

Catalysis

A Liquid Derivative of Phosphotungstic Acid as Catalyst for Benzyl Alcohol Oxidation in Water: Facile Separation and Stability of Benzaldehyde at Room Temperature[†]Rama R. Bhattacharjee,^{*,[a]} Thangamani S,^[a] and Sib S. Mal^[b]

Polyetheramines belong to a class of green di-block copolymer with ethylene oxide and propylene oxide moieties along with terminal amine functionality. The polymers are biocompatible and show temperature dependant phase separation properties. Herein, we report the effect of a polyetheramine (Jeffamine[®]) on the catalytic properties of a well studied polyoxometalate catalysts, phosphotungstic acid (PTA). The catalytic reaction chosen for the test is the hydrogen peroxide-mediated oxidation of benzyl alcohol (BzOH). Modification of PTA with Jeffamine[®] (PTA-Jeffamine[®]) resulted in a solvent-less liquid-like material accessible to a wide range of solvents. The PTA-Jeffamine[®] catalyst was observed to enhance the conversion of

BzOH compared to that of pristine PTA and facilitated easy separation of benzaldehyde (BzH) and catalyst from reaction mixture. Stability of synthesized BzH was studied with gas chromatography attached with mass spectrometry (GC-MS). Synthesis of the catalyst is cost-effective and scalable due to easy availability of the individual components and nature of the synthetic protocol. UV-visible spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and field emission scanning electron microscopy (FE-SEM) were used to characterize the catalyst. Surface tension experiment, FE-SEM, ICP-MS and controlled experiments were performed to understand the effect of Jeffamine[®] in the catalytic process.

Introduction

Benzaldehyde (BzH) is an important organic intermediate in the family of aromatic carbonyl compounds.^[1] It is used as a raw material in the production of perfumes^[2] and dye stuffs,^[3] in pharmaceutical industries for curing cancers^[4] and in agro-chemical products.^[5] Literature reports suggest that the liquid-phase oxidation of benzyl alcohol (BzOH) is preferred in industry as it saves energy, enhances selectivity for the desired product and prevents catalyst deactivation.^[6,7,8] The progress in green chemistry have encouraged the use of ecofriendly reactants and allowed modifications in existing chemical process. Current focus is on the design of eco-friendly protocols for liquid-phase oxidation of BzOH to BzH in water with hydrogen peroxide (H₂O₂) as a clean oxidizing agent.^[1,9] It has been observed that H₂O₂ is preferred over conventional oxidants for oxidation of BzOH.^[9,10] Conventional and cheaper oxidants such as sodium permanganate,^[11] bromide,^[12] and chromium based compounds^[13] can leave behind traces of metal impurities/wastes in various oxidation states. These species are highly water soluble.^[13] Such transition-metal ions can initiate secondary reactions even after oxidation process gets over and that can lead to over-oxidation and auto-degradation of BzH.^[13] Combination of both solvent-less and

solvent media with various catalyst systems have been used previously for BzOH oxidation.^[7,8] In 2014, Wang *et al.* have reported the oxidation of BzOH in water using amino tethered guanidinium ionic liquid [TMGHA]Cl combined phosphotungstic acid.^[14] Very next year, Shiwei *et al.* have reported epichlorohydrin modified Fe₃O₄ microstructures as catalyst for oxidation of alcohols.^[15] In 2011, Caprio *et al.* have been reported oxidation of BzOH using TiO₂/Cu(II)/UV solar system.^[16] Fe(Cu) containing coordination polymers are used as benzyl alcohol oxidation catalyst with hydrogen peroxide (H₂O₂) as oxidant in aqueous medium.^[17] Room temperature catalytic oxidation of alcohols with polyoxovanadate salt has been reported in aqueous medium.^[18]

Among the above mentioned catalytic systems, polyoxometalates (POMs) are the most efficient.^[19,20] The advantage of POMs over other inorganic catalysts is the stability of the metal center present in the cage. POMs do not show leaching of metal ions in the reaction medium and hence can be superior compared to other metal-ligand complexes used as catalysts.^[21] Both homogeneous and heterogeneous POM species have been reported for BzOH oxidation in water.^[22–24] Heterogeneous reactions are preferred as they facilitate easy separation of products and re-cycling of the catalyst. Chen *et al.* have reported mesoporous POM based ionic hybrid triphasic catalyst for oxidation of BzOH.^[14] Jing and co-workers have worked with POM based amphiphilic catalyst functionalized by cationic surfactants for BzOH oxidation.^[25] Oxidation of BzOH with novel vanadium POMs have been studied in the presence of PTSA (p-toluene sulphonic acid).^[26] Carraro *et al.* reported organic-inorganic hybrids synthesized from lacunary POMs as oxidation catalysts for alcohol oxidation with H₂O₂ under MW irradiation.

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tion.^[27] Organic solvent-free direct selective oxidation of BzOH to BzH with aqueous 15% H₂O₂ have been reported using tetra-alkylpyridinium octamolybdate catalysts.^[28]

POMs combined with amphiphilic supports can show better catalytic activity compared to other types of support materials for H₂O₂ oxidation reactions. Sato *et al.* have reported that H₂O₂ forms an intermediate peroxo complex with POMs in water which acts as the active species for oxidation.^[29] The efficiency of the reaction may depend upon the facile phase-transfer of the active species to the organic layer.^[29] For bi-phasic reactions like BzOH oxidation in water, amphiphilic POMs may lead to better interaction of BzOH with H₂O₂ at the water-oil interface and may improve the conversion rate.^[30] A few reports on the use of amphiphilic supports used in combination with POMs are available where the catalyst modification required multiple steps.^[14,25] Such reports site tedious extraction and purification of BzH often with the use of external organic solvents. The catalyst preparation and separation processes may further limit its industrial applications. In the present manuscript, we choose to study the effect of a biocompatible polyetheramine (Jeffamine[®]) on the catalytic property of phosphotungstic acid (PTA). We selected the oxidation of BzOH in water as the catalytic process to test the effect of the PTA catalyst. The catalyst may pave away to the development of greener synthetic protocols in water based oxidation processes.

Results & discussions

Tungsten as free WO₄²⁻ and as PTA is a well studied catalyst system.^[31-34] In the next sections we have documented the catalytic properties of PTA modified with Jeffamine[®] (PTA-Jeffamine[®]) in details and compared with that of pure PTA.

Synthesis and characterization of the liquid-like solvent-less catalyst

The Jeffamine[®] polymer is a di-block copolymer with ethylene oxide (EO) and propylene oxide (PO) moieties along with terminal amine functionality (Figure 1).

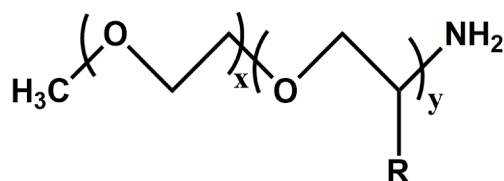


Figure 1. Structure of Jeffamine[®] (M2070).

It is a biocompatible polymer and has been used to reduce cytotoxicity of phosphazenes and aqueous-in-oil droplets.^[35,36] The PTA-Jeffamine[®] catalyst preparation was achieved through a simple acid-base titration process. A plot of pH against volume of Jeffamine[®] added to PTA is shown in Figure 2. The plot indicates the removal of three protons from PTA in three

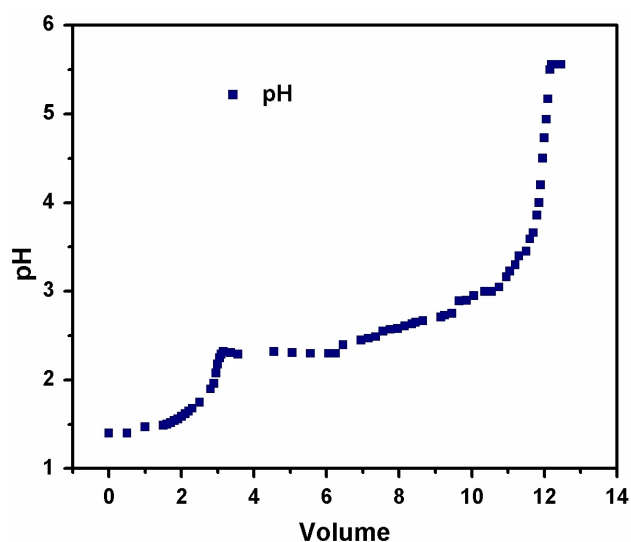
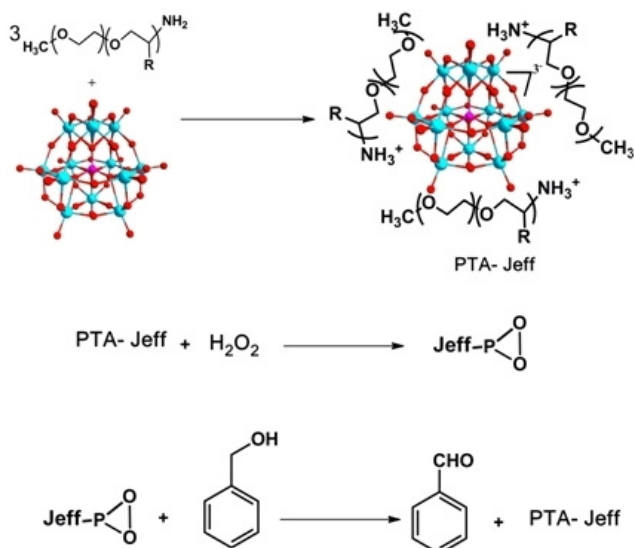


Figure 2. Plot showing variation in pH against volume of Jeffamine[®] added to a fixed amount of PTA.

stages of titration. During the course of titration, each surface proton of PTA was exchanged with the amine group of Jeffamine[®] that resulted in the formation of water soluble PTA-Jeffamine[®] liquid derivative. The surface protons of PTA are assumed to be in dynamic equilibrium and fluctuates between the PTA surface and the amine group of Jeffamine[®]. Similar concept of dynamic surface exchange is provided by Giannelis *et al.* for the preparation of nano ionic materials.^[37] Once all the protons have been exchanged, the pH of the catalyst solution increased linearly with increasing concentrations of added Jeffamine[®] as shown in Figure 2. The catalyst or liquid-derivative formed out of the titration process can be envisaged as composed of an anionic PTA electrostatically conjugated with three cationic Jeffamine[®] (ammonium form) (Scheme 1). Mal *et al.* have reported similar type of 'salt' formed from ion exchange process.^[38] Strong electrostatic interactions between the ammonium cations of Jeffamine[®] and anionic oxygen of PTA may be responsible for the enhanced solubility and stability of PTA in water phase.^[14]

After titration, the PTA-Jeffamine[®] catalyst solution was obtained as a clear liquid in water. Different liquid-mixtures with varying PTA: Jeffamine[®] were used as catalyst in the BzOH oxidation process. pH of the final catalyst depend on the volume of Jeffamine[®] added. Freeze-drying the catalyst yield a liquid-like transparent and homogeneous material. Bhattacharjee *et al.* reported the preparation of nano ionic materials where Jeffamine[®] was used as base or counter-ion.^[39,40] The liquid nature of the dried PTA-Jeffamine[®] catalyst is due to the low glass transition temperature of the polymer ($T_g = -55^\circ\text{C}$).^[39] The advantage of the liquid-nature is that, it increase the dispersibility of PTA in a any given solvent which may in turn improve the catalytic properties of PTA.

The PTA-Jeffamine[®] catalyst was characterized with Fourier transform Infrared spectroscopy (FT-IR), UV-vis spectroscopy and field emission scanning electron microscope (FE-SEM).FT-IR



Scheme 1. Pictorial representation of the PTA-Jeffamine[®] catalyst and mechanistic picture of the BzOH oxidation process.

and UV-Vis spectroscopic data indicated that the structure of PTA remained literally unchanged after modification with Jeffamine[®] (Figure 3, Table 1 & S1). The catalyst mixtures were

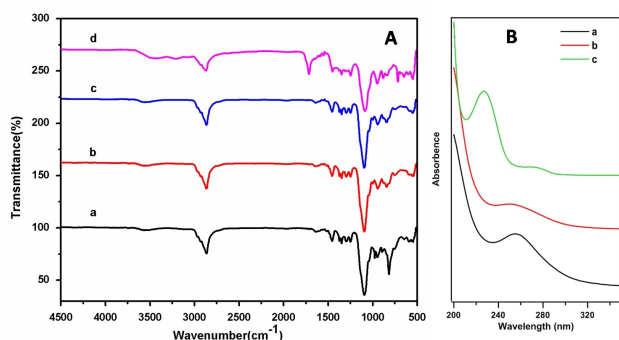


Figure 3. (A) FT-IR spectra of PTA-Jeffamine[®] prepared at three different pH (a) 6.5 (b) 7.5 (c) 8.5 (d) FT-IR spectrum of phase separated aqueous part freeze dried after first catalytic cycle; (B) UV-vis spectra of aqueous PTA in different conditions. (a) pristine PTA, (b) PTA-Jeffamine[®] (pH-7.5), (c) cycle 1 (catalyst part after reaction).

made at a fixed concentration of PTA and varying concentrations of Jeffamine[®]. Variation of Jeffamine[®] resulted different pH values. Figure 3 A shows FT-IR spectrum of PTA-Jeffamine[®] at three different concentrations of Jeffamine[®] (pH 6.5, 7.5 & 8.5). The characteristic FT-IR peaks of PTA are observed at 1093 cm⁻¹ (P–O), 943 cm⁻¹ (W–O), 879 cm⁻¹ (W–O_b-W) and 842 cm⁻¹ (W–O_c-W) in all samples (Table 1). UV-vis spectrum of pure PTA and PTA-Jeffamine[®] is shown in Figure 3B (a & b). Absorption bands at 257 nm for pure PTA and at 246 nm for PTA-Jeffamine[®] are observed (Figure 3B (a & b)). The blue shift from 257 nm to 246 nm indicate strong interaction between

Nature of Sample	Nature of bond	Peak position [cm ⁻¹]
PTA-Jeffamine [®] (pH-7.5) before reaction	P-O	1093
	W-O	943
	(W-O _b -W)	879
	(W-O _c -W)	842
	(C-O in ether)	1249
	(C-H stretching)	2866
Phase separated aqueous part after first catalytic cycle	(C-H bending)	1456
	(N-H stretching)	3566
	P-O	1087
	W-O	948
	(W-O _b -W)	883
	(W-O _c -W)	842
	(C-O in ether)	1247
	(C-H stretching)	2872
	(C-H bending)	1450
	(C=O in acid)	1714
	(C-O stretching in acid)	1247
	(N-H stretching)	3435

Jeffamine[®] and PTA (Table S1) as reported in literature.^[41] The shift in UV-vis bands and the presence of the characteristic peaks in FT-IR indicate that the structure of PTA remained almost intact after addition of Jeffamine[®] without the formation of any lacunary polyanions under change in pH.^[42] The presence of strong electrostatic interactions discussed in previous section might be responsible for the hydrolytic stability of PTA observed here at varying pH.

The structure of PTA-Jeffamine[®] catalyst was further characterized by FE-SEM (Figure 4). Pure-PTA shows crystalline

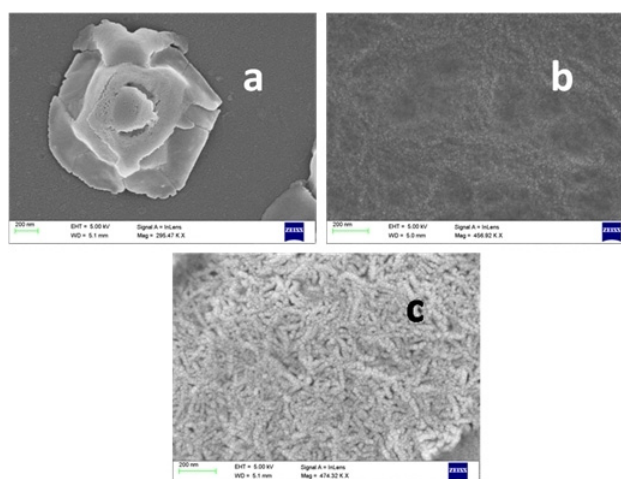


Figure 4. FE-SEM images of (a) PTA, (b) PTA-Jeffamine[®] mixture at pH 3.5 and (c) at pH 7.5.

aggregates in Figure 4a. Similar crystalline structures for PTA drop-casted from aqueous solution have been reported by

Giannelis *et al.*^[37] Interestingly, the FE-SEM images of PTA-Jeffamine[®] catalyst do not show any crystalline aggregate (Figure 4b &c). At low concentration of Jeffamine[®] (pH 3.5), FE-SEM image shows uniform distribution of PTA aggregates throughout the polymer matrix (Figure 4b). The images indicate that PTA was unable to crystallize in presence of Jeffamine[®] may be due to the surface modification of PTA. Giannelis *et al.* reported similar observations based on X-ray diffraction data.^[37] They have reported that the crystalline properties of PTA diminish in presence of partially protonated composites. The structure of the PTA-modified with Jeffamine[®] at pH 7.5 has been identified as worm-like micelles as shown in FE-SEM image (Figure 4c). Similar micellar structures are well reported in literature for self-assembled polymer and surfactant molecules.^[43,44] The formation of "worm-like" micellar structures can be explained from the pH vs. Jeffamine[®] volume curve shown in Figure 2. From the curve, we observe that the titration between PTA (strong acid) and Jeffamine[®] (weak base) reaches end point around pH 3.5. Beyond a certain volume of added Jeffamine[®] to PTA solution, the pH increases steeply. Hence, we can imagine that at pH 7.5 there is excess Jeffamine[®] present along with the salt like (PTA- Jeffamine[®]) species shown in Scheme 1. The higher concentrations of Jeffamine[®] might result in supramolecular self-assembly induced by counter ions resulting in worm like micelles as reported in literature.^[43,44] Such micellar self-assembly may also respond to changes in surfactant and salt concentrations as per literature reports and may influence the course of the present catalytic reaction.

The catalytic reaction and facile separation of BzH: Effect of Jeffamine[®]

At first, BzOH oxidation reaction was studied with and without pure-PTA as catalyst. The oxidation product of BzOH was monitored by gas chromatograph fitted with mass spectra (GC-MS). The GC-MS data showed very low conversions of BzOH for reaction with and without pure-PTA (Table 2, S.no.1&2). The

Table 2. Summary of GC-MS results obtained from reactions performed at various conditions *				
S.no	pH	Catalyst	% Conversion	% Selectivity
1	-	No catalyst	2.9	5.0
2	2.5	PTA(0.5 g)	9	100
3	7.5	Potassium salt of PTA(0.5 g)	5	100
4	7.5	PTA-Jeffamine [®] (0.5 g)	100	74
5	3.5	PTA- Jeffamine [®] (0.5 g)	25	73
6	4.5	PTA- Jeffamine [®] (0.5 g)	100	63
7	6.5	PTA-Jeffamine [®] (0.5 g)	100	59
8	8.5	PTA- Jeffamine [®] (0.5 g)	100	73

*Amount of catalyst (PTA) taken is mentioned in brackets, Medium-water, Temperature - 90 ° C, Time - 1.5 h

conversion and selectivity of the BzOH oxidation depends on the pH of the reaction medium as well as on the phase transfer efficiency of the active intermediate Venturello ion.^[29,38,45] Although pH was suitable for the reaction with pure-PTA, it was the absence of efficient phase transfer of the active intermediate that may have limited conversion of BzOH.^[30] In order to induce phase transfer, a cationic surfactant (CTAB) was introduced in the reaction medium along with pristine-PTA. Addition of CTAB did not help the formation of BzH as observed by thin layer chromatography (TLC) and Tollens' tests.

Next, pure-PTA was replaced by PTA-Jeffamine[®] as catalyst. The catalyst mixtures were made at a fixed concentration of PTA (0.5 g) and varying concentrations of Jeffamine[®]. The reaction time was monitored and finally optimized by TLC and Tollens' tests. The catalytic process is schematically shown in Figure 5. Prominent TLC spots indicated the formation of BzH

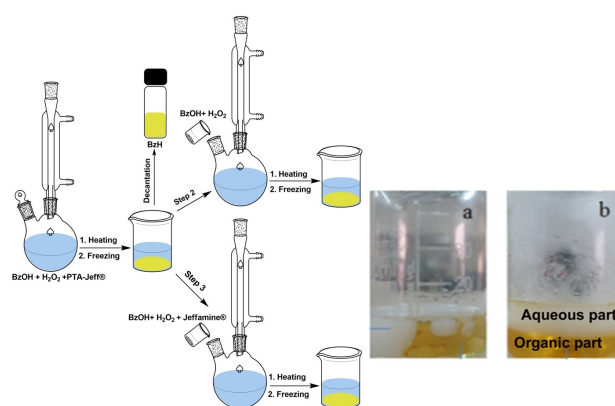


Figure 5. Schematic representation of the BzOH oxidation reaction, and (a) & (b) represents the reaction mixture obtained before and after freezing respectively.

along with un-reacted BzOH (Figure S1). TLC spots for specific products were confirmed by comparing the TLC of known standards (Figure S1). A heterogeneous suspension was observed after end of reaction as shown in Figure 5a. It consisted of the products and the catalyst past. The reaction mixture was kept in a freezer at -5°C . Two separate layers were observed after 24 h namely the phase separated organic part (yellowish) and the aqueous part as shown in Figure 5b. Jeffamine[®] exhibits upper critical solution temperature (UCST) characteristics due to the presence of both hydrophilic (EO) and hydrophobic (PO) moieties.^[46,47] Hence, it phase separates when cooled along with electrostatically attached PTA molecules, leaving behind the organic layer as shown in Figure 5b. The organic layer was manually separated by simple decantation, dried over sodium sulphate, was kept in ambient conditions for 5 days and finally analyzed with GC-MS (Figure S2). At low Jeffamine[®] concentration (pH 3.5), the conversion is only 25% after 1.5 h, but increase dramatically to 100% at higher Jeffamine[®] contents (pH 4.5, 6.5, 7.5 & 8.5) (Table 2). Such high conversion values for BzOH oxidation in water at 1.5 h has not been reported earlier. With some minor fluctuations, maximum

selectivity towards BzH (~ 74%) was observed above pH 6.5. Thus from Table 2, it is clear that BzOH conversion increases with increase in Jeffamine[®] for the fixed amount of PTA until maxima observed at pH 7.5. For comparison, the trend in conversion and selectivity values at different conditions with PTA-Jeffamine[®] catalyst are shown with the help of bar diagram (Figure S3).

Kinetic studies performed at pH 7.5 shows higher selectivity towards BzH beyond 1.5 h (Figure S4). Maximum selectivity ~ 83% was observed for BzH after 2 h (Figure 6, Table S2).

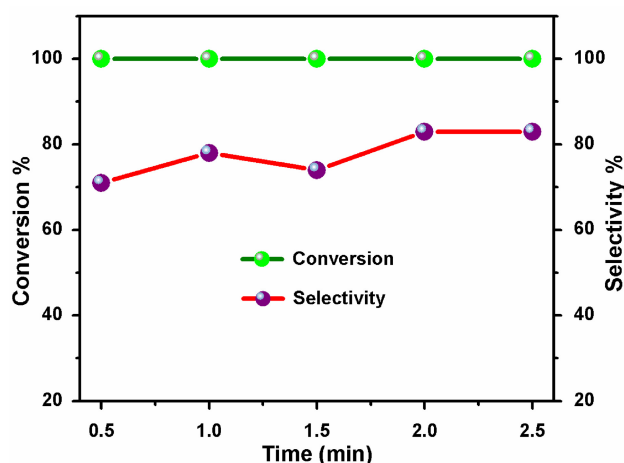


Figure 6. Kinetic study of conversion of BzOH and selectivity for BzH with PTA-Jeffamine[®] catalyst at pH 7.5.

Figure 6 & Figure S4 shows that 100% conversion of BzOH was achieved within 30 min of initiation of reaction. The GC-MS results were compared with reported literature on BzOH oxidation with POMs.^[48] Similar reaction conditions and use of POM has already been reported by Saini and co-workers with 70% BzH conversion after 3 h of reaction.^[48]

Stability of BzH formed in the organic layer

BzH undergo slow and spontaneous autoxidation to benzoic acid (BzA) simply upon exposure to air at ambient conditions.^[49,50] Hence it is always a challenge to obtain the product in pure form and keep it stable. Literature reports on the use of specific catalyst modification methods designed for separation and purification of BzH in water are available.^[14,25] Literature reports have suggested that BzH can be separated from water with external solvent like ethyl acetate (EAc).^[15,19] During evaporation of EAc, BzH can readily get oxidized to BzA.

In the present work, it was observed that the GC-MS of the phase separated organic part remained unchanged even after a week which indicates that the BzH produced in the reaction is stable against oxidation. GC-MS traces obtained from the phase separated organic part for all reactions did not detect unreacted BzOH except at pH 3.5 (Figure S2). The data indicate that 100% conversion of BzOH was achieved beyond pH 3.5 and that the BzH formed with PTA-Jeffamine[®] as catalyst was

stable towards auto-oxidation in absence of unreacted BzOH. This is largely in contrast to the report of Hutchings and coworkers, where they had designated stability of BzH to the presence of BzOH. They reported that the presence of low concentrations of unreacted BzOH prevent the auto-oxidation of BzH by intercepting radicals formed during the oxidation reaction.^[49] Possible reason can be attributed to the single step phase separation of PTA-Jeffamine[®] catalyst and by-products from the organic part as described in previous section. Further reasoning was provided from the analysis of the GC-MS traces obtained from the organic phase separated part (Figure S2). At pH 3.5, peaks for BzH and unreacted BzOH were observed along with a peak C. The MS data of peak C shows resemblance with BzH and/or mono-substituted benzene compound (Figure S5). GC-MS data for the reactions at pH 4.5 and 6.5 shows BzH, peak C and a new peak D. MS data of peak D also indicate a mono-substituted benzene compound (Figure S5). The GC-MS results of the reactions at pH 7.5 and 8.5 show presence of BzH and peak C (Table S3). No BzA peak was detected throughout the kinetic studies. So, we believe that the stability of BzH against auto-oxidation can be attributed to the formation of the intermediate compounds designated as peak C and D (see mechanism section). Interestingly, iodimetric titration (as detailed in experimental section) shows presence of organic peroxide in the separated organic layer (Figure 5). The present of organic peroxides at low concentration may be the reason of the appearance of peak C & D in GC-MS and might inhibit the auto-oxidation of BzH.^[49]

When the organic part was diluted with methanol or acetone and analyzed in GC-MS, peaks of BzOH and BzA were observed whereas peaks C and D disappeared (Figure S6). We assume that, few molecules of Jeffamine[®] stabilized Venturello ions may be present in the organic phase after phase separation. This has evidenced in ICP-MS studies where trace amounts of PTA was detected (Table S4). The Venturello ions may not react with the compounds C and D in absence of external solvent. When acetone or methanol was added, the active Venturello intermediate may react quickly but unselectively with the compounds (C & D) to form BzA and BzOH. Similar disproportionation reactions for BzH have been reported in literature.^[51] We are working on to isolate and characterize the intermediates C and D which can help us to understand the fundamental reasons behind the stability of BzH.

Isolation and reusability of catalyst PTA from reaction mixture: Role of Jeffamine[®]

The above catalytic results were obtained from the phase separated organic part. Analysis of the organic part with ICP-MS shows the presence of a meager amount of PTA. ICP-MS data reveal the presence of 1.2 ppb phosphorous and 12.8 ppb tungsten of PTA (Table S4). Due to strong electrostatic interactions with the PTA molecules, Jeffamine[®] can remove most of the PTA molecules from organic part and bring them into the aqueous part. Since according to literature, 0.3% of BzH is soluble in water, there are chances for some trace

amounts of PTA to mix into the organic phase during the manual decantation process as explained in experimental section.^[52] ICP data also indicate that, almost all the PTA is separated into the aqueous phase during separation. This further justifies the role of Jeffamine® in easy separation of the products, reactants and catalyst. ICP data also reveal that the structure of PTA after reaction is intact as the ratio of P to W ~ 1:12.

After the oxidation reaction was over, the phase separated aqueous part containing the PTA-Jeffamine® catalyst was kept under observation separately in normal laboratory condition and at $-5\text{ }^{\circ}\text{C}$. The sample kept under normal temperature shows formation of BzA crystals, whereas the sample stored inside the freezer did not show any phase separation or crystallization. The aqueous part separated after first reaction cycle (Figure 5) was freeze-dried and used for characterization. FT-IR spectroscopy and UV-Vis spectroscopic techniques were used to detect the presence of PTA along with Jeffamine® in the phase separated aqueous part (Figure 5). FT-IR shows peaks at 1247 cm^{-1} (ether) and 3435 cm^{-1} (amine) that indicate the presence of Jeffamine® along with four characteristic peaks of PTA at $1087, 948, 883, 842\text{ cm}^{-1}$ (Figure 3 A, Table 1). The four FT-IR peaks of PTA were observed to be slightly blue shifted as compared to that of pure PTA-Jeffamine® catalyst. The shift in FT-IR peak position indicates changes in characteristics of the bridge-oxygen present in PTA (Table 1).^[41,42,53] UV-vis spectrum of phase separated aqueous part shows PTA band at 269 nm which is considerably red-shifted compared to that of pure mixture of PTA and Jeffamine® (Figure 3B, Table S1). The characteristic changes observed in the FT-IR and UV-vis data of PTA can be attributed to the presence of BzA in the aqueous part. Sharp FT-IR peak at 1714 cm^{-1} corresponds to $-\text{CO}$ of COOH and sharp UV band at 227 nm indicated presence of BzA in the separated catalyst mixture (Figure 3, Table 1 & Table S1).

In order to check the stability and recyclability of the isolated PTA-Jeffamine® obtained from phase separated aqueous layer, two catalytic cycles were performed as detailed in experimental section. GC-MS data for recoverability tests performed with the used catalyst present in the phase separated aqueous part showed conversion of BzOH to BzH (Figure S7). The conversion values indicated that PTA is catalytically active in the recycled catalyst. It also indicates that the PTA molecules are hydrolytically stable even after three cycles of catalysis. FT-IR data of recycled PTA-Jeffamine® catalyst further supports the same. The observation is significant as literature reports hydrolytic instability of simple and lacunary Keggin type POMs in the presence of H_2O_2 .^[19] The enhanced stability of the catalyst may be attributed to the stabilizing effect of cationic Jeffammonium ions as indicated in the work by Mal *et al.*^[38]

Although conversion of BzOH was observed in all the catalytic cycles, there was a gradual decrease in conversion values as well as selectivity (Figure S7). This is due to the decrease in catalytic efficiency of the recycled PTA-Jeffamine® catalyst may be attributed to the partial decomposition of the catalyst in the acidic environment of the recycled aqueous phase. Formation of BzA in the aqueous phase as observed in

FT-IR and UV-vis studies (Figure 3) might aggravate the catalytic conditions by decreasing the pH considerably (pH 2.5). Similar hindrance by acid attack on POM catalyst is reported by Mal *et al.*^[38]

Controlled reactions

Controlled reactions were carried out to establish the role of Jeffamine® and PTA. Oxidation of BzOH with H_2O_2 and pure-PTA was performed. The pH of the catalyst was adjusted with KOH to 7.5. GC-MS data indicated a very low conversion ~ 5% (Table 2, S. No. 3). Details on controlled reactions are provided in experimental section. Since Jeffamine® exists as quaternary ammonium cation in presence of PTA, it was replaced with CTAB which had similar ammonium groups.^[37] The reaction of BzOH and H_2O_2 in presence of CTAB was monitored by TLC (Figure S8). TLC and Tollens' test results showed the absence of BzH after 1.5 h (Figure S8 & S9). Literature reports suggest that the interaction of H_2O_2 with PTA to form active PTA species decreases with increasing alkyl chain length.^[25] Hence CTAB with longer chain length than Jeffamine® may be ineffective for BzOH oxidation. Effect of PTA in the oxidation process was evaluated by carrying out BzOH oxidation reactions in presence of Jeffamine® with a conventional acid (HCl) instead of PTA (Figure S10 & S11). Reaction between BzH and H_2O_2 with only Jeffamine® were also performed (Figure S12). TLC and Tollens' test showed absence of BzH after 1.5 h in all cases.

Mechanism of the catalytic process

From the experimental results, it is apparent that PTA shows catalytic effect for the selective conversion of BzOH to BzH in water only in presence of Jeffamine®. That is, the liquid-derivative of PTA is more effective in the oxidation process. The conversion and selectivity values towards BzH showed improvements as Jeffamine® content was increased against a fixed PTA concentration in the liquid-derivative. Before we venture into the mechanistic aspect of the current reaction, it is worth mentioning that, the classic Ishii-Venturello system is important when considering catalytic oxidation reactions with PTA and H_2O_2 .^[45] Literature reports also suggest that, in the Ishii-Venturello system, the Venturello anion ($\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$) is combined with a quaternary ammonium cation in the formation of an inorganic-organic hybrid salt. The "salt" was used as a phase transfer catalyst for alcohol oxidation under mild conditions.^[45] In the present work, we have shown that in absence of Jeffamine®, the pure-PTA act as a poor catalyst with H_2O_2 as oxidant. This may be due to the fact that the Venturello ion formed was not stable in absence of Jeffamine®. Effect of cations stabilizing anionic structures is well known in biological systems where proteins and various cellular structures are found to be stabilized in presence of certain cationic materials.^[54] In case of the liquid-derivative of PTA, the Jeffammonium species might be responsible in stabilizing the Venturello ion formed in the reaction medium (Scheme 1). The stabilized complex may have further reacted with BzOH to form BzH as shown in Step 3, Scheme 1.

The conversion of BzOH and rate of reaction depends on the smooth transfer of Venturello ion to the organic phase.^[30] As Jeffamine® is amphoteric in nature, we measured the surface tension (S.T.) values of PTA- Jeffamine® at pH 3.5 and 7.5 respectively and compared the S.T. values with that of pure PTA in water (Table 3). PTA solutions containing Jeffamine® shows

S. no	Sample	Surface tension (N/m)
1	Water	75.64
2	PTA-Jeffamine® (pH 3.5)	44.28
3	PTA-Jeffamine® (pH 7.5)	36.5

lower S.T. values compared to that in pure water (Table 3).^[55] Increasing Jeffamine® concentration (i.e. increasing pH from 3.5 to 7.5) results in further decrease in S.T. (Table 3). The low S.T. value can be a result of "worm-like" micellar structures formed as shown in FE-SEM images (Figure 4). Formation of such micellar structures may allow more H₂O₂ molecules to interact with BzOH across the water-oil interface resulting in increased conversion to BzH at high pH (pH 7.5). Low S.T. values may also induce PTA molecules to orient at the water-oil interface and result in improved selectivity towards BzH formation.^[30] Thus, the Venturello ion formed in the reaction medium can be efficiently transferred to the organic phase by Jeffamine® resulting in high conversion and improved selectivity.

Based on the experimental evidences and the trend in GC-MS data, we can draw a mechanistic picture of the BzOH oxidation process as shown in Scheme 1. In case of pure PTA, the reactive Venturello intermediate formed by the reaction of H₂O₂ and PTA is not stable and cannot effectively phase-transfer. This results in low conversion values of BzOH as shown in Table 2. For PTA- Jeffamine® catalyst, the Jeffamine® molecules stabilized the Venturello ion and consecutively reduces the S.T. of the medium by formation of micellar structures (Figure 4). The electrostatic complex formed between PTA & Jeffamine® allowed quick and quantitative transfer of the active Venturello ion to the organic phase to react efficiently with BzOH. The reaction rate thus increased with increase in Jeffamine® concentration (pH > 4.5) as shown in the kinetic studies (Figure S3). At higher Jeffamine® content, i.e., at pH 7.5, 100% conversion takes place within 30 min as shown in Figure 6. This fast kinetics enabled us to formulate the mechanism.

Conclusion

The catalytic activity of Jeffamine® modified PTA was investigated in detailed for H₂O₂-mediated oxidation of BzOH in water. Experimental data obtained from various techniques ranging from FT-IR, UV-vis spectroscopy, FE-SEM, surface tension, ICP-MS and GC-MS indicated that addition of Jeffamine® increased conversion rate of BzOH, facilitated easy separation of BzH and PTA catalyst from the reaction medium and provided hydrolytic stability to the structure of PTA at a

wide range of pH. GC-MS data revealed that the BzH obtained from the catalytic process was stable owing to the presence of intermediates formed during the oxidation process. Formation of BzA hindered the catalytic conversion of BzOH to BzH in consecutive catalytic cycles.

Supporting Information Summary:

Additional experimental section, TLC studies of BzOH oxidation, GC-MS data for reactions performed at various conditions, Bar diagram showing pH dependence of conversion, GC-MS data for kinetic study of BzOH oxidation with liquid PTA derivative® at pH 7.5, MS data for selected GC peaks, GC-MS data for diluted samples, Data for recoverability tests, TLC studies of controlled reactions, UV-vis data summarised from Figure 3, Summary of kinetics experiments performed at pH 7.5, Tabular representation of Figure S4 and ICP-MS data of organic layer after first reaction cycle.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Benzyl alcohol oxidation • Jeffamine® • Phase separation • Phosphotungstic acid • Venturello ions

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