Cs salt of tungstophosphoric acid-promoted zirconium titanium phosphate solid acid catalyst: An active catalyst for the synthesis of bisphenols

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Abstract. A series of novel $x\text{CsTPA-ZTP}$ ($x = 30, 40, 50, 60$ and 80 wt%) solid acid composite catalysts were synthesized by ion-exchange process using cesium nitrate, tungstophosphoric acid (TPA), zirconium titanium phosphate (ZTP) with varied surface areas, acidities and microstructures. Detailed characterizations of the composite catalysts were done by Powder X-ray Diffraction (PXRD), Fourier Transform Infrared (FTIR) Spectroscopy, N_2 adsorption desorption, Scanning Electron Microscopy (SEM-EDS) analysis, X-ray Photoelectron Spectroscopy (XPS) and Temperature Programmed Desorption (TPD). We have studied the catalytic activities, kinetics and reusability of the catalysts. 60CsTPA-ZTP is found to be an effective and re-usable catalyst for the synthesis of bisphenol A (BPA) and bisphenol F (BPF) using acetonitrile as solvent.

Keywords. Solid acid catalyst; CsTPA-ZTP composite; condensation reaction; bisphenol A (BPA); bisphenol F (BPF).

1. Introduction

Bisphenol A (BPA) and bisphenol F (BPF) are the important chemicals and/or intermediates for the preparation of industrially useful epoxy resins, phenolic resins, polycarbonates, etc. in the moulding, casting, sealing, coating, encapsulating, adhesives, laminating, reinforced plastics and other industrial chemicals. BPA and BPF are conventionally produced through acid-catalysed condensation reaction between phenol and acetone/formaldehyde (scheme 1) by using ion-exchange resins promoted by mercapto compounds. BPA is industrially produced using ion-exchange resin such as Amberlyst. It was reported that ion-exchange resins or modified ion-exchange resins are used worldwide to produce BPA in industry which show good catalytic functions. However, thermal stability of resin catalysts is very limited and they cannot be used at higher reaction temperature.^{1–3}

Again fouling of resin catalysts in the reaction medium is a problem. Some attempts have been made on the use of inorganic solid acids for BPA synthesis such as heteropolyacids,⁴ zeolites,⁵ acid functionalized mesoporous silica⁶ and clays.¹ Hou *et al.* reported the

design of inorganic mixed oxide catalyst for bisphenol A synthesis.⁷ They made a successful demonstration of the mixed oxide of phosphoric, boric and sulphuric acids (P:B:S ratio is 1:2:3) calcined at 100°C in vacuum which showed 81.6% of bisphenol A yield. However, this catalyst had a drawback of deactivation due to loss of sulphuric acid.^{5,8} It is well-known that Keggin-type tungstophosphates, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, possess super acidity and are effective in many catalysed reactions such as alkylation of aromatics,^{9,10} skeletal isomerisation of n-butane,¹¹ hydrolysis of esters in excess water,¹² hydration of olefins in a solid-water reaction systems,¹³ esterification of palmitic acid and transesterification of tributyrin.¹⁴ It is acknowledged that the substitution of H^+ with Cs^+ in Keggin-type $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can significantly influence its acidity and microstructure.¹⁵ Recently, Ide *et al.* reported an effective and selective bisphenol A synthesis on a layered silicate with spatially arranged sulphonic acid.¹⁶

Previously, we have prepared CdS-pillared zirconium–titanium phosphate (ZTP),¹⁷ CdS–ZnS/zirconium–titanium phosphate (ZTP)¹⁸ and silver-exchanged zirconium titanium phosphate (Ag-ZTP)¹⁹ composites for different catalytic applications. Recently, we have developed CdSe QD/ZTP composite material²⁰ for hydrogen production under visible light irradiation

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Scheme 1. Schematic representation of the formation of bisphenol A and bisphenol F.

without using any co-catalyst. In the present investigation, we have successfully synthesized $x\text{CsTPA-ZTP}$ ($x = 30\text{--}80$ wt%) composites by ion-exchange process with varied surface areas, acidities and microstructures. Catalytic performance of these samples for the synthesis of BPA and BPF by coupling of phenol with acetone/formaldehyde has been studied.

2. Experiment details

2.1 Materials

Cetyltrimethyl ammonium chloride ($\text{C}_{16}\text{TMACl}$, Aldrich), Zirconium n-propoxide (Aldrich), Phosphoric acid (Merck), Titanium isopropoxide (Aldrich), 2-propanol (S.d. fine-Chem. Ltd.), Hydrochloric acid (Finar Chemicals Ltd.), Ethanol (Jiangsu Huaxi International Trade Co Ltd.), Cesium nitrate (Fluka), Tungstophosphoric acid (TPA, Himedia), Acetone (S.d. Fine-Chem. Ltd.), Formaldehyde (Qualigen), Acetonitrile (Merck), Phenol (S.d. Fine-Chem. Ltd.). All chemicals were of analytical grade (AR) and used as received without further purification.

2.2 Preparation of zirconium–titanium phosphate

ZTP with Zr:Ti molar ratio 1:3 was prepared as reported by Parida *et al.*¹⁷ In a typical synthesis, cetyltrimethyl ammonium chloride was first dissolved in deionised water (90 g, 5 mol) by heating at $50\text{--}60^\circ\text{C}$. Zirconium n-propoxide as zirconium precursor was then added followed by a dropwise addition of H_3PO_4 . The gel immediately formed was homogenized by vigorous stirring for 30 min. Titanium isopropoxide dissolved in 2-propanol was added very slowly maintaining Zr:Ti ratio 1:3. The pH of the gel was adjusted to 6.5 after 1 h of stirring. Finally, the gel was stirred at room temperature for 3 days. The product was filtered, washed with distilled water and dried under vacuum at room temperature. Surfactant was removed by extracting with HCl/ethanol solution (2 M HCl in ethanol) at 80°C for 12 h. This is designated as ZTP.

2.3 Preparation of Cs salt of tungstophosphoric acid-ZTP ($x\text{CsTPA-ZTP}$) composite

$x\text{CsTPA-ZTP}$ composites were prepared by varying the wt% of Cs salt of tungstophosphoric acid from 30–80 ($x = 30, 40, 50, 60$ and 80 wt%) by ion-exchange

process. In a typical experiment, different wt% of Cs⁺ was exchanged using CsNO₃ as precursor onto the support ZTP by stirring for 24 h. After subsequent washing and drying, CsTPA-ZTP was prepared by stirring stoichiometric amount of tungstophosphoric acid in a suspension of Cs-ZTP (Cs⁺-exchanged ZTP) for 12 h. These samples were dried and designated as *x*CsTPA-ZTP (where *x* = 30, 40, 50, 60 and 80 wt%).

2.4 Characterizations

The samples were characterized by BAXS, FTIR, N₂ adsorption desorption studies, SEM-EDS, XPS and TPD studies. Broad angle X-ray diffraction (BAXS) patterns were recorded on a Rigaku Miniflex (set at 30 kV and 15 mA) powder diffractometer using Cu K α radiation within the 2 θ range from 10 to 70 ° at a rate of 5 °/min in step of 0.01 °. N₂ adsorption-desorption studies were carried out by ASAP 2020 (Micromeritics) instrument at liquid nitrogen temperature (−196 °C). Prior to analysis, the particles were subjected to vacuum (10^{−5} torr) at 110 °C for 5 h to ensure a clean surface. Surface area was calculated with Brunauer–Emmett–Teller (BET) method using the adsorption data within the (*P/P*_o) range from 0.05 to 0.33. The pore volumes were taken at a relative pressure (*P/P*_o) of 0.95. Pore size distribution was obtained using Barrett–Joyner–Halenda (BJH) model using desorption branch of isotherm. Scanning electron microscopic (SEM) images and semiquantitative EDS microanalyses were taken by Hitachi S-3400N. Prior to the analyses, the samples were sputtered with a thin film of gold. Fourier Transform Infrared (FTIR) spectra were recorded on Varian FTIR spectrophotometer (FTS 800) in the range 4000–400 cm^{−1} using KBr wafers. Each spectrum was recorded at 4 cm^{−1} resolution with 30 scans. X-ray photoelectron spectroscopy (XPS) measurements were performed by VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatic Mg–K α X-ray source. Energy resolution of the spectrometer was set at 0.8 eV with Mg–K α radiation at pass energy of 50 eV. The binding energy correction was performed using the C1s peak of carbon at 284.9 eV as reference. Temperature programmed desorption (TPD) profiles were obtained by AutoChem 2920 (Micromeritics). About 0.05 g of the sample was housed in a quartz U-tube. Prior to analysis, the samples were degassed at 110 °C for 2 h under N₂ flow (50 mL/min). It was cooled down to 40 °C. The samples were saturated with NH₃ by the flow of 20% NH₃/balanced He for 30–40 min (25 mL/min). The N₂ gas was flowed over catalyst (50 mL/min) for 30 min to remove the

physisorbed NH₃. The temperature was increased from 40 ° to 900 °C with the flow of N₂ (50 mL/min) to get the TPD profile. The amount of NH₃ consumed was determined by TCD detector which gives the amount of Bronsted and Lewis acid sites in the sample. Before the experiment, the above said equipment was calibrated by 20% NH₃/balanced He to know the exact amount of gas consumed during the experiment.

2.5 Catalytic activity

Catalytic activity of the catalysts was studied at different parametric conditions such as wt% loading of CsTPA onto ZTP, temperature, time, molar ratio of phenol to acetone, etc. Synthesis of bisphenol A/bisphenol F was carried out in a two-necked round bottom flask charged with 50 mg of the composite catalyst, 8 mmol of phenol and 1 mmol of acetone/formaldehyde using acetonitrile as solvent which was stirred at 70 °C for 7 h. From the said condition, we obtained the maximum conversion and selectivity of BPA and BPF, respectively. After the reaction, the product was separated from the catalyst by filtration and analysed by Shimadzu GC-2010 with a capillary column; ZB-5. Conversion (%) of phenol and selectivity (%) of BPA and BPF are calculated with the following formulae.

$$\text{Conversion}(\%)_{\text{reactant}} = \left(\frac{\text{Reactant converted (moles)}}{\text{Reactant used (moles)}} \right) \times 100$$

$$\text{Selectivity}(\%)_{\text{product}} = \left(\frac{\text{Product formed (moles)}}{\text{Reactant converted (moles)}} \right) \times 100$$

3. Results and discussion

3.1 Characterization of catalysts

The PXRD pattern of *x*CsTPA-ZTP (figure 1a) showed that the composites are crystalline in nature. There is not much change in the crystallinity with increase in the wt% of CsTPA salt onto the support which is in agreement with Zhang *et al.*²¹ Diffraction patterns matched with the patterns of CsTPA reported by Satsuma *et al.*²² which confirmed that the composite of CsTPA-ZTP was formed. The indexed peaks are for CsTPA, some of the peaks of ZTP overlap with these CsTPA peaks and the un-indexed peaks are for neat ZTP. The peak with *d* value of 3.9 Å (JCPDS-34-1237) in figure 1b shows the formation of ZTP.

Textural characterization of *x*CsTPA-ZTP composite was determined by N₂ BET surface area and pore analysis (table 1). The nitrogen adsorption-desorption

Figure 1. PXRD patterns of (a) x CsTPA-ZTP composite, and (b) neat ZTP.

isotherms of all samples are shown in figure 2(a). For all the samples, it shows type IV isotherm and H1 hysteresis loop as defined by IUPAC which confirms the mesoporosity of all the composite samples.^{17,18} In the isotherms, two clear distinct phases can be recognized (i) a slow enhance in nitrogen uptake at low relative pressures, resulting in monolayer–multilayer adsorption on pore walls and (ii) relatively sharp step at higher relative pressures associated with multilayer adsorption. Also, the pore size and pore volume distribution of the catalysts are shown in figure 2(b). The BJH average pore size and pore volume of neat ZTP are 4.0 nm and 0.55 cm³/g, respectively. Also, the BJH average pore size and pore volume are found to be in the range of 7.9 to 9.4 nm and 0.25 to 0.33 cm³/g for all the x CsTPA-ZTP composite samples. The composite materials do not follow the specific trend. It is found that the pore size and pore volume are nearly same from 30CsTPA-ZTP to 60CsTPA-ZTP, i.e., 8.0 to 8.1 nm and 0.28 to 0.25 cm³/g, respectively.²³ In the case of 80CsTPA-ZTP, the pore size and pore volume are slightly greater than the other composites, i.e., 9.4 nm and 0.33 cm³/g. Pore sizes of all the catalysts lie in the mesostructured region. It can be observed that the pore-size distribution curve becomes somewhat broader; however, pore-size distribution still remains very narrow with major fractions of

pores lying within the 7.9 Å region. From table 1, it was found that the neat ZTP and x CsTPA-ZTP (where x = 30, 40, 50, 60 and 80 wt%) composite have surface area 102 m²/g and 54–72.3 m²/g, respectively. It is examined that the surface areas are nearly same from 30CsTPA-ZTP to 60CsTPA-ZTP, i.e., 54.0 to 53.4 m²/g.²³ Surface area of 80CsTPA-ZTP is 72.3 m²/g which might be due to the presence of some extra CsTPA salt on the surface of the catalyst. Surface area of composite materials in comparison to the neat ZTP is reduced which suggests that the catalysts just physically block the pore structure of the ZTP.^{18,20}

Figure 3(a) depicts the FTIR spectra of the neat ZTP and x CsTPA-ZTP composites. Broad bands in the hydroxyl region (3600–3200 cm⁻¹) with largely at 3400 cm⁻¹ were consigned to the O-H stretching vibration of the remaining water, transferable OH⁻, and imperfect OH groups with significant hydrogen bonding. Owing to the C-H stretching vibration, no absorption peaks at 1480 and 2800–3000 cm⁻¹ were detected which indicated that the surfactant was fully taken away by HCl/EtOH solvent extraction. The pointed peak in the area 1600–1700 cm⁻¹ shows the existence of H₃O⁺ (Bronsted acidity).²⁴ The typical band at 1072.63 cm⁻¹ (P-O in the central tetrahedral) is present in Keggin ion. The existence of δ(POH) is

Table 1. Surface properties of x CsTPA-ZTP composite.

Catalyst	Surface area (BET, m ² /g)	Average pore size (nm)	Pore volume (cm ³ /g)	CsTPA (wt%) ^a
ZTP	102	4.0	0.55	0
30CsTPA-ZTP	54	8.0	0.28	20.52
40CsTPA-ZTP	50	7.9	0.29	26.32
50CsTPA-ZTP	51	7.9	0.26	31.54
60CsTPA-ZTP	53.4	8.1	0.25	33.95
80CsTPA-ZTP	72.3	9.4	0.33	33.02

^aDetermined by EDX studies

Figure 2. (a) N₂ adsorption–desorption studies. (b) BJH-pore size distribution of *x*CsTPA-ZTP.

Figure 3. (a) FTIR spectra of *x*CsTPA-ZTP (*x* = 0–80 wt%) composite. (b) FTIR spectra of the composites designating the important band positions.

Figure 4. (a) Total survey, (b) O1s, (c) W4f, and (d) Cs3d spectra of CsTPA-ZTP.

Figure 5. NH_3 TPD profile of CsTPA-ZTP composites.

known from the standard intensity peak at 1400 cm^{-1} . These bands specify the presence of structural hydroxyl groups/protonic sites in the material. In these composites, the small band (ca. 953 cm^{-1}) become visible in the P–O stretching region was assigned to Ti–O–P or Zr–O–P vibrations.¹⁹ From the observation of figure 3(a), it is clear that all the composites show no structural loss. It is visible that the bands at 992 (terminal W=O) cm^{-1} , 889 and 812 cm^{-1} (W–O–W) asymmetric vibrations are associated with Keggin ion (figure 3b). The Cs-DTP is specifically illustrated by a split in the W=O band. This doublet signifying that a direct contact among the polyanion and Cs^+ exists.^{25–29}

Figure 4(a) depicts the total XPS survey of CsTPA-ZTP and few major individual elements. Binding energy of O1s is decreased to 529.9 eV (figure 4b) which shows that Cs is getting exchanged.³⁰ The bands of W 4f electron are visible at 34.7 and 36.3 eV . The band at 36.3 eV may be interpreted due to presence of

W^{6+} and the band at 34.7 eV is mainly due to presence of reduced species of tungsten which might be due to the high vacuum ESCA studies (figure 4c).³¹ The bands of Cs 3d electron are noticeable at 722.3 and 742 eV (figure 4d). Apart from that, a less intense band is observed at 78.03 eV for Cs 4d electrons (figure 4a).³²

Figure 5 shows the NH_3 TPD profile of CsTPA-ZTP with varied concentration of CsTPA onto ZTP composite. The NH_3 TPD profile shows peaks which are observed in low temperature range (LT < $500\text{ }^\circ\text{C}$) and high temperature range (HT > $500\text{ }^\circ\text{C}$). It possesses mainly two peaks which indicate the presence of two types of acid sites, i.e., Bronsted and Lewis acid sites in the composite materials. The mainly two peaks are around at $250\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$. At higher temperature (> $760\text{ }^\circ\text{C}$), some peaks are detected. As cesium-substituted dodecatungstophosphoric acid-based materials mainly contains Bronsted acid sites, the present material may acquire a large amount of these acid sites.²⁴ From table 2, it is found that the concentration of acid sites increases (0.56 to $1.29\text{ }\mu\text{mol/g}$) with the increase of the CsTPA up to $60\text{ wt\%}$ and thereafter it decreases slightly ($0.91\text{ }\mu\text{mol/g}$). This might be due to the reduction of exchange of Cs^+ during ion exchange process at $80\text{ wt\%}$ concentration which is also evidenced from the EDX data presented in table 1. Concentration of acidic sites for composite materials in high temperature region (> $500\text{ }^\circ\text{C}$) is very low (0.06 to $0.12\text{ }\mu\text{mol/g}$) comparison to the concentration of acidic sites in low temperature region (< $500\text{ }^\circ\text{C}$). Details of acid strengths are summarized in table 2.

3.2 Performance of the catalysts

Tables 3 and 4 depict the activities of various solid acid catalysts toward the coupling reactions for the formation of (BPA) and (BPF) with rate of formation of

Table 2. NH_3 TPD^a results of xCsTPA-ZTP.

Catalyst	Acid sites/unit surface area ($\mu\text{mol s}^{-1}$)	TPD of NH_3 ($\mu\text{mol/g}$)	
		LT-Peak (< $500\text{ }^\circ\text{C}$)	HT-Peak (> $500\text{ }^\circ\text{C}$)
30CsTPA-ZTP	27.4	0.56	0.11
40CsTPA-ZTP	105.32	0.79	0.08
50CsTPA-ZTP	43.0	0.83	0.11
60CsTPA-ZTP	89.79	1.29	0.06
80CsTP-ZTP	16.95	0.91	0.12

^aValues determined after deducting the amount of physisorbed NH_3 at temperature < $150\text{ }^\circ\text{C}$.

Table 3. Conversion of phenol and selectivity towards the formation of BPA and BPF.

Catalysts	BPA conversion (%)	BPF conversion (%)	BPA selectivity (%)	BPF selectivity (%)
ZTP	3	6.5	5	6.25
CsTPA	10	10	5	7.20
30 CsTPA-ZTP	25	28.9	30.3	33.45
40 CsTPA-ZTP	38.95	41.23	52	55.3
50 CsTPA-ZTP	50.23	58.52	68.92	73.9
60 CsTPA-ZTP	60.87	69.73	83.82	87.95
80 CsTPA-ZTP	61.9	70	85	90

Table 4. Rate of formation of BPA and BPF as a function of wt% of CsTPA onto ZTP.

Catalysts	Rate of BPA formation (mmol/g/h)	Rate of BPF formation (mmol/g/h)
ZTP	0.57	0.714
CsTPA	1.23	1.56
30 CsTPA-ZTP	3.46	3.82
40 CsTPA-ZTP	5.94	6.32
50 CsTPA-ZTP	7.88	8.45
60 CsTPA-ZTP	9.57	10.05
80 CsTPA-ZTP	9.71	10.28

Reaction condition: (Catalyst) = 0.05 g; Phenol:Acetone/formaldehyde = 8:1; Temperature = 70 °C.

Figure 6. Conversion and selectivity of (a) BPA and (b) BPF as a function of reaction time. Reaction condition: [60CsTPA-ZTP] = 0.05 g; Phenol:Acetone/formaldehyde = 8:1; Temperature = 70 °C.

BPA and BPF. As observed, the pristine ZTP¹⁷ having highest surface area, i.e., 102 m²/g shows the lowest phenol conversion, i.e., 3% and 6.5%, lowest selectivity, i.e., 5% and 6.25% towards the formation of BPA and BPF, respectively. This is because of the fact that ZTP contains strong acidic sites at high temperature (HT),^{33,34} which are not effective for the formation of *p,p'*-BPA. Also, CsTPA shows the conversion, i.e., 10% towards BPA and BPF with 5% selectivity for BPA and 7.2% BPF. It is clearly observed from

tables 3 and 4, the selectivity as well as the rate of formation of BPA increases from 5–83.82% and 0.57–9.71 mmol/g/h, respectively with increase in the wt% of CsTPA onto the pristine ZTP up to 60 wt%. This is very much coherent with the low temperature acid concentration (1.45%) which is maximum for 60CsTPA-ZTP. Our observation is in agreement with the report published by Rode *et al.*³⁴ Similar observations were noticed on the formation of BPF with selectivity enhancement from 6.25–87.95% and

Table 5. Temperature-dependent conversion and selectivity for coupling reactions.

Temperature (°C)	Phenol conversion (%)		Selectivity (%)	
	Phenol–acetone coupling	Phenol–formaldehyde coupling	BPA	BPF
60	55.62	62.59	78.23	81.36
70	61.73	71.20	85.00	88.35
80	65.39	72.93	79.49	81.43
90	70.43	78.45	70.2	77.95

Reaction conditions: (60CsTPA-ZTP) = 0.05 g; Phenol:Acetone/formaldehyde = 8:1; Reaction time = 7 h

rate of BPF formation from 0.714–10.28 mmol/g/h. With further increase in the wt% of CsTPA onto ZTP, the selectivity and rate of formation remain almost same. In case of BPA, biproducts such as chromans and triphenols were not identified, rather a minor quantity of o,p'-BPA was observed at higher wt% of CsTPA (>50 wt%) supported ZTP. In case of BPF formation, carbinol was identified as the side product since the trimer formation is favoured at HT acidic concentration.³⁴

The activity of 60 CsTPA-ZTP was studied towards the formation of BPA and BPF as a function of reaction time (figure 6). The experiments were carried out in the time range of 1–10 h. One can see, the conversion of phenol and selectivity towards the formation of p,p'-BPA and BPF are rapidly increasing. At 7 h, the phenol conversion reached maximum, i.e., 61.73% and selectivity towards p,p'-BPA at 85% (figure 6a). Thereafter, with increase in the reaction time, the conversion and selectivity drop to 40.2% and 78.9% at 10 h (figure 6a). Similarly, at 7 h, maximum phenol conversion, i.e., 71.2% and selectivity, i.e., 88.35% towards p,p'-BPF formation drop to 33.92% and 78.3%, respec-

tively, at 10 h (figure 6b). This is mainly due to the deactivation of catalyst with the formation of water during the reactions (scheme 1).⁷

Also, to know the effect of reaction temperature on the conversion of phenol and selectivity towards BPA and BPF, we have carried out the experiments with fixed catalyst concentration, molar ratio of phenol to ketone/aldehyde in a range of reaction temperatures from 60–90 °C. As mentioned in table 5, conversion of phenol in both the coupling reactions is increases with increase in temperature, but the selectivity of BPA and BPF decreases which is in good agreement with the report by Das *et al.*⁶

Recyclability test was performed thrice by activating the used 60 CsTPA-ZTP catalyst. After the first experiment, the catalyst was washed several times with acetonitrile and dried at 110 °C overnight. The same procedure was followed during the second and third time. It was observed that the said catalyst showed nearly same conversion and selectivity compared to fresh one. Again, the used catalysts were tested using FTIR technique. It is well-observed from figure 7(a) that there is not much difference in the spectra of the fresh and

Figure 7. (a) FTIR spectra of used 60CsTPA-ZTP catalyst for BPA and BPF synthesis process. (b) Designation of important band positions from 1000–700 cm⁻¹.

Scheme 2. Plausible mechanism for the formation of bisphenols over CsTPA-ZTP catalysts.

used catalysts. From figure 7(b), it is observed that there is no change in the important bands of the Keggin ion moiety in used composite compared to unused one (figure 3b). This shows the stability of the catalyst towards the reaction conditions.

Scheme 2 shows that the condensation reaction occurs with two moles of phenolic compounds and one

mole of aldehyde or ketone. The aldehyde or ketone undergoes chemisorption onto the catalyst surface. As seen in the TPD profiles (figure 5) and data analysis (table 2), the catalysts contain mainly Bronsted acid sites which help in forming electrophile. There is a first electrophilic attack on the phenol and formation of intermediate occurs. The second electrophilic attack

Table 6. Comparison table for the formation of BPA/BPF over different catalysts.

Entry	Catalyst	Temp (°C)	Time (h)	Conversion (%)	References
1	60CsTPA@ZTP	70	7	61.73 (BPA) 71.20 (BPF)	Present study
2	MPS-8	70	24	29.6	8
3	15 Al:MCM-41 having a Si/Al ratio of 70 mol mol ⁻¹	90	4	- 93.1	23
4	MCM-SO ₃ H	70	24	30 -	10
5	Laccase from <i>Trametes versicolor</i> (120 IM BPA, 0.15 U/ml laccase)	25	1	59.1 - pH 5.0 (25 mM acetate buffer)	35
6	BPA with EC	180	20 min	37 -	36
7	Amberlyst XE-717p	135	4	60 -	1
8	CsHPW/MCM-41	160	6	42 -	5
9	Al:MCM-41	90	1	- 63.2 (Yield)	37
10	20% DTP/SiO ₂	80	1	- 34.2% (Yield)	38

takes place with a release of water molecule forming bisphenols. Catalysts having strong Bronsted acid sites can favour the formation of bisphenols. Hence, the supported catalysts are employed for this purpose.

Table 6 shows the BPA/BPF formation over other catalysts and comparison with the present study. It is observed that the present catalyst is comparable to that of the reported catalysts.

4. Conclusion

In summary, the present study emphasizes on a novel solid acid catalyst (60CsTPA–ZTP) which has been used in the liquid phase condensation reaction. Our recent results indicate that 60CsTPA–ZTP is an efficient catalyst for the condensation of 8 mmol phenol and 1 mmol acetone/formaldehyde at relatively low temperature (70 °C) in 7 h to synthesize bisphenol A/bisphenol F. It gives the highest conversion of 61.73% and 71.20% with selectivity of 85% and 88.35% towards bisphenol A/bisphenol F, respectively. Further, this study extends the possibility of using CsTPA–ZTP composite in other liquid phase acid-catalysed reactions.

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