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Styrene Epoxidation in Aqueous over Triazine-Based Microporous Polymeric Network as a Metal-Free Catalyst

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ABSTRACT

Tirazine based microporous polymeric (TMP) network was found to be an efficient metal-free catalyst for the epoxidation of styrene. The reactions were performed in water as an environmentally benign medium using H_2O_2 as a green oxidant at ambient temperature. The reaction afforded higher yield with 90% conversion of styrene and 98% selectivity to styrene oxide in 6 h. The triazine based microporous polymeric network can be readily recovered and reused up to 4 cycles without significant loss in catalytic activity and selectivity.

Keywords: Triazine Microporous Polydendritic Network; Metal-Free Catalyst; Aqueous Medium; Epoxidation; Styrene

1. Introduction

Design and development of nitrogenous materials and their utilization in catalysis is of great interest. Depending upon the type of N-moieties these materials have been enormously utilized in catalyzed organic transformations such as Knoevenagel condensation [1], aldol condensation [2], C-H bond activation [3], isomerization [4], oxidation [5] and epoxidation [6]. Recently nitrogen based molecules such as guanidine [7], cinchonidine [8], urea [9], aminoacids [10], 1, 4-diazabicyclo [2.2.2] octane (DABCO) [11] and proline derivatives have drawn substantial attention in catalysis due to their green nature. However the use of these nitrogenous material as an organocatalysts have a number of formidable problems such as corrosion, deposition on reactor walls and moreover tedious product/catalyst separation procedure due to their homogenous modus operandi. To overcome these problems efforts have been made towards immobilization of nitrogenous materials onto organic, polymeric, or inorganic nanoporous supports [12]. Although immobilization of the homogenous catalyst reduces several drawback but are prone to problems like less number of active sites, high loading and leaching of anchored organocatalyst during reaction.

In this context it is highly desirable to design a nanoporous catalyst which possess in built catalytic functionalities as a part of framework. One such promising design of catalyst is porous polymers due to their metal free nature, high surface properties and flexible framework, compared to inorganic siliceous materials. Moreover the monomeric units in these polymeric networks can be tuned according to the desired catalytic reaction. It has been reported by Chehardoli *et al.* that melamine have potential to catalyze the chemo- and homoselective oxidation of thiols and sulfides [13] by hydrogen peroxide. With respect to these viewpoints we have synthesized high surface area polymeric network containing terephthalaldehyde and melamine as monomeric unit and were intrigued by possibility to utilize this triazine based microporous polymeric (TMP) network as a heterogeneous catalyst in epoxidation of styrene to styrene oxide.

Conventionally styrene oxide is prepared via two homogenous routes, namely dehydrochlorination of styrene chlorohydrin with a base or oxidation of styrene using organic peracids with transition metals. Both these methods are hazardous and show poor selectivity for styrene epoxide and produce copious amount of undesirable wastes, leading to disposal problem of toxic solid and liquid wastes. Since last few decades Payne epoxidation system [14] have been enormously used [15], this system operates via Radziszewski reaction in which hydrolysis of an organic nitrile by alkaline hydrogen peroxide occurs via peroxycarboximidic acid intermediate leading to end products amide, water and oxygen. The presence of olefin in this reaction mixture acts as a better reducing agent and potentially eliminates the hydrolysis of the intermediate with hydrogen peroxide thereby accomplishing epoxidation of the olefin.

In last decade Richardson *et al.* have introduced bicarbonate-activated peroxide (BAP) system which operates

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in water for oxidation of sulfides [16] and also for water-soluble olefins [17], however this system have limitation for hydrophobic olefins. Later Burgess *et al.* [18] made further progress in BAP system for epoxidation of hydrophobic olefins using various transition metal salts, additives and also co-solvents. Tong *et al.* have also developed an epoxidation protocol for lipophilic olefins based on manganese sulphate and BAP system in which ionic liquid served as solvent media as well as phase transfer agent [19]. These systems are associated with drawbacks like use of buffer, additive, co-solvent, phase transfer agent and moreover tedious product/catalyst separation procedure. In this context here we report a designed eco-friendly protocol using BAP system for epoxidation of styrene in water at room temperature using triazine based polymeric network as metal-free heterogenous catalyst.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used without further purification. Styrene was purchased from Sigma Aldrich. $NaHCO_3$ and 28% H_2O_2 were purchased from Duksan chemicals South Korea. The water was deionized by aqua Max^{TM} basic water purification system, Young Lin, Korea.

2.2. Catalyst Preparation

Synthesis of TMP-Network: The 1,3,5-triazine based microporous network was synthesized by slightly modified procedure as reported earlier [20]. A flame dried two necked round bottom flask fitted with a condenser and a magnetic stirring bar, was charged with terephthalaldehyde dissolved in dimethyl sulfoxide and heated up to 100˚C and temperature was maintained till a yellow colour solution was observed. Warmed melamine solution in dimethyl sulfoxide was added to hot terephtahaldehyde solution under nitrogen atmosphere. The hot solution is maintained at 100˚C with sonication for 3 h. The resulting mixture was heated at 180˚C up to 48 h under an inert atmosphere. After cooling to room temperature the precipitated TMP network was isolated by filtration over a Buchner funnel and washed with excess acetone followed by tetrahydrofuran and dichloromethane. The isolated TMP network was dried under vacuum for overnight at 60˚C and gave 75% yield.

2.3. Characterization

Fourier transform infrared (FT-IR) spectroscopy (Nicolet 6700) and Raman spectroscopy (HR 800, Horiba/Jobin-Yvon) were employed to analyze the chemical structure of the catalyst. The NMR (Nuclear Magnetic Resonance) spectra were recorded on Varian UnityNOVA solid state 600 MHZ spectrometer. The Brunauer-Emmett-Teller (BET) nitrogen adsorption and desorption were measured at –196˚C using a Micromeritics porosimeter (model AS-AP-2020). Prior to the measurement, the samples were degassed at 160˚C for 5 h. Scanning electron microscopic (SEM) image was collected with a JEOL 630-F microscope. The aliquot of reaction mixture were analyzed by GC and GC-MS (Agilent technologies 5975).

2.4. Catalytic Activity

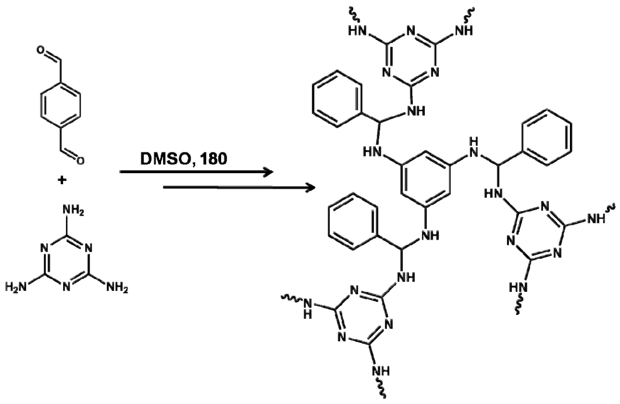
Styrene 1 mmol along with 2 ml of H_2O and 20 mg of catalyst were taken in a vial with magnetic bar. Appropriate amount of $NaHCO_3$ (0.5 - 2.0 mol) in one ml water was added to this reaction mixture. The reaction mixture was stirred for 30 min followed by drop wise addition of H_2O_2 at room temperature. After completion of reaction the reaction mixture was separated by the addition of diethyl ether and separated using separating funnel. The ether layer was collected dried over anhydrous sodium sulphate, filtered, concentrated by rota-evaporator and subjected to GC analysis. The obtained products were characterized by GC-MS.

The conversions were calculated on the basis of mole percent of styrene, the initial mole percent of styrene was divided by initial area percent (CYA peak area from GC) to get the response factor. The unreacted moles of styrene remained in the reaction mixture were calculated by multiplying response factor with the area percentage of the GC peak for CYA obtained after the reaction. The conversion was calculated as Styrene Conversion (mol%) = [(Initial mol% − Final mol%)/initial mol%] × 100 and selectivity was calculated as Styrene oxide Selectivity % = (GC peak area of styrene oxide/ΣGCpeak area of all products) × 100.

3. Results and Discussion

3.1. Catalyst Preparation and Characterization

The TMP network was synthesized by catalyst free polymerization via condensation of terephthalaldehyde and melamine with modified procedure as reported earlier (**Scheme 1**). The modified procedure contributed to improved yield (75%) and as well as reduced the reaction time from 72 h to 48 h [20]. Fourier transform infrared (FTIR) spectroscopy (**Figure 1**) of TMP network depicted the absence of the bands at 3470 cm^{-1} and 3420 cm^{-1} (NH_2 stretching) which corresponds to the primary amine group of melamine [21]. The absence of band at 1690 cm^{-1} (C=O stretching) corresponding to carbonyl function of the aldehydes confirmed the formation of TMP network. The well distinct quadrant vibrations at (1550 cm^{-1}) and semicircle stretching vibrations (1480 cm^{-1}) of heteroaromatic ring systems are observed in FTIR spectra. No band corresponding to imine linkages such as the



Scheme 1. Synthesis of TMP network.

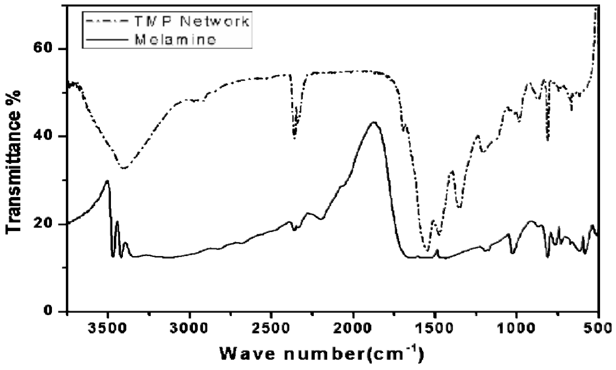


Figure 1. Fourier transform infrared (FTIR) spectra of Melamine and TMP network.

C=N stretching vibration around 1600 cm^{-1} are observed. The UV spectrum (**Figure 2**) depicted K and B bands which arise from π to π* transitions as a result of a group containing multiple bond being attached to the aromatic ring. The incorporation of melamine showed bathochromic shift in K band from 220 nm to 250 nm and in B band it shifted from 300 nm to 350 nm [22]. The above all characteristics depicted the incorporation of melamine and formation of TMP framework.

The ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR (**Figure 3**) spectrum shows three resonances which appears at 167, 114, and 54 ppm. The peak at 167 ppm is assignable to the carbon atoms present in the triazine ring of the melamine, while the signal at 114 ppm corresponds to C-H aromatic carbons of the benzene and resonance at 54 ppm originates from the tertiary carbon atoms formed upon the addition of the primary amine groups of melamine. The ^{15}N CP-MAS spectrum (**Figure 4**) of TMP network showed two major resonances at –215 and –287 ppm, respectively. The peak at –215 ppm is assigned to the nitrogen atoms in the triazine ring, whereas the peak at –287 ppm may be attributed to the secondary amine present in the aminal motif. All the characterization results were in consonance with those reported earlier [20].

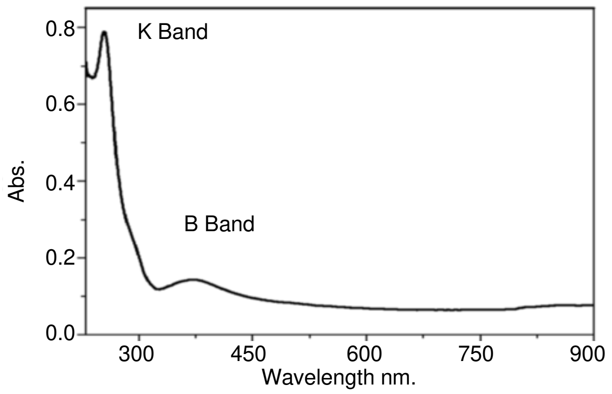


Figure 2. U.V. spectra of TMP network.

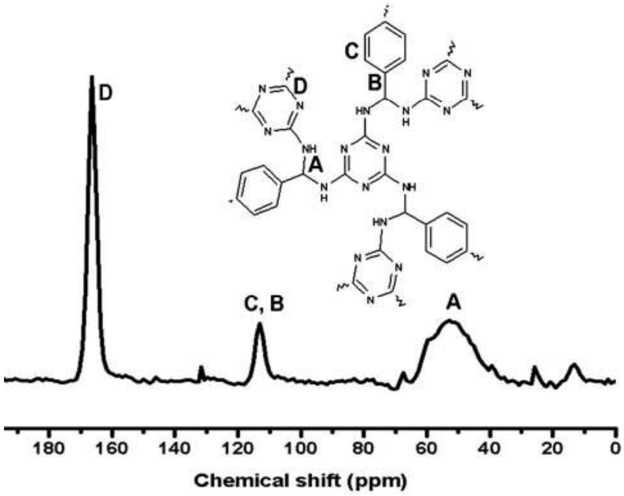


Figure 3. Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of TMP network.

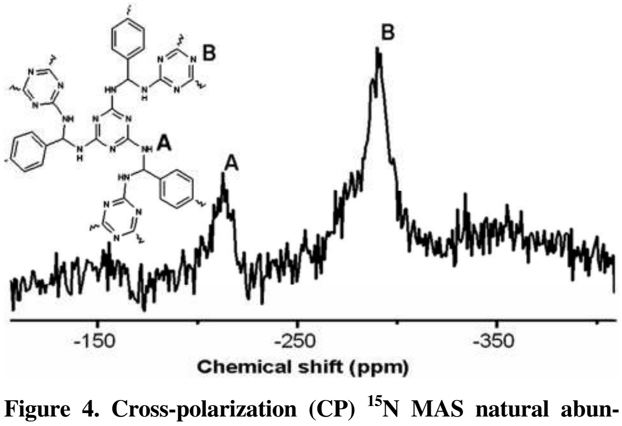


Figure 4. Cross-polarization (CP) ^{15}N MAS natural abundance NMR spectrum of TMP network.

The surface properties of TMP networks were analyzed by nitrogen sorption analysis. The adsorption isotherm (**Figure 5**) showed a steep gas uptake at low relative pressures and also flat course in the intermediate section, which reflects the microporous nature of the polymeric networks [23]. The Brunauer-Emmet-Teller (BET) surface

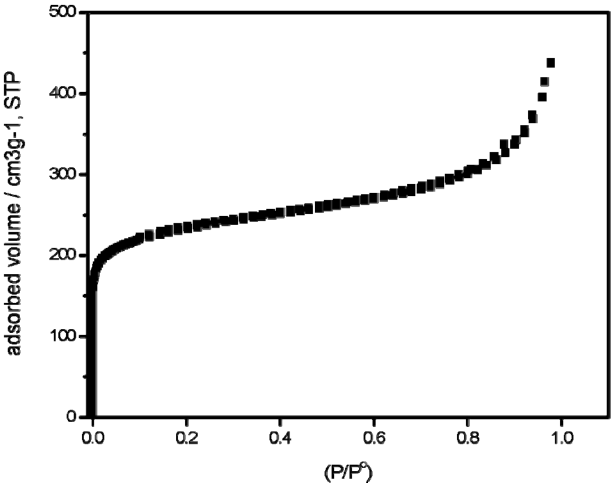


Figure 5. Nitrogen adsorption and desorption isotherm of TMP network.

area found to be 738 m^2/g indicated high degree of cross-linking in TMP network which is also evidenced by SEM image showing globular aggregates of TMP network (**Figure 6**). The micropore volume calculated by nonlocal density functional theory (NLDFT) found to be 0.22 cm^3/g indicated conformational flexibility of TMP network.

3.2. Catalytic Results

The TMP network was used as catalyst for the epoxidation of styrene with various oxidants in the presence and absence of promoter. Initially the optimization of molar ratio of oxidant to substrate was investigated in presence of $NaHCO_3$ as promoter using acetonitrile as solvent system and the results are listed in **Table 1**.

Low conversion of styrene was observed for unimolar ratio of substrate to oxidant (**Table 1**, Entry 1) further increase in molar ratio was very effective to increase the conversion of styrene to styrene oxide (**Table 1**, Entries 2-4). The highest conversion (50%) and selectivity (90%) was observed at molar ratio 1:5 (**Table 1**, Entry 5), however further increase in amount of oxidant increases the conversion but dropped selectivity (**Table 1**, Entry 6). After optimization of oxidant to substrate molar ratio reactions were carried out in aqueous and organic (acetonetrile, DMF, DMSO) solvent systems (**Table 2**). Interestingly, conversion of styrene to styrene oxide was found 60% with good selectivity (98%) in aqueous conditions (**Table 2**, Entry 4). Surprisingly acetonitrile (**Table 2**, Entry 1) gave better conversion (50%) and high selectivity (90%) among the non-aqueous solvents, whereas moderate conversion and selectivity was observed in DMF and DMSO (**Table 2**, Entries 2 and 3).

The selectivity and conversion in aqueous media were higher; therefore further studies were performed in aqueous using various oxidants namely H_2O_2, tert-Butyl hydroperoxide (TBHP) and iodosylbenzene. However the conversion and selectivity was poor with TBHP and iodosylbenzene compared with H_2O_2, which may be due to lesser degree of solvation of oxidant in reaction media. To further optimize the amount of promoter variation in $NaHCO_3$ concentration from the range of 0.0 - 2.0 mole % was used. In absence of $NaHCO_3$ the conversion was low (5%). The maximum conversion (90.8%) and selectivity (97.8%) was achieved at 1 mole% of $NaHCO_3$ (**Table 3**, Entry 3), further increase in concentration of

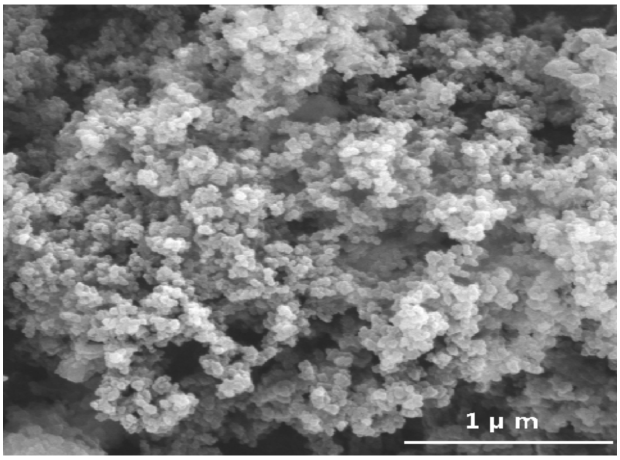


Figure 6. Scanning electron microscopy image of TMP network.

Table 1. Optimization substrate to H_2O_2 molar ratio.

Entry	Styrene:H_2O_2	Conversion of Styrene %	Selectivity for Styrene Oxide %
1	1:1	10	96
2	1:2	22	96
3	1:3	30	94
4	1:4	36	93
5	1:5	50	90
6	1:6	54	85

Reaction condition: 20 mg catalyst, Styrene 1 mmol, 1 - 6 mmol 30% H_2O_2, 0.5 mmol $NaHCO_3$, acetonitrile 2 ml, 25˚C, 6 h.

Table 2. Influence of solvent and oxidant on conversion.

Entry	Solvent	Oxidant	Conversion of Styrene %	Selectivity for Styrene Oxide %
1	ACN	H_2O_2	50.0	90.0
2	DMF	H_2O_2	45.5	75.0
3	DMSO	H_2O_2	38.9	65.0
4	H_2O	H_2O_2	60.3	98.7
5	H_2O	TBHP	30.1	45.0
6	H_2O	PhIO	15.3	ND

Reaction condition: 20 mg catalyst, Styrene 1 mmol, 5 mmol oxidant, 0.5 mmol $NaHCO_3$, solvent 2 ml, 25˚C, 6 h.

Table 3. Effect of base and temperature on conversion.

Entry	$NaHCO_3$ (mmol)	Time	Conversion of Styrene %	Selectivity for Styrene Oxide %
1	0	12	5.0	ND
2	0.5	6	60.3	98.7
3	1	6	90.0	97.8
4[a]	1	6	30.3	99.0
5[b]	1	6	>99	59.2
6	1.5	6	92.2	70.2
7	2	6	97.1	65.2
8[c]	1	12	10.0	ND

Reaction condition: 20 mg catalyst, Styrene 1 mmol, 5 mmol H_2O_2, 0.5 mmol $NaHCO_3$, 25˚C, H_2O 2 ml, 6 - 12 h, [a]15˚C, [b]40˚C, [c]absence of catalyst.

Table 4. Recyclability of the catalyst.

Entry	No. of Cycle	Conversion of Styrene %	Selectivity for Styrene Oxide %
1	1	90.9	98.0
2	2	89.1	98.0
3	3	87.9	97.5
4	4	88.6	97.4

Reaction condition: 20 mg catalyst, Styrene 1 mmol, 1 - 6 mmol 30% H_2O_2, 0.5 mmol $NaHCO_3$, acetonitrile 2 ml, 25˚C, 6 h.

$NaHCO_3$ increases the conversion but selectivity for epoxide was dropped (**Table 3**, Entries 6 and 7). The Optimized amount of base was found to be one mole % of $NaHCO_3$. To know the effect of temperature for the conversion of styrene to styreneoxide, the reaction was also conducted at different temperatures (**Table 3**, Entries 3-5). At lower temperature (15˚C) the selectivity was higher (98%), however the conversion (30.3%) was low (**Table 3**, Entry 4). At higher temperature (40˚C) the conversion was 100% however, the selectivity of styrene oxide was dropped down to 59.2% and the diol was other product which was formed due to ring opening at high temperature (**Table 3**, Entry 5).

The ideal temperature was found to be 25˚C (**Table 3**, Entry 3) where high conversion (90.8%) and excellent selectivity (97.8%) was obtained, further increase in temperature causes poor selectivity (**Table 3**, Entry 5).

The catalyst was recycled up to 4 cycles without significant loss of activity and selectivity (**Table 4**).

3.3. Role of H_2O

The higher activity in aqueous condition may be attributed to stabilization of catalytic active species peroxymonocarbonate ion, (HCO_4^-) [19] which is also in agreement with earlier report. We have also able to demonstrate by ^{13}C NMR the formation of peroxymonocarbonate species (**Figure 7**). The NMR spectra in absence of hydrogen peroxide depicted peak corresponding to bicarbonate anion HCO_3^- at 160.5 ppm (**Figure 7(a)**). When hydrogen peroxide was added to the solution a peak at 157.7 ppm (**Figure 7(b)**) could be observed suggesting the formation of peroxymonocarbonate species [17-19].

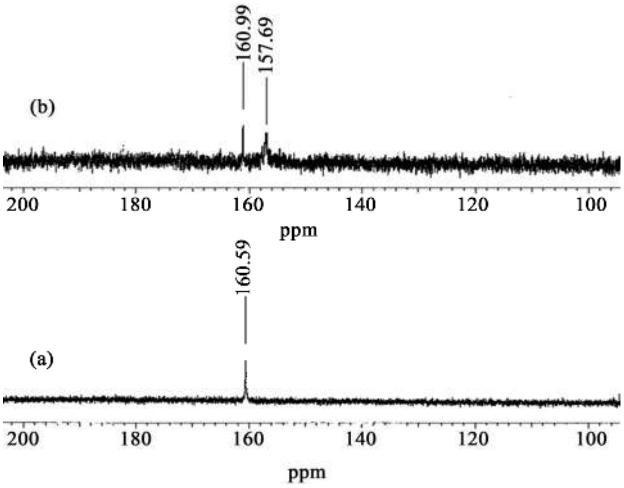
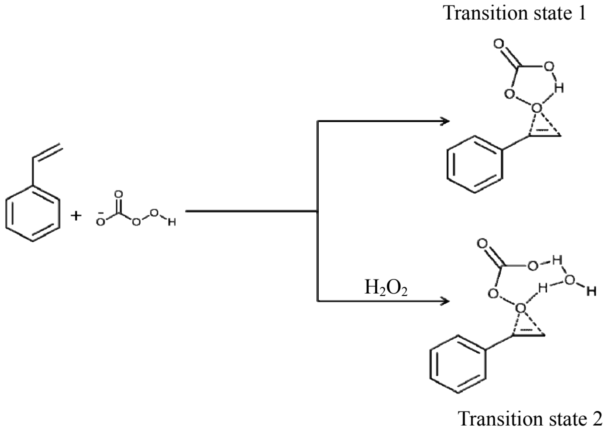


Figure 7. ^{13}C NMR spectra for a solution at 25˚C in D_2O. (a) $NaHCO_3$; (b) $NaHCO_3$:H_2O_2 (1:5).



Scheme 2. TMP network catalyzed epoxidation of styrene and transition states.

Richardson et al. have proposed the formation of peroxymonocarbonate species leads to two transition states in BAP system as depicted in (**Scheme 2**) transition state 1 and transition state 2 [17]. The two transition states proposed earlier are different compositionally; transition state 1 involves olefin, peroxymonocarbonate species whereas the transition state 2 involves H_2O in addition (**Scheme 2**). This suggests that the mechanism in water proceeds via two different pathways increasing the conversion.

In addition to lower transition state energy the reaction of organic molecules in water are prone to "Breslow effect" [24]. In line of this effect it is presumed that styrene molecules repel water molecules and are forced to form aggregates in order to decrease the organic surface area exposed to water. Organic reactions arising from these hydrophobic aggregates in water will have reduced activation energies and significant rate enhancements. In addition to this the water medium brings the styrene molecule in close proximity of TMP network by π-π stacking interactions which influences the contact times of substrate with catalyst [25].

4. Conclusion

TMP-network has been synthesized and its role as an efficient catalyst towards styrene epoxidation has been demonstrated with effective performance in aqueous medium. The better performance in water is accredited to dual pathway and "Breslow effect". This eco-friendly epoxidation protocol afforded 90.9% conversion of styrene with 97.8% selectivity to styrene oxide under aqueous conditions using hydrogen peroxide as an oxidant at ambient temperature. The catalyst can be easily recycled and used several times without significant loss in conversion and selectivity.

5. Acknowledgements

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