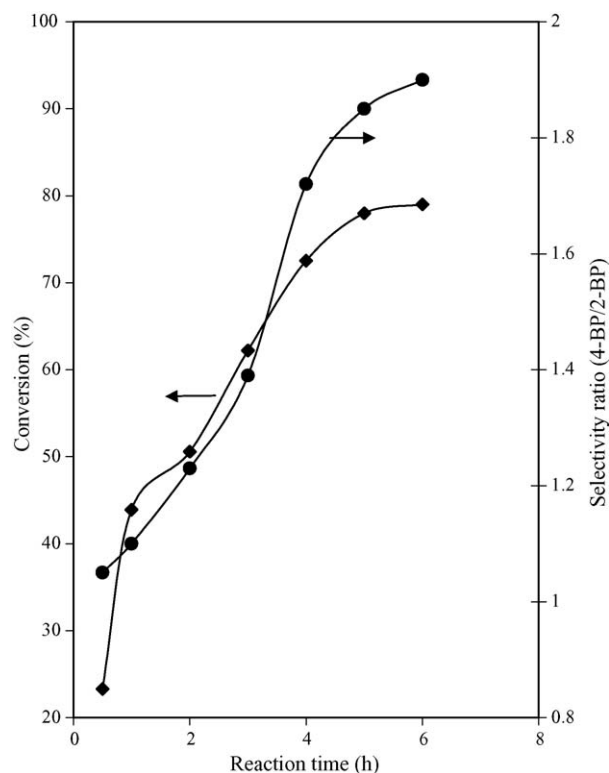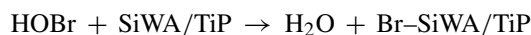
3.2.3. Effect of catalyst concentration

Fig. 12 shows the effect of catalyst concentration[1] on selectivity (4-BP/2-BP) and conversion (%) over 400 °C heated 15 wt.% SiWA/TiP. With increase in the catalyst concentration from 25 to 125 g/mol, the percentage of conversion and selectivity ratio (4-BP/2-BP) increase from 38.92 to 78% and from 1.23 to 1.85, respectively. Thereafter these values remain constant.

4. Possible mechanism

The possible mechanism is similar to that mentioned by Das et al. [40]. The SiWA/TiP with hydrogen peroxide forms peroxo species [41] in presence of acetic acid. The formed peroxometal species enhances the oxidation of Br$^-$ (KBr) to Br$^+$ (HOBr) which reacts in presence of acidic centers of SiWA/TiP with phenol to give brominated compounds (Scheme 1).

The best results were obtained by taking acetic acid compared to other solvents. This is because of the fact that in presence of H_2O_2, acetic acid forms peracetic acid which is a stronger oxidant than H_2O_2 and effective for the oxidation of Br$^-$ to Br$^+$ [31]. This may be the reason for which acetic acid is preferred as solvent over others.

$$HOBr + SiWA/TiP \rightarrow H_2O + Br-SiWA/TiP$$

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[1] Catalyst concentration means the amount of catalyst being changed with the phenol concentration remaining the same and is expressed as g/mol of phenol.
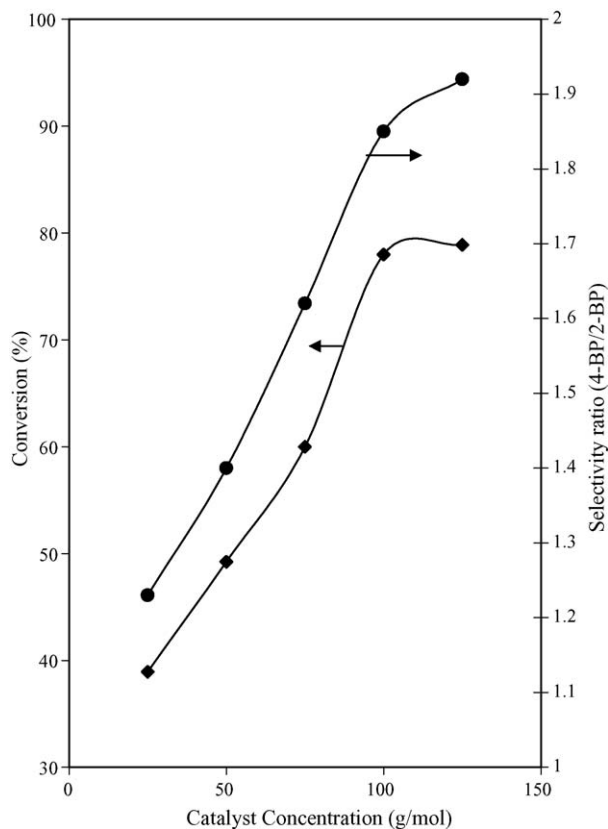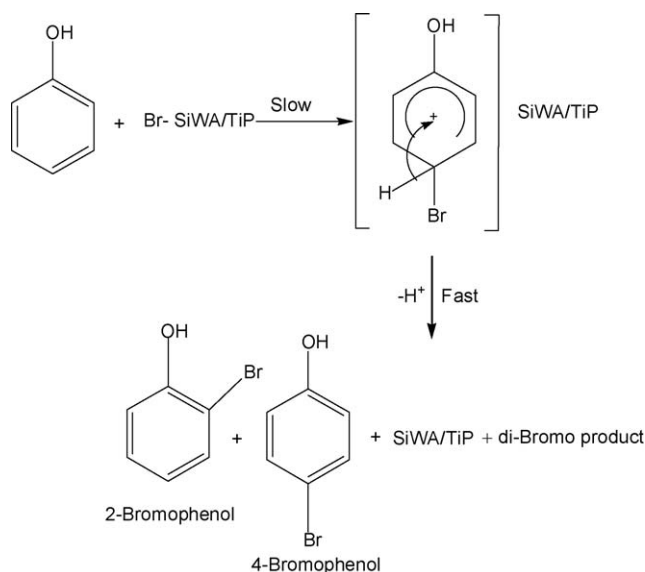
Fig. 12. Effect of catalyst concentration (g/mol) on conversion (%) and selectivity ratio (4-BP/2-BP). Phenol = 2 mmol; KBr = 2.2 mmol; 30% H_2O_2 = 2.2 mmol; acetic acid = 4 ml and reaction time = 5 h.

Scheme 1.

5. Conclusions

1. Higher conversion of phenol with *ortho*-selectivity was observed in the case of different weight percent of HPA/TiP dried at 110 °C and a good *para*-selectivity was observed by using KBr and H_2O_2 over 15 wt.% SiWA/TiP activated at 400 °C.

2. A 15 wt.% PWA/TiP and SiWA/TiP, dried at 110 °C show the conversion (%) 98% and 97%, respectively with low *para*-selectivity.

3. A 15 wt.% SiWA/TiP was found to show the conversion 78%, with the highest selectivity ratio (4-BP/2-BP) of 1.85.

4. With increase in the catalyst concentration from 25 to 125 g/mol and reaction time from 0.5 to 6 h, the selectivity ratio increased from 1.23 to 1.85 (38.92 to 78% conversion) and from 1.05 to 1.76 (23.29 to 78% conversion), respectively. But as far as reaction time is concerned, no trend was observed in cases of 2-BP and di-BP.

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