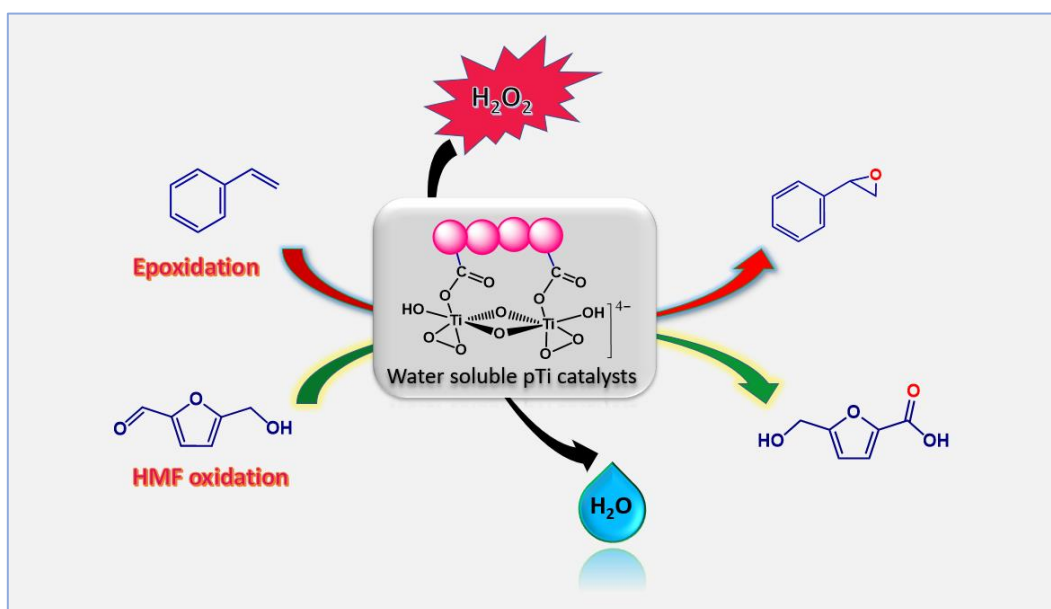


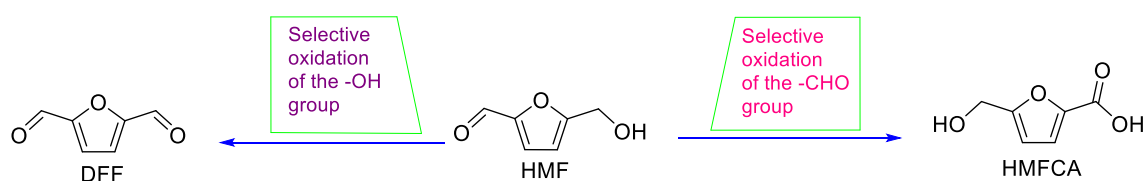
CHAPTER 6

Polymer anchored peroxidotitanates as novel and versatile catalysts for selective oxidation of 5-hydroxymethyl-2-furfural and solvent free epoxidation of olefins with H_2O_2



6.1 Introduction

Biomass derived 5-hydroxymethyl-2-furfural (HMF) has been widely recognized as a versatile platform molecule as it can be used as a sustainable precursor for the preparation of a broad range of valuable chemicals and liquid transportation fuels [1-3]. The oxidation of HMF can generate several kinds of furan compounds, as shown in **Scheme 1.10** of Chapter 1, such as 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), 5-formyl-2-furancarboxylic acid (FFCA) or levulinic acid (LA) [4-14]. In addition to these, 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) is another important product formed by the selective oxidation of the aldehyde group in HMF [15-21]. The compound serves as an important monomer for various polyesters [22] as well as a starting material for synthesis of FDCA. Also, it has been proved that HMFCFA has therapeutic properties like antitumor as well as antimicrobial activities [23]. However, reports pertaining to HMFCFA synthesis from HMF oxidation is still limited compared to the overwhelming research on synthesis of FDCA and DFF from HMF. This may be due to the difficulty in the selective oxidation of the formyl group into carboxylic acid [17], without affecting the alcohol functional group in HMF (**Scheme 1**).



Scheme 1 Possible products obtained from selective oxidation of HMF.

A number of efficient methodologies have been developed in recent years to obtain HMFCFA *via* oxidation of HMF using various homogeneous or heterogeneous catalysts based on metals such as Mo, Au, Ag, Pd etc. [12,15-18,24,25]. A heterogeneous catalyst developed by Zhang *et al.* by immobilizing molybdenum acetylacetonate complex on montmorillonite K-10 clay showed high catalytic activity in oxidation of HMF with molecular oxygen to HMFCFA, with 87% selectivity in toluene [17]. Using a gold catalyst, 95% yield of HMFCFA was obtained *via* oxidation of HMF with 690 kPaO₂ pressure [11]. Another selective HMFCFA formation protocol was established by

Zhou *et al.* using Au/TiO₂ catalyst which afforded 90–95% yield of HMFCa under ultraviolet and visible light within 8 h of reaction [16]. Schade *et al.* have recently shown that HMFCa was produced with 98% yield after 5 h reaction time at 50 °C, 10 bar air pressure, 4 equivalents of NaOH in water by supported gold and silver-based catalysts [15]. We have come across only three research articles discussing the synthesis of HMFCa from HMF oxidation through the classic Cannizzaro reaction [26-28]. Although yield obtained was >90%, complete product selectivity was not achieved in these reactions.

A perusal of literature thus revealed that despite the development of several promising methodologies to obtain HMFCa *via* oxidation of HMF using various metal catalysts, in majority of cases 100% selectivity of HMFCa could not be achieved even after a prolonged reaction time [13,17]. Moreover, most of the metal catalyzed oxidations utilized molecular oxygen or air as oxidant which is difficult to control [12,13]. Requirement of high pressure and temperature, high cost of the catalyst are additional difficulties in some of the procedures [13,15,17,24]. In fact, we are yet to come across any report on metal catalyzed oxidation of HMF to HMFCa using H₂O₂ as oxidant. Moreover, to the best of our knowledge, activity of peroxidotitanates as catalysts in HMF oxidation remains yet to be explored. Thus the development of efficient and sustainable catalytic procedure for selective oxidation of HMF into HMFCa still remains a challenging research area.

Among various types of organic oxidations catalyzed by titanium based systems, epoxidation of olefins ranging from small to large molecules is most well known [29-31]. Epoxides are one of the most valuable intermediates used in synthetic chemistry [32-36]. As has been mentioned in Chapter 1, although there are myriads of reports available that deal with the synthesis of epoxides using titanium based catalysts, most of them suffer from disadvantages like long reaction time, high cost of the method, difficulty in regeneration of catalyst, generation of toxic waste due to use of halogenated or hazardous organic solvents and oxidants. Recently, solvent-free reactions have been receiving great deal of importance as such systems contribute significantly towards the development of clean, environmentally benign and cost-effective procedures [37]. So far, we have come across only few reports of titanium catalyzed solvent-free epoxidation of alkene [38,39] including only one report of homogeneous titanium system [40].

Encouraged by the aforementioned observations and in continuation of our previous work presented in Chapter 3, in the present study we have focused on exploring the catalytic potential of the WSP supported **pTi** catalysts **3.1-3.3** in selective oxidation of HMF as well as olefin epoxidation using H_2O_2 as oxidant under mild condition. In fact, we have endeavoured to expand the substrate scope of these highly efficient catalyst systems which have already demonstrated excellent activity and selectivity in sulfide oxidation under very mild condition, as shown in Chapter 3.

The present chapter contains the findings of our studies on catalytic activity of the water soluble polymer anchored peroxidotitanium(IV) complexes $[\text{Ti}_2(\text{O}_2)_2\text{O}_2(\text{OH})_2(\text{carboxylate})]$ -PA (**PATi**) (**3.1**), $[\text{Ti}_2(\text{O}_2)_2\text{O}_2(\text{OH})_2(\text{carboxylate})]$ -PMA (**PMATi**) (**3.2**) and $[\text{Ti}_2(\text{O}_2)_2\text{O}_2(\text{OH})_2(\text{sulfonate})]$ -PSS (**PSSTi**) (**3.3**) in oxidation of 5-hydroxymethyl-2-furfural (HMF) with H_2O_2 in water. In addition, this chapter also describes the activity of these **pTi** complexes as efficient catalysts in olefin epoxidation under solvent free condition.

6.2 Experimental section

6.2.1 General procedure for catalytic oxidation of HMF

The oxidation reaction was carried out in a 50 mL round bottom flask. Typically, (0.4 mmol, 50.4 mg) of HMF was dissolved into water (3 ml) with stirring. Then the catalyst containing 0.004 mmol of Ti [**PATi** (1.1 mg) or **PMATi** (1.5 mg) or **PSSTi** (2.4 mg)] was added to the system. After that, NaOH, 1.6 mmol (64 mg in 3 mL water) was added drop wise followed by addition of aqueous 12% H_2O_2 (1.13 mL) to the system in 1:10 substrate: oxidant molar ratio. The temperature of the system was kept at 80 °C at a constant stirring rate. After reaction, the reaction mixture was diluted with water. The progress of the reaction was followed by HPLC method (**Appendix IV**).

Samples were analyzed by a Thermo Scientific Dionex Ultimate 3000 HPLC System equipped with a UV detector. Furan compounds were well separated by a reversed-phase C18 column (250 × 4.6 mm) at the wavelength of 280 nm at 25 °C. The peak area of each furan compound has a good linear relationship with its concentration at the wavelength of 280 nm. HMF, LA, HMFCa, DFF and FDCA were well separated under the analytic conditions, and their retention times were 14.3, 13.8, 25.6, 14.8 and 26.9 min, respectively in the 40 minutes run. The mobile phase was composed of

methanol, water, acetonitrile and 0.1 wt% acetic acid aqueous solutions. Gradient method was applied.

6.2.2 General procedure for catalytic epoxidation of olefins

To a reaction mixture of catalyst (containing 0.005 mmol of Ti) [**PATi** (1.4 mg) or **PMATi** (1.8 mg) or **PSSTi** (2.9 mg)] and styrene (5.0 mmol), 30% H₂O₂ (1.13 mL, 10 mmol) was added in portion. The system was kept at 80 °C under stirring. The Ti:substrate:oxidant molar ratio was maintained at 1:1000:2000. The progress of the reaction was monitored by HPLC. After completion of the reaction, the product and unreacted substrates were extracted by ethyl acetate.

The quantitative analysis of styrene and its oxidized products were performed on a Thermo-Scientific Dionex Ultimate 3000 HPLC system equipped with a UV detector. The products were detected at a wavelength of 254 nm and well separated by the use of a reversed phase C18 column (250 × 4.6 mm). The mobile phase was composed of acetonitrile, methanol and water in a volume ratio of 2:3:5 with a flow rate of 1 mL/min and an injection volume of 20 µL. The substrate and products were identified by using authentic samples (**Appendix III**). The content of the compounds in the sample was determined directly from the interpolation of the calibration curves.

6.2.3 Regeneration of the catalyst

The regeneration of the catalyst was carried out for the epoxidation reaction using styrene as the model substrate. After performing the reaction up to the stipulated reaction time as mentioned in the above section, the product, as well as unreacted substrates, were extracted with ethyl acetate. To the aqueous part of the system, fresh batch of substrate was added followed by the addition of 30% H₂O₂, maintaining the standard reaction condition. The reaction was repeated up to three cycles for each catalyst.

6.3 Results and discussion

6.3.1 Catalytic activity of 3.1-3.3 in oxidation of HMF to HMFCA

The WSP anchored **pTi** compounds were screened for their catalytic performance in oxidation of 5-hydroxymethyl-2-furfural (HMF) with H₂O₂ as oxidant. In line with our goal to achieve the targeted transformation under mild reaction

condition, we have performed oxidation of HMF in water with aqueous 12% hydrogen peroxide. To obtain the desired product in maximum yield, we investigated the influence of various reaction parameters including reaction temperature, HMF: catalyst ratio, base additive, HMF : oxidant molar ratio etc., using **PATi** as representative catalyst.

6.3.1.1 Effect of temperatures

The reactions were carried out at four different temperatures starting from room temperature to 90 °C, under similar reaction condition to evaluate the effect of temperature on the HMF oxidation (**Fig. 6.1**). From the data presented in **Table 6.1**, it can be seen that with increase of temperature, formation of HMFCFA increases resulting in 71% HMF conversion with complete HMCA selectivity at 90 °C, within a short stipulated reaction time of 15 min resulting in a high TOF of 710 h⁻¹. However, we have decided to perform the subsequent reactions at 80 °C instead of higher 90 °C, considering the environmental aspect.

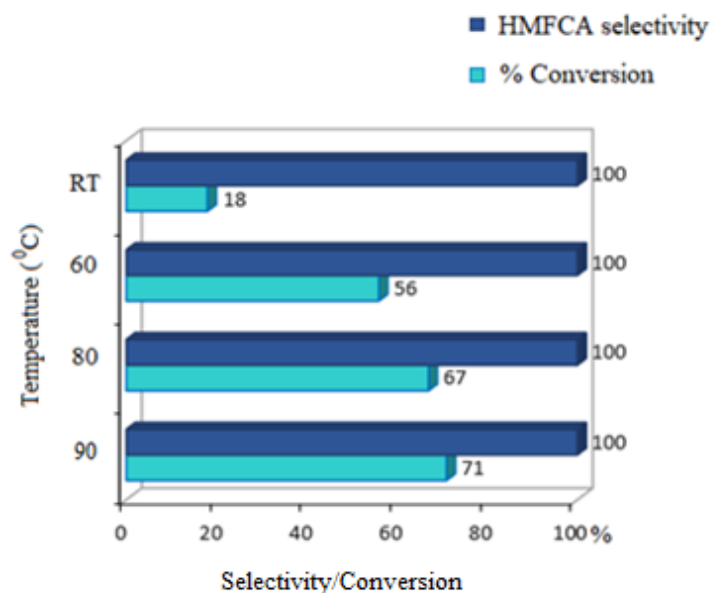


Fig. 6.1 % HMF conversion vs. temperature for catalyst **PATi**. Reaction condition: 0.4 mmol of HMF (50 mg), catalyst (0.0016 mmol of Ti), 1.6 mmol of NaOH (dissolved in 3 mL H₂O) in 3 mL water.

Table 6.1 HMF oxidation at different temperature^a

Entry	Temperature (^o C)	Time (min)	Conversion (%)	Selectivity (%)	TON ^b	TOF ^c (h ⁻¹)
1	RT	15	≥18	100	45	180
2	60	15	≥56	100	140	560
3	80	15	≥67	100	168	670
4	90	15	≥71	100	177	710

^aReaction condition: HMF (0.4 mmol, 50.4 mg), 12% H₂O₂ (4 mmol), catalyst (0.0016 mmol of Ti), NaOH solution (1.6 mmol, 64 mg in 3 mL H₂O) in 3 mL water. ^bTON (turnover number) = mmol of product per mmol of catalyst. ^cTOF (turnover frequency)= mmol of product per mmol of catalyst per hour.

6.3.1.2 Effect of base amount

Previous literature revealed that the presence of base in the reaction mixture was required in order to control the formation of byproducts from the side reactions of HMF oxidation [12,41,42]. Thus, in order to minimize the side-product formation during oxidation process concentration of base was optimized. Sodium hydroxide was used to facilitate the reaction because an earlier report indicated that hydroxide was more effective than carbonate [12]. All the other reaction parameters were kept constant for each experiment. The experimental results described in **Table 6.2** shows that, the reaction was sluggish and provided poor conversion without product selectivity in absence of base (Entry 1). Addition of base accelerated the reaction indicating that the base plays an important role in selective and fast oxidation of HMF. Although with increasing amount of base led to improved conversion at faster rate, 4 equivalents of NaOH was found to be effective to obtain 100% of HMFCAs selectivity. Moreover, higher base concentration was avoided in order to minimize the alkaline waste.

Table 6.2 HMF oxidation using different amount of base^a

Entry	HMF:NaOH	Time (min)	Conversion (%)	Selectivity (%)	TON ^b	TOF ^c (h ⁻¹)
1 ^d	--	15	≥4	--	10	40
		60	≥9	--	22	22
2	1:2	15	≥10	100	25	100
		60	≥28	100	70	70
3	1:4	15	≥67	100	168	670
		60	≥92	≥97	230	230
4	1:6	15	≥87	≥91	217	868
		60	≥96	≥54	240	240
5	1:8	15	≥97	≥95	243	970
		60	100	≥8	250	250

^aReaction condition: HMF (0.4 mmol, 50.4 mg), 12% H₂O₂ (4 mmol), catalyst (0.0016 mmol of Ti) at 80 °C in 3 mL water. ^bTON (turnover number)= mmol of product per mmol of catalyst. ^cTOF (turnover frequency)= mmol of product per mmol of catalyst per hour. ^dReaction performed without base.

6.3.1.3 Effect of catalyst amount and reaction time

The data presented in the **Table 6.3**, show that with increase in the amount of catalyst the conversion of HMF could be improved considerably within shorter reaction time without compromising HMFCA selectivity. Thus, 98% HMF conversion with 100% HMFCA selectivity was achieved within 30 min of reaction time when catalyst:HMF molar ratio was increased to 1:100. However, the highest TOF value of 880 h⁻¹ with complete HMFCA selectivity could also be obtained at 10-fold lower catalyst(Ti):HMF ratio of 1:1000, with a lower conversion 22% within 30 min. In a control experiment carried out in absence of catalyst under identical condition, only 27% HMF was oxidized by H₂O₂ within 30 min with a much lower HMFCA selectivity of 54%. Some byproducts from the oxidative cleavage of furan ring were also detected, which resulted in reduced HMFCA selectivity. Thus the important role played by the catalyst in achieving the desired selective oxidative transformation of HMF is amply evident.

Table 6.3 Effect of catalyst amount and reaction time on HMF oxidation using **PATi** as catalyst ^a

Entry	Cat:HMF	Time (min)	Conversion (%)	Selectivity (%)		TON ^b	TOF ^c (h ⁻¹)
				HMFCFA	Others		
1	1:1000	15	≥12	100	--	120	480
		30	≥22	100	--	220	880
		60	≥37	≥61	39	370	370
2	1:250	15	≥67	100	--	168	670
		30	≥86	100	--	215	430
		60	≥92	≥97	3	230	230
3	1:100	15	≥74	100	--	74	296
		30	≥98	100	--	98	196
		60	100	≥95	5	100	100
4 ^d	--	15	≥8	≥54	46	--	--
		30	≥27	≥54	46	--	--
		60	≥48	≥43	57	--	--

^aReaction condition: HMF (0.4 mmol, 50.4 mg), 12% H₂O₂ (4 mmol), NaOH solution (1.6 mmol, 64 mg in 3 mL H₂O), at 80 °C in 3 mL water. ^bTON (turnover number)= mmol of product per mmol of catalyst. ^cTOF (turnover frequency)= mmol of product per mmol of catalyst per hour. ^dBlank experiment without any catalyst.

Furthermore, reaction time of 30 min consistently provided better results both in terms of conversion as well as HMCA selectivity, irrespective of the amount of catalyst used. As evident from the data in **Table 6.3** (entry 3), prolonging the reaction up to 1 h, led to formation of byproducts which lowered the selectivity of the process.

6.3.1.4 Effect of oxidant concentration

Effect of oxidant concentration on HMF oxidation was next examined using various amounts of hydrogen peroxide. The results are summarized in **Table 6.4**. It is seen that HMF conversion increased dramatically from 37% to 98% (entries 1 and 4) as the HMF:oxidant molar ratio was increased from 1:4 to 1:10, while the product selectivity of 100% remained remarkably unaffected by these changes. Thus, HMF:H₂O₂ molar ratio of 1:10 was found to be ideal to attain complete HMFCFA selectivity

Table 6.4 HMF oxidation using different amounts of oxidants^a

Entry	HMF:H ₂ O ₂	Time (min)	Conversion (%)	Selectivity (%)	TON ^b	TOF ^c (h ⁻¹)
1	1:4	30	≥37	100	37	74
		60	≥43	100	43	43
2	1:6	30	≥67	100	67	134
		60	≥71	100	71	71
3	1:8	30	≥85	100	85	170
		60	≥89	100	89	89
4	1:10	30	≥98	100	98	196
		60	100	≥95	100	100

^aReaction condition: HMF (0.4 mmol), catalyst **PATi** (0.004 mmol of Ti, 1.1 mg), NaOH solution (1.6 mmol NaOH in 3 mL H₂O) at 80 °C in 3 mL water.

^bTON (turnover number)= mmol of product per mmol of catalyst. ^cTOF (turnover frequency)= mmol of product per mmol of catalyst per hour.

with highest HMF conversion of 98% within a fairly short reaction time of 30 min which, led to the best TOF value of 196 h⁻¹. The conversion and selectivity of the catalytic process with respect to different amounts of oxidant are shown in **Fig. 6.2**.

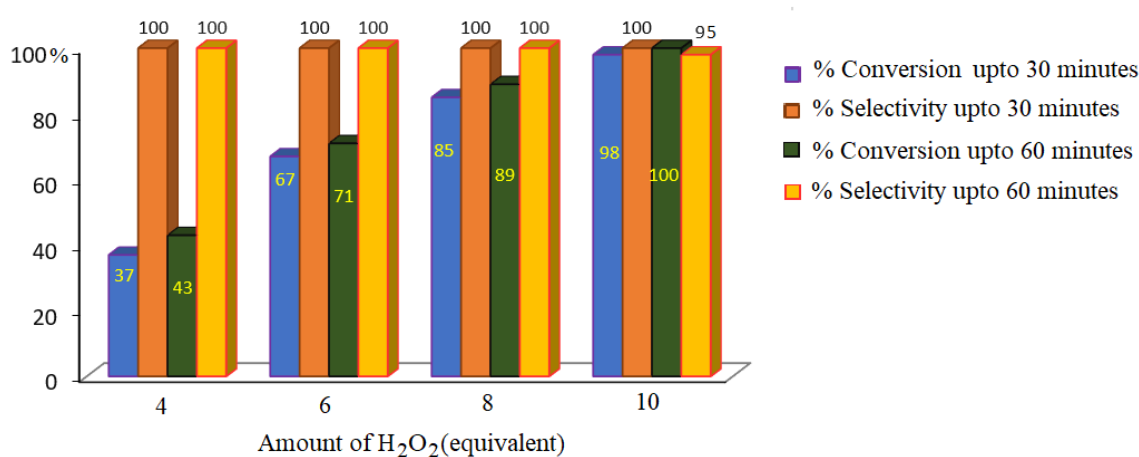


Fig. 6.2 % HMF conversion vs. amount of H₂O₂ (eq.) for catalyst **PATi**. Reaction condition: 0.4 mmol of HMF (50 mg), catalyst (0.004 mmol of Ti, 1.1 mg), 1.6 mmol of NaOH (dissolved in 3 mL H₂O), 80 °C in 3 mL water.

Table 6.5 Selective oxidation of HMF with 12% H₂O₂ catalyzed by **PATi**, **PMATi** and **PSSTi**^a

Entry	Catalyst	Time (minutes)	Conversion (%)	Selectivity (%)	TON ^b	TOF ^c (h ⁻¹)
1	PATi	30	≥98	100	98	196
2	PMATi	15	≥99	100	99	396
3	PSSTi	40	≥98	100	100	148

^aReaction condition: HMF (0.4 mmol), catalyst (0.004 mmol of Ti), 12% H₂O₂ (4 mmol), NaOH solution (1.6 mmol NaOH in 3 mL H₂O) at 80 °C in 3 mL H₂O.

^bTON (turnover number)= mmol of product per mmol of catalyst. ^cTOF (turnover frequency)= mmol of product per mmol of catalyst per hour. .

Our findings depicted in **Table 6.5** demonstrate that in addition to catalyst **PATi**, the other two WSP anchored **pTi** catalysts **PMATi** and **PSSTi** also serve as highly efficient catalysts in H₂O₂ induced oxidation of HMF into HMFCa. In fact, catalyst **PMATi** displayed superior activity in comparison to the other two catalysts, as nearly complete conversion of HMF occurred within a short period of 15 min although, the HMFCa selectivity was essentially identical in all the cases.

6.3.2 Catalytic activity of **PATi** (3.1), **PMATi** (3.2) and **PSSTi** (3.3) in epoxidation of alkene

First, we optimized various reaction parameters to attain the best conversion and selectivity, using **PMATi** as catalyst and styrene as substrate.

6.3.2.1 Effect of solvent

The encouraging results achieved in alkene epoxidation using polymer immobilized **pMo** catalysts under solvent free condition as described in Chapter 4, motivated us to explore the efficacy of the WSP bound **pTi** catalysts in styrene oxidation in absence of solvent, as well as in presence of variety of solvents. Initially a set of reactions were performed with 5 mmol of styrene, 0.005 mmol of **PMATi**, 30% H₂O₂ (10 mmol) as oxidant at 60 °C for 3 h in different solvents including water, to examine the effect of solvents on the epoxidation reaction (**Fig. 6.3**).

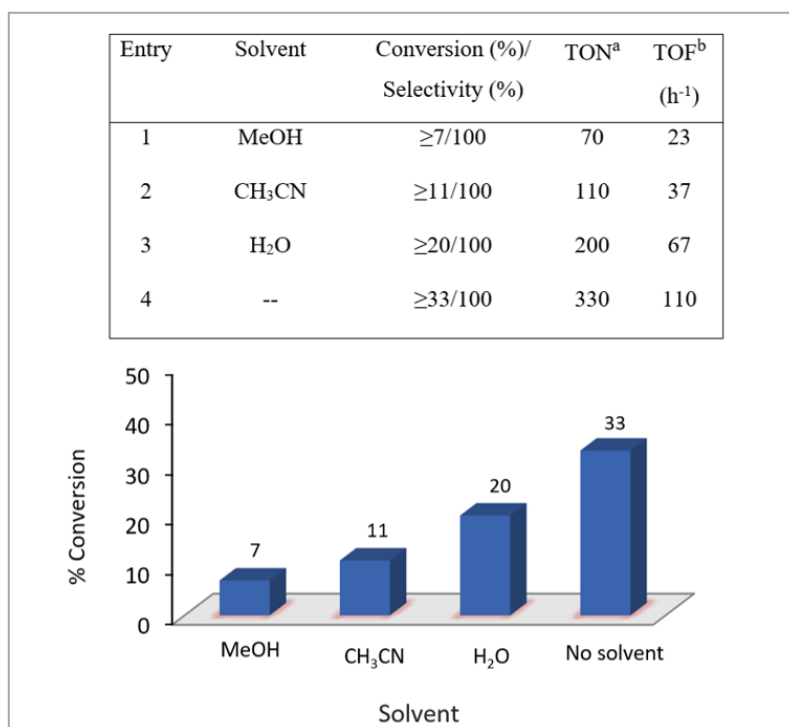


Fig. 6.3 Effect of solvent on styrene conversion over product selectivity and TON/TOF. Reaction conditions: Styrene (5 mmol), catalyst **PMATi** (0.005 mmol of Ti, 1.88 mg), 30% H₂O₂ (10 mmol, 1.13 mL), solvent (5mL), at 60 °C, 3 h. ^aTON (turn over number)= mmol of product per mmol of catalyst. ^bTOF (turn over frequency) = mmol of product per mmol of catalyst per hour.

To our delight, each of the reactions led to clean conversion of styrene to the targeted epoxide, however, solvent free reaction condition provided the highest styrene conversion under identical reaction condition [**Fig. 6.3** (inset, entry 4)]. Therefore, solvent free condition was preferred for the subsequent experiments.

6.3.2.2 Effect of temperature

Next, we performed the epoxidation reaction at different temperature ranging from room temperature to 80 °C. The experimental results revealed that under identical reaction condition it is easier to obtain maximum product conversion within the same reaction time at an elevated temperature. As shown in **Fig. 6.4** (inset entry 4), the catalyst displayed the best catalytic performance with highest conversion at 80 °C temperature along with 100% product selectivity. Therefore, 80 °C temperature was found to be optimal for further investigations.

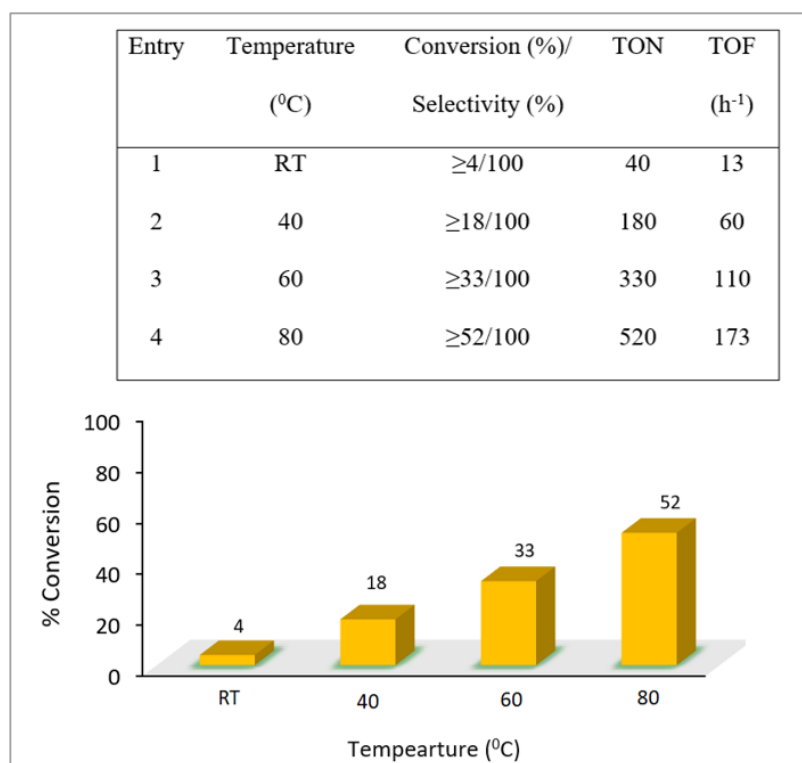


Fig. 6.4 Effect of temperature on styrene conversion over product selectivity and TON/TOF (inset). Reaction conditions: Styrene (5 mmol), catalyst **PMATi** (0.005 mmol of Ti, 1.88 mg), 30% H₂O₂ (10 mmol, 1.13 mL), 3 h.

6.3.2.3 Effect of H₂O₂ concentration

To assess the effect of oxidant amount on styrene epoxidation, we carried out the reactions using different amount of aqueous 30% H₂O₂. As illustrated in **Fig. 6.5**, although an increase in oxidant amount from 1 to 2 equivalents led to an enhancement of reaction rate resulting in higher TOF, further increase of oxidant amount to more than two equivalents led to lower conversion. Notably, the observation is in accord with findings in styrene epoxidation catalyzed by supported **pMo** catalysts **MRAsnMo** and **MRNAMo** mentioned in Chapter 5. Thus a catalyst:H₂O₂ ratio of 1:2 could be considered as ideal for attaining maximum conversion with high TOF.

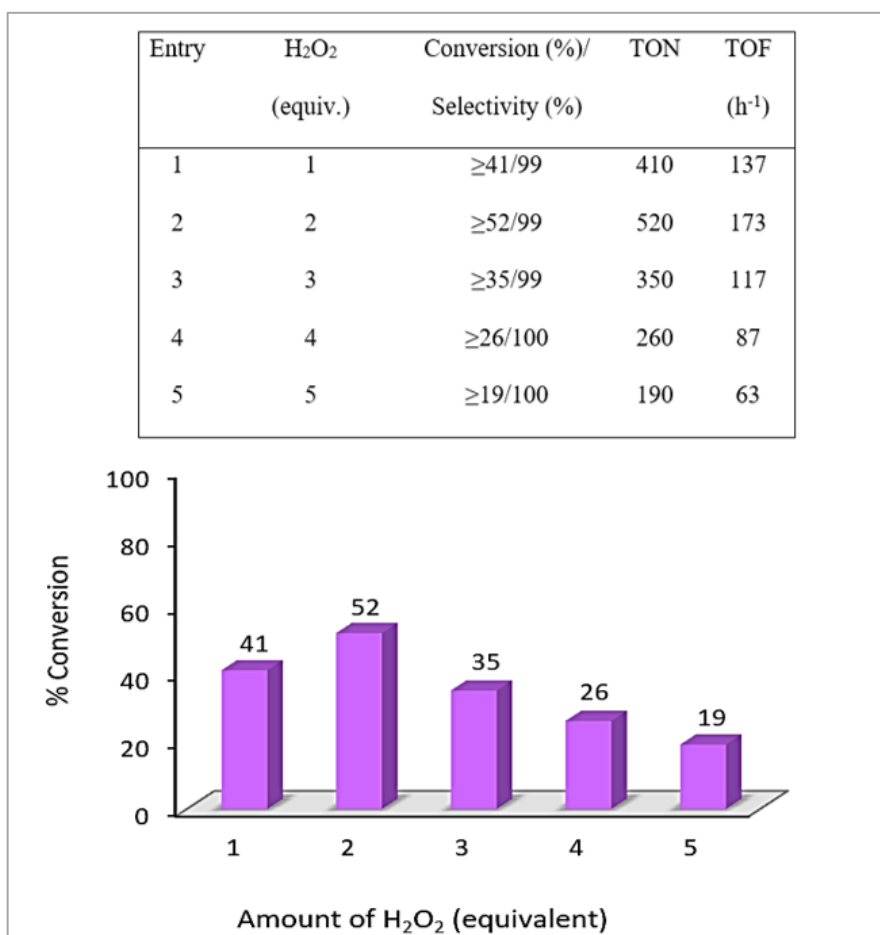


Fig. 6.5 Effect of H₂O₂ concentration on styrene conversion over product selectivity and TON/TOF (inset). Reaction conditions: Styrene (5 mmol), catalyst **PMATi** (0.005 mmol of Ti, 1.88 mg), 80 °C, 3 h.

6.3.2.4 Effect of catalyst amount

Amount of catalyst has been found to have an enormous effect on the rate of epoxidation reaction without any noticeable influence on the epoxide selectivity, as seen from the results shown in **Fig. 6.6**. In absence of the catalyst in a blank experiment, styrene conversion was recorded to be only 7% whereas, in presence of the 0.0025 mmol catalyst (1:2000::Ti:Styrene molar ratio) led to a dramatic rise in conversion to 31% under analogous condition. Reasonably good TOF value with high conversion was also obtained at 1:1000::Ti:Styrene molar ratio [**Fig. 6.6** (inset, entry 3)] and this amount of catalyst was regarded as optimal for styrene conversion.

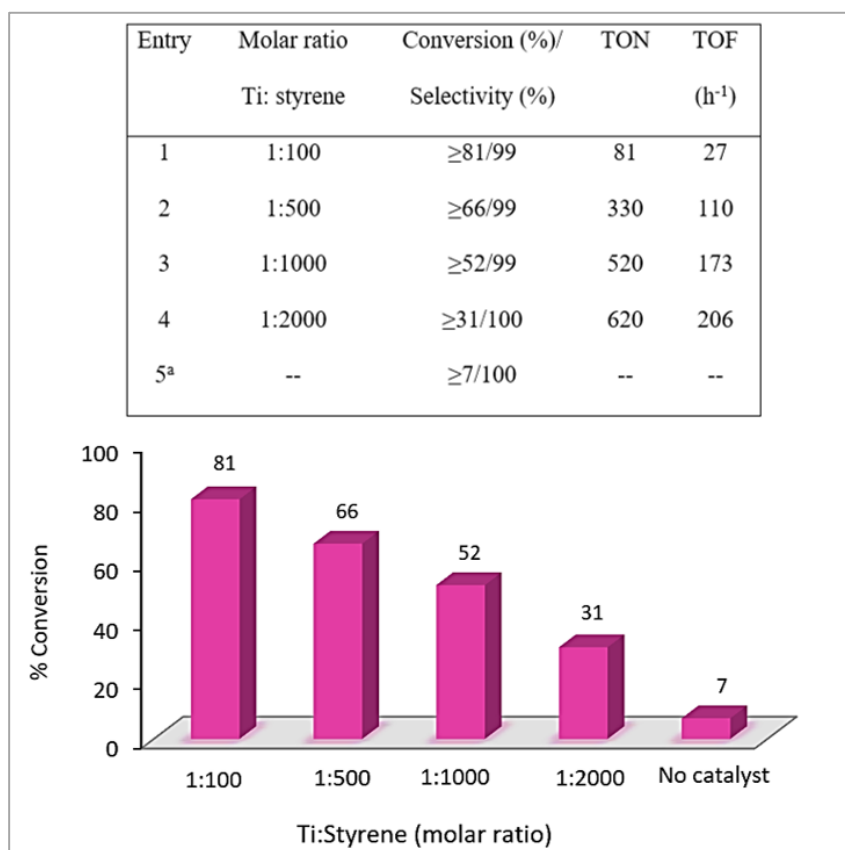


Fig. 6.6 Effect of catalyst amount (**PMATi**) on styrene conversion over product selectivity and TON/TOF (inset). Reaction conditions: Styrene (5 mmol), 30% H₂O₂ (10 mmol, 1.13 mL), 80 °C, 3 h. ^aBlank experiment without any catalyst.

6.3.2.5 Effect of reaction time

We have next probed the % conversion of styrene as a function of time. As expected, a gradual increase in conversion on prolonging the reaction time was observed, without any significant change in epoxide selectivity. Complete conversion of styrene with selectivity above 98% was achieved finally at 7.5 h [**Fig. 6.7** (inset, entry 9)]. Thus it is evident that the catalysts can withstand an elevated temperature of 80 °C and remain stable and retain their activity and selectivity with respect to styrene oxidation even on prolonging the reaction beyond 7 h.

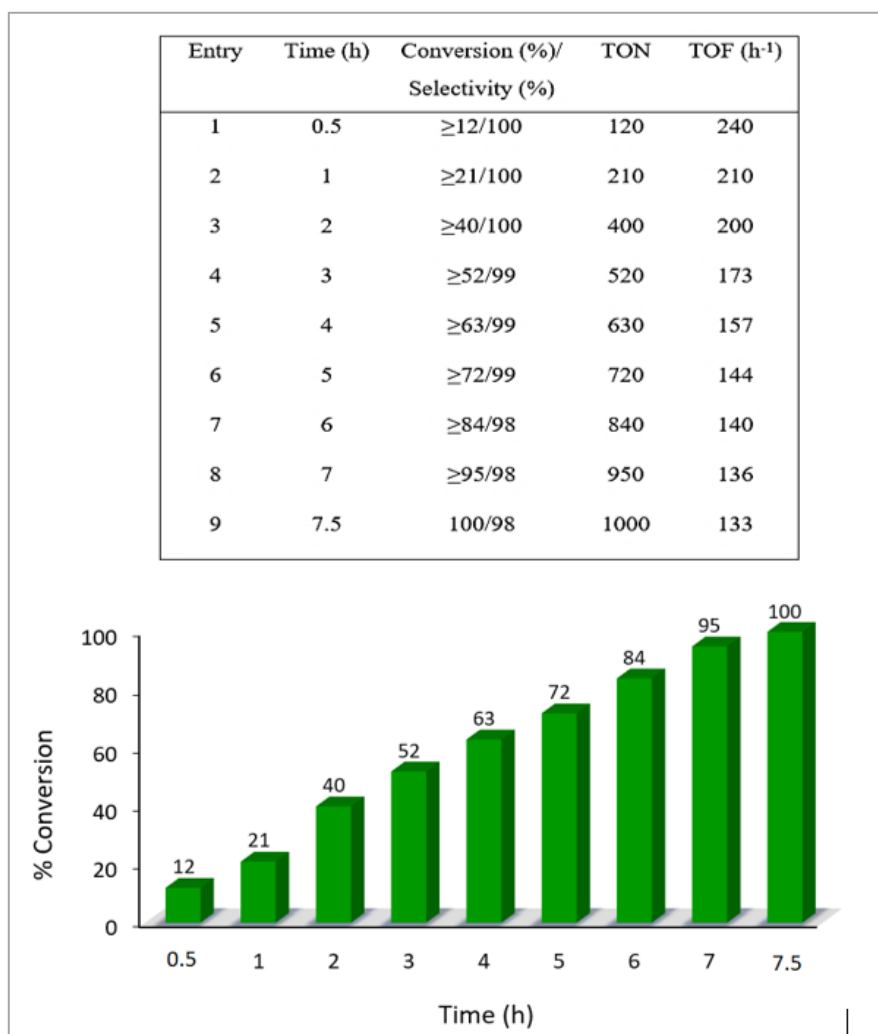
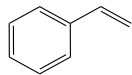



Fig. 6.7 Effect of reaction time on styrene conversion over product selectivity and TON/TOF (inset). Reaction conditions: Styrene (5 mmol), **PMATi** (0.005 mmol of Ti, 1.88 mg), 30% H₂O₂ (10 mmol, 1.13 mL) at 80 °C.

The optimized conditions were then utilized to examine the catalytic activity of the other two **pTi** catalysts *viz.*, **PATi** (**3.1**) and **PSSTi** (**3.3**) in alkene epoxidation to explore the applicability of the developed protocol in epoxidation of another unfunctionalized alkene *viz.*, cyclooctene. The results depicted in **Table 6.6** demonstrate that all the three catalysts are active in epoxidation of styrene as well as cyclooctene in presence of H₂O₂ under the standardized solvent free reaction condition, although **PMATi** was found to display relatively superior activity in terms of higher conversion within the stipulated reaction time of 7.5 h.

Table 6.6 Selective oxidation of alkenes to epoxides with 30% H₂O₂, catalyzed by **PATi**, **PMATi** and **PSSTi**^a

Entry	Substrate	PMATi					PATi				PSSTi			
		Time (h)	Conversion (%)	Selectivity		TOF ^b	Conversion (%)	Selectivity		TOF ^b	Conversion (%)	Selectivity		TOF ^b
				epoxide	others			epoxide	others			epoxide	others	
1		7.5	100	≥98	2 ^c	131	≥94	≥99	1 ^c	125	≥89	≥99	1 ^c	119
			≥83	≥95 ^d	5 ^c	111	≥72	≥98 ^d	2 ^c	96	≥68	≥97 ^d	3 ^c	91
2		4	100	100	--	250	≥87	100	--	217	≥82	100	--	205

^aReactions were carried out with 5 mmol substrate, 10 mmol of 30% H₂O₂ without solvent at 80 °C. Catalyst (0.005 mmol of Ti), ^bTOF (turn over frequency) = mmol of product per mmol of catalyst per hour. ^cBenzaldehyde. ^d% Conversion for 3rd reaction cycle.

6.3.2.6 Recyclability of the catalyst

One of the major drawbacks of homogeneous catalytic systems is their difficulty in regeneration and reuse. Interestingly however, as reported in Chapter 3, (Section 3.3.2.4) during catalytic oxidation of sulfide the water soluble immobilized **pTi** catalysts, afforded easy *in-situ* regeneration which could be reused for at least 10 reaction cycles with consistent activity and selectivity. Following a similar methodology, in the present case, the recycling experiments were performed under optimized reaction condition using styrene as model substrate (**Section 6.2.3**). After completion of the reaction, and separation of the product and unreacted substrates by extraction with ethyl acetate, fresh lot of substrate and 30% H₂O₂ were added to the reaction mixture containing the soluble catalyst. In this case however, as shown in the **Fig. 6.8**, conversion of styrene gradually decreased with each consecutive cycle of reaction. Dilution of the reaction system due to increment in oxidant volume after each reaction cycle, is likely to be responsible for the observation, as mentioned under section 6.3.2.3. It is noteworthy that, the product selectivity remained consistent during the recycling experiments for each system.

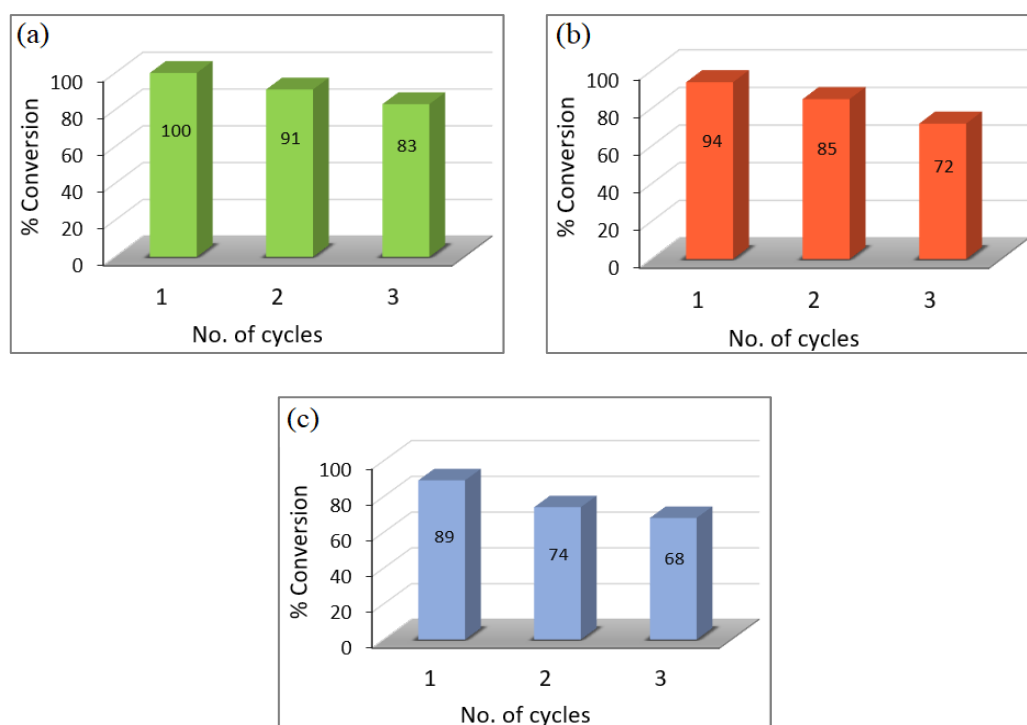


Fig. 6.8 Recyclability of catalyst (a) **PMATi**, (b) **PATi** and (c) **PSSTi** for the selective oxidation of styrene.

The IR and raman spectra of the recovered catalysts isolated after 3 recycling runs, did not show any significant change compared to the fresh catalysts, confirming that the catalysts retained their structural integrity during the catalytic process. However, elemental and EDX spectral data recorded for the recovered catalysts revealed slight decrease in peroxide as well as metal content, indicating some amount of metal leaching out of the polymer support during repeated reaction cycles.

6.3.2.7 Proposed catalytic cycle

Several reports are available addressing the nature of chemical transformation that takes place in the process of various oxidation reactions catalyzed by titanium based catalysts in the presence of hydrogen peroxide [31,43-46]. Katsuki and his co-workers synthesized the first dinuclear μ -oxido- μ -peroxido titanium salan complexes which they used as catalyst in the epoxidation of unfunctionalized olefins [43]. Recently Bryliakov and co-workers have examined epoxidation of styrene with a series of titanium salan catalysts [31,44,45]. The authors mentioned the specific role of the structure of catalyst present in the system. It has been observed that formation of an intramolecular hydrogen bonding between one of the peroxido oxygen of μ -oxido-peroxidotitanium salan type catalysts and nearby amino hydrogen leads to the activation of the peroxido moiety [31,43-46]. It is pertinent to mention that presence of a H-bond between the metal bound peroxido group and a neighbouring -COOH group has been indicated in the optimized structure of the complex **PATi** derived from DFT studies (Chapter 3, Section 3.3.1.6).

Although in absence of detailed kinetic data it is difficult to comment on the exact mechanism of the observed epoxidation reaction, nevertheless, taking into account the afore mentioned literature information and our experimental results, a proposed catalytic cycle for the epoxidation of alkene mediated by **pTi** complexes **3.1-3.3** in presence of H_2O_2 is shown in **Fig. 6.9**. The first step is the coordination of the alkene to the active titanium center (reaction a). In the next step, intramolecular oxygen transfer from the catalyst to the substrate takes place, leading to the formation of the product along with oxidotitanium intermediate (reaction b). This intermediate then combines with the H_2O_2 present in the system, thus generating the original catalyst (reaction c).

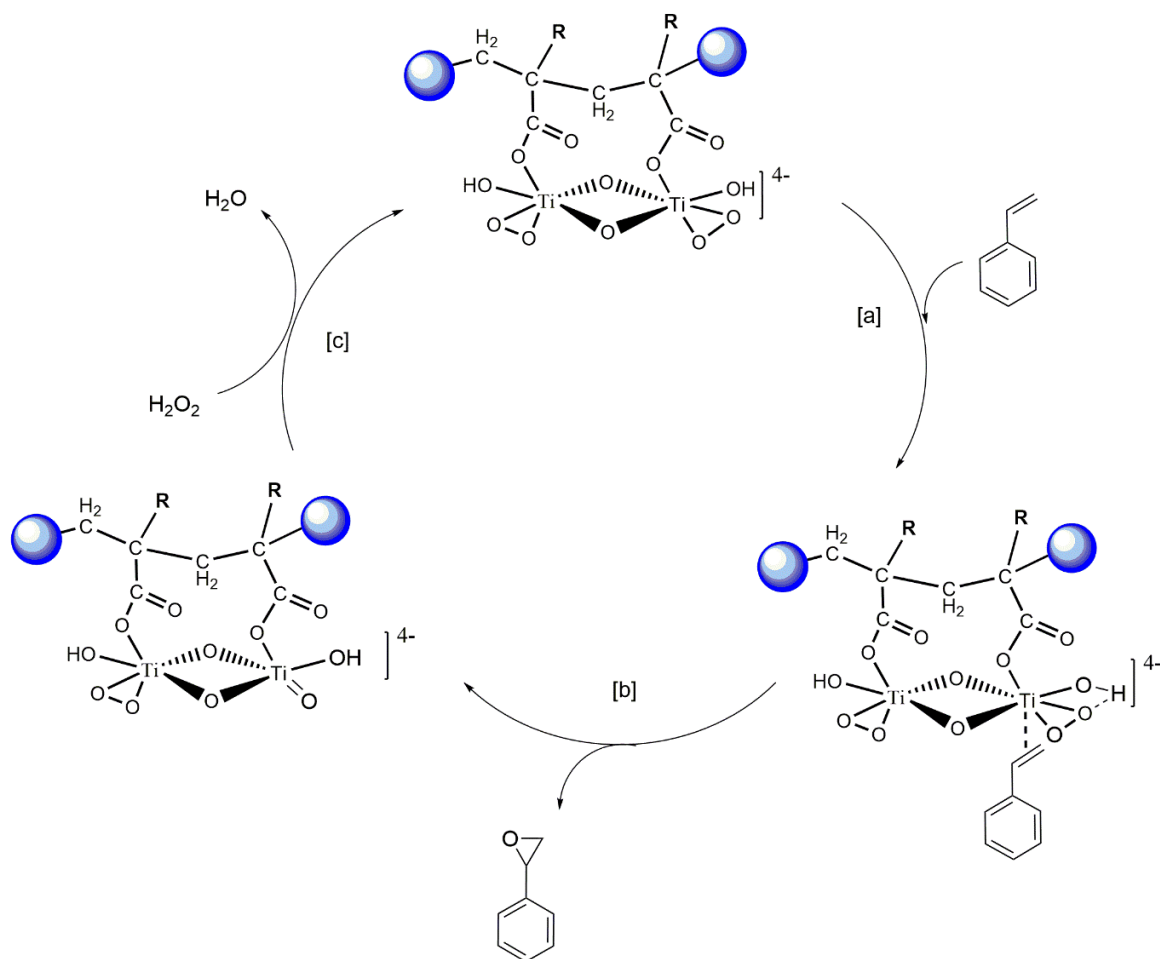


Fig. 6.9 Proposed catalytic cycle for epoxidation of styrene in presence of peroxidotitanium catalyst/ H_2O_2 system.

6.4 Conclusions

We have developed a new system for the highly selective oxidation of HMF to HMFCFA using a set of peroxidotitanium complexes supported on linear water soluble polymers as catalysts. Results obtained after investigating a number of important reaction parameters demonstrated that under optimized condition it was possible to attain nearly 99% HMF conversion with 100% HMFCFA selectivity within 15-40 min of reaction, using H_2O_2 as oxidant at 80°C , in water. The maximum TOF of 396 h^{-1} was obtained in presence of the catalyst **PMATi**. Thus compared to several reported methods on metal catalyzed HMFCFA synthesis from HMF [17,24,42,47], our catalytic

protocols offered a number of advantages with respect to conversion, selectivity and reaction conditions employed.

Further, employing the same catalyst systems it was possible to achieve clean and selective oxidation of unfunctionalized olefins such as styrene and cyclooctene with H₂O₂ as terminal oxidant under solvent-free condition. Thus, it has been demonstrated that the developed **pTi** catalysts have a great potential for application in epoxidation of alkene under mild condition.

Each of the developed catalytic oxidation protocols *viz.*, HMF oxidation and alkene epoxidation are operationally simple, safe and easy to control as these are carried out in aqueous medium or without solvent, under atmospheric pressure at temperature below 100 °C, using green oxidant H₂O₂. Thus, catalytic oxidation procedures adhere to green and sustainable chemistry. It is believed that our findings will be useful in the synthesis of value-based chemicals from renewable resources and will stimulate the design of efficient immobilized peroxido metal catalysts supported on linear water soluble polymers.

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