Kinetics studies and mechanism evolution of the epoxidation of styrene over nanoporous Au doped TS-1

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A kinetic investigation of the slurry phase epoxidation of styrene with hydrogen peroxide has been carried out, for the first time, over nanoporous Au doped TS-1 catalyst, in a batch reactor, in the temperature range of 313-333 K. It was found that product selectivity and the rate of reaction are greatly influenced by concentrations of styrene and hydrogen peroxide. Kinetics studies reveal that the mechanism of the reaction is of the "Redox" type. The rate equation, $r = k_1 k_2 P_O P_H / (k_1 P_O + k_2 P_H)$ deduced, assuming a steady state involving two stage oxidation-reduction process, represent the data most satisfactorily for the conversion of styrene to styrene oxide. A tentative mechanism of the process has also been suggested.

Keywords: Kinetics, Epoxidation, Au/TS-1, styrene, Styrene Oxide.

SOLVENT-FREE PRESSURE-SENSITIVE ADHESIVES

Catalytic epoxidation of olefins is an important issue from a practical as well as a mechanistic point of view. Epoxides as chemical intermediates find use in a wide variety of applications such as synthesis of several perfume materials, epoxy resins, plasticizers, drugs, sweeteners and other fine chemicals. Epoxidation of olefin compounds like styrene over titanium silicates molecular sieves; TS-1 (MFI)[1-2] or TS-2 (MEL)[3-4] using hydrogen peroxide[5-7] and anhydrous urea-hydrogen peroxide[8] as oxidant has gained considerable interest.

Metallic nanoparticles, finely dispersed onto high surface area supports are increasingly playing an important role in heterogeneous catalysis. In the liquid phase application, small gold particles (2 – 7nm) deposited over different solid supports has received a growing interest as a catalyst for the selective oxidation of organic molecules[9-10]. Direct epoxidation of propene using Au dispersed on TS-1 and other titanium containing supports has been reported by Nijhuis et al[11].

Although there are numerous publications on epoxidation of styrene[12], to my knowledge, only two reports on the kinetics of the process over Au/TiO2 and methyl rhenium trioxide catalysts have been found and no report on the kinetics of the process over Au-doped TS-1 was found. The present study was therefore undertaken to collect data on the rate of styrene oxide formation as a function of concentrations of reactants at various temperatures with a view to (1) finding a suitable model which could best explain the observed data and to (2) predicting the mechanism of the reaction.

MATERIALS AND METHODS

Styrene was procured from Aldrich, USA. Hydrogen peroxide and solvents like acetone, acetonitrile, methanol, carbon tetrachloride and isopropyl alcohol were procured from Merck. Tetrapropyl ammonium hydroxide, tetraethyl orthosilicate and tetrabutyl orthotitanate were also procured from Merck.

Preparation of Gold Doped TS-1

The catalyst was prepared as follows: To an aqueous solution of 25.25 g of Tetrapropyl ammonium hydroxide (TPAOH), 16.75 g of Tetraethyl orthosilicate (TEOS) was added slowly under vigorous stirring for 45 min in order to hydrolyze TEOS. A slight increase in the temperature was observed. To the resultant mixture (pH=12.5), a solution of 1.3 g of tetrabutyl orthotitanate (TBOT) in 5 g of dry isopropyl alcohol was added dropwise with stirring for 45 min in order to avoid its instantaneous hydrolysis to stable TiO_2 resulting in poor incorporation of titanium. The clear liquid thus obtained was stirred for 1 h in order to complete hydrolysis of TEOS and TBOT. Further, 13 g of double distilled water was added slowly to the above mixture and the final gel mixture was further stirred for 45 min to remove the alcohol. The reaction mixture was then transferred into a stainless steel autoclave and heated at 443 K for 24 hrs. The autoclave was quenched and the solid product was separated by centrifugation at 15000 rpm in 20 min. The product was dried at 393 K for 4-5 hrs and calcined at 813 K for 16 hrs. For the preparation of Au/TS-1, 1g TS-1 was added to a 10 ml of 5% solution of Gold (III) chloride under vigorous stirring at ambient temperature and pH was adjusted between 9 and 10 by adding ammonium hydroxide solution. The resulting mixture was stirred for 2 hrs, filtered and repeatedly washed with distilled water till it was free from chloride ions. Then the product was oven dried and calcined at 813 K.

Epoxidation experiments

Catalytic runs were performed in a 250-ml three-necked round bottom flask fitted with a magnetic stirrer, a condenser, a thermometer pocket and the third neck was used for sampling of the liquid phase. The whole assembly was housed in a water bath. This arrangement ensured the kinetic measurement at a constant temperature.

In a typical batch experiment the water bath was heated to 313 K and 1 g of hydrogen peroxide, 1 g of styrene, and 0.1g of catalyst Au/TS-1 were taken in the flask and stirred for the period of 4 hr. After the completion of the reac-

tion, the reaction mixture was cooled down to room temperature and the catalyst was separated by filtration. The liquid samples were subjected to analysis time to time using a Gas Liquid Chromatography (Chemito Gas Chromatograph 7610) equipped with Flame Ionization Detector. The conditions of the GC analysis were: FID Detector temperature 473 K, Injector temperature 473 K, and Column temperature ranges from 353 – 473 K. Nitrogen was used as a carrier gas with flow rate of 3 X10^{-5} m^3 / min.

RESULT AND DISCUSSION

Preliminary Studies:

The overall reaction can be written as shown in Scheme 1. Several runs were performed to screen the effect of differ-
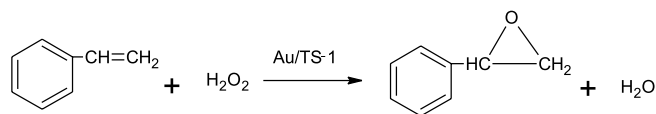
Scheme 1. Epoxidation of styrene to styrene over Au/TS-1

ent solvents, and the results are graphically shown in Figure 1. Acetone was found to be the best solvent, perhaps due to higher adsorption of styrene[13]; hence all the kinetic investigations were performed in this solvent. Byproducts such as benzaldehyde and phenyl acetaldehyde were not found with the present catalyst system. Analysis of the reaction mixture was repeated time to time to ensure that material balance according to equation 1 was > 98%. The summary of the operating conditions for the kinetic investigation is listed in Table 1. No epoxide was detected in the
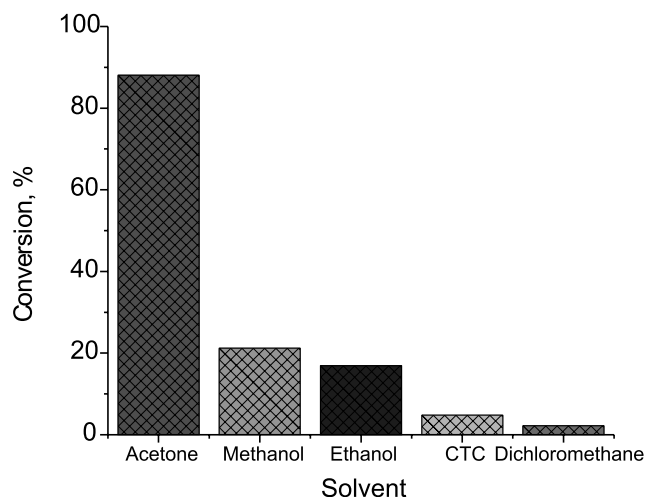

Figure 1. Effect of Solvent on Conversion of Styrene

Table 1. The range of the operating conditions

Conditions	Range
Temperature	313-333 K
Hydrogen Peroxide Concentration	3.3x10^{-4}-13.3x10^{-4} kmol/m^3
Concentration of styrene	3.3x10^{-4}-13.3x10^{-4} kmol/m^3
Concentration of catalyst	0.5x10^{-4}-1.5x10^{-4} kg/m^3
Time	1-4 hours
Volume	1.5x 10^{-5} m^3

absence of the catalyst, indicating the absence of any homogeneous reaction.

The analysis of the initial rate data provides a first approximation in understanding the dependency of the reaction rate on individual parameters. Liquid samples were drawn time to time and were analyzed on GC for the concentrations of styrene and styrene oxide during the whole epoxidation reaction. Typical concentration-time profiles for three temperatures are presented in Figure 2. The slope at initiation (t = 0) was taken as the initial rate of epoxidation.
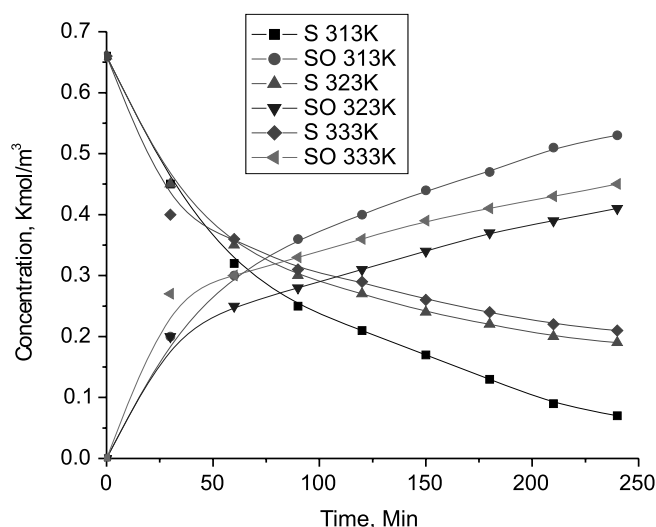
Figure 2. Variation of concentration of styrene and styrene oxide as a function of time

The effect of catalyst loading on the initial rates, in the temperature range of 313 – 333 K, styrene concentration 6.6 X 10^{-4} kmol/m^3 and hydrogen peroxide concentration 6.6 X 10^{-4} kmol/m^3, is shown in Figure 3. At all temperatures, the initial rates were found to be proportional to catalyst concentration, up to the catalyst concentration of 1 kg/m^3 indicating the absence of mass transfer limitation through the catalyst surface in this range. Subsequent reactions were performed at the catalyst concentrations < 1 kg/m^3.

The effect of rate of stirring on the initial rates, in the temperature range of 313 – 333 K, with styrene concen-
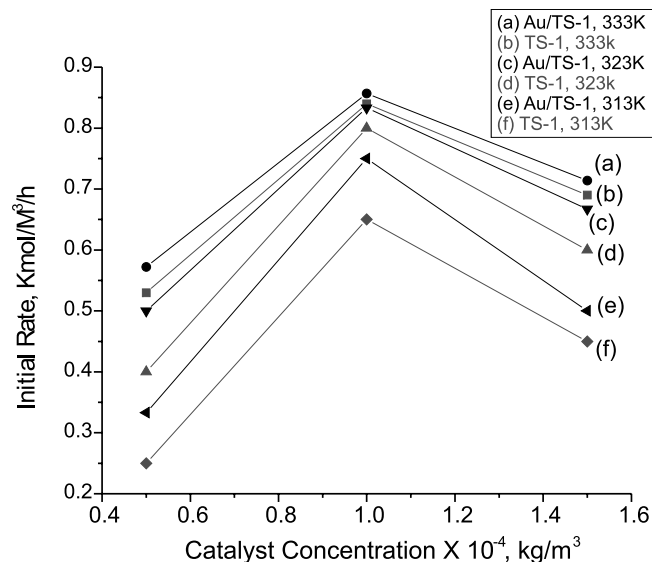
Figure 3. Effect of catalyst (TS-1 and Au/TS-1) concentration on initial rate of epoxidation

tration of 6.6×10^{-4} kmol/m^3, hydrogen peroxide concentration of 6.6×10^{-4} kmol/m^3, and catalyst loading in the range 0.5×10^{-4}-2×10^{-4} kg/m^3, is shown in Figure 4. Constant initial rates at all agitation speeds, at a particular temperature, confirm the absence of liquid, liquid diffusional mass transfer limitation.
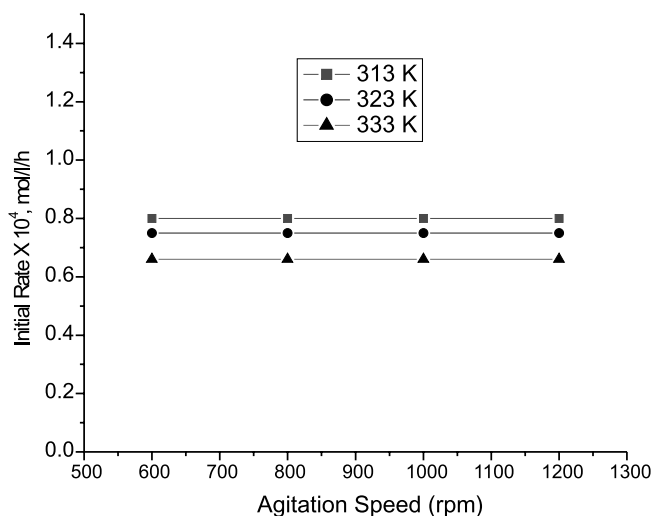

Figure 4. Effect of Agitation Speed on Initial Rate of epoxidation

Effect of concentration of hydrogen peroxide and styrene

The effect of concentrations of styrene and hydrogen peroxide on the initial rate of reaction, at 313 K, using Au/TS-1 as a catalyst is shown in Figure 5. It was found that the initial rate increases with an increase in the concentration of hydrogen peroxide, however, the rate of the increase was faster at a lower concentration and decreased with increase in concentration perhaps due to the loss of oxygen with concentration. In general, rates increase with an increase in styrene concentration.
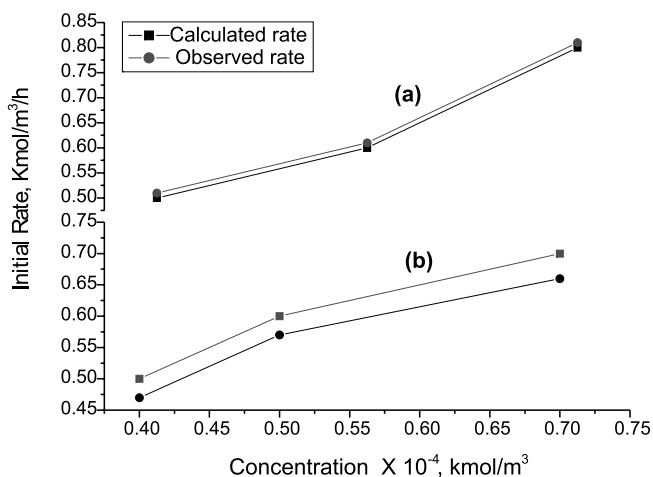

Figure 5. Effect of variation of concentration of (a) styrene and (b) hydrogen peroxide on initial Rate of epoxidation

Effect of temperature on rates

The effect of temperature on the initial rate of epoxidation was studied in the temperature range of 313 – 333 K. The study reveals that the initial rate increases with an increase in temperature. Further increase in temperature led to a decrease in initial rates perhaps due to

low availability of hydrogen peroxide due to its decomposition.

Treatment of rate data

Mass transfer to the catalyst, diffusion of reactants in the catalyst pores, adsorption, surface reaction and desorption of the products from the catalyst surface are the five steps responsible for a surface reaction. Under the present experimental conditions, the initial rates were found to be independent of the catalyst loading and stirring speed, indicating that mass transfer and diffusion were not rate controlling, thus leaving the possibility of adsorption, surface reaction and desorption as the possible processes controlling the rates of reaction.

Thus rate equations based on adsorption, surface reaction and desorption of the products were derived and tested for their validity in the present reaction. The list of such models tested is shown in Table 2. Kinetics studies reveal that the mechanism of the reaction is of the "Redox" type[14]. The derivation of rate equations, based on the two-step and three-step mechanisms, are as follows. In these derivations, the following notations are used; H= hydrocarbon (styrene), S= surface and O= oxidants (hydrogen peroxide), P_O = conc. of oxidant, P_H = conc. of hydrocarbon, S_{OX} = oxidized surface, S_{red} = reduced surface, SO = Styrene oxide, $S = S_{OX} + S_{red}$.

Table 2. Redox models tested for the epoxidation of styrene with Hydrogen peroxide

Model	Mechanism	Resulting rate equation
1.	Two stage mechanism k_1 H + S_{ox} ---------> SO + S_{red} k_2 S_{red} + O ----------> S_{ox}	$R = k_1P_Hk_2P_O /$ $(k_2P_O + k_1P_H)$
2.	Three stage mechanism k_1 H + S_{ox} ----------> TS-S_{red} k_2 TS-S_{red}----------> SO + S_{red} k_3 S_{red} + O -----------> S_{ox}	$R = k_1k_2k_3P_HP_O /$ $k_2k_3P_O + k_1k_3P_HP_O +$ $k_1k_2P_H$

R = rate of formation of styrene oxide, k_1, k_2, k_3 = rate constants, PO = concentration of oxidant, PH = concentrations of hydrocarbon.
H= hydrocarbon, O= oxidant
Sred = reduced surface, Sox= oxidized surface.

Two step mechanism.
$$k_1$$
$$H + S_{ox}----------> SO + S_{red}$$
$$k_2$$
$$S_{red} + O----------> S_{ox}$$
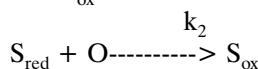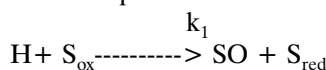
Rate of reduction of surface = $k_1 S_{ox} P_H$
Rate of oxidation of surface = $k_2 (1 - S_{ox}) P_O$
Here k_1 and k_2 are adsorption rate constants. In the steady state condition,
$$k_2 (1 - S_{ox}) P_O = k_1 S_{ox} P_H$$
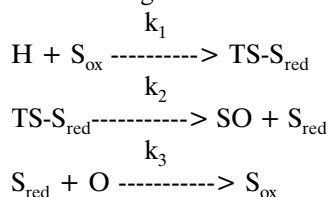$$k_2 P_O = (k_2 P_O + k_1 P_H) S_{ox}$$

$S_{ox} = k_2 P_O / (k_2 P_O + k_1 P_H)$

Rate of reaction $= k_1 P_H S_{ox}$ (1)

Or

$r = k_1 k_2 P_O P_H / (k_2 P_O + k_1 P_H)$ (2)

Three stage mechanism

$$H + S_{ox} \xrightarrow{\quad k_1 \quad} TS\text{-}S_{red}$$

$$TS\text{-}S_{red} \xrightarrow{\quad k_2 \quad} SO + S_{red}$$

$$S_{red} + O \xrightarrow{\quad k_3 \quad} S_{ox}$$

Applying steady state condition for TS-S_{red} and S_{red}

$k_1 P_H S_{ox} = k_2 [TS\text{-}S_{red}]$

$[TS\text{-}S_{red}] = k_1 PH\, S_{ox} / k_2$

$k_2 TS\text{-}S_{red} = k_3 PO S_{red}$

$S_{red} = k_2 TS\text{-}S_{red} / k_3.P_O$

$1 = S_{Ox} + S_{red} + TS\text{-}S_{red}$

$\quad = SO_x + k_2 TS\text{-}S_{red} / k_3.P_O + k_1 P_H\, S_{ox} / k_2$

$\quad = SO_x + k_2\; k_1 P_H\, S_{ox} / k_2 k_3.P_O + k_1 P_H S_{ox} / k_2$

$\quad = SO_x + k_1 P_H\, S_{ox} / k_3.P_O + k_1 P_H S_{ox} / k_2$

$S_{ox} = 1/(1 + k_1 P_H / (k_3.P_O) + k_1 P_H / k_2)$

Rate $= k_1.P_H\, S_{ox}$

$\quad = k_1 P_H /(1 + k_1 P_H/(k_3.P_O) + k_1 P_H / k_2)$ (3)

Rate equations derived for the two-stage and three-stage mechanisms were linearized and solved for the constants employing the method of the least squares, with the help of the observed data on the rate and the concentration of reactants. The rate law emerging with positive values of the constants is supposed to be the most representative of the reaction mechanism. In the present investigation model assuming the two-stage processes came out with positive coefficients of 2.82 and 1.73 and these can be accepted. Model 2 (three-stage mechanism) with the negative coefficients was rejected. Further support for model 1 (two-stage mechanism) is demonstrated in Figure 5 where the observed rates are plotted against the calculated rates. Reasonable matching between the observed and the calculated rates demonstrates the correctness of the model.

Evolution of the mechanism

Several works on the liquid phase epoxidation of hydrocarbons are based on the concept that metal peroxo species serve as a more versatile and functional oxidizing agent than hydrogen peroxide or hydrogen peroxide urea adduct .and follow the oxidation-reduction type of mechanism. According to this mechanism, peroxo oxygen is consumed in the reaction and the reduced site formed is reoxidized by hydrogen peroxide. In order to confirm the participation of metal- peroxo complex we (1) treated styrene with Au/TS-1 (2) styrene with HP and (3) styrene with Au/TS-1 pretreated with HP and found that styrene oxide is formed in step 3 only. We again repeated these reactions with the exhausted catalyst and repeatedly found that styrene oxide is formed when styrene is reacted with the catalyst pretreated with HP. This indicates that oxygen insertion into the double bond is not directly from hydrogen peroxide but through formation of peroxo compounds with hydrogen peroxide. In order to confirm the formation of peroxo species we recorded the FTIR spectrum of the complex in the range of 400 – 4000 cm^{-1} on Shimadzu 460 infrared spectrometer and it is reproduced
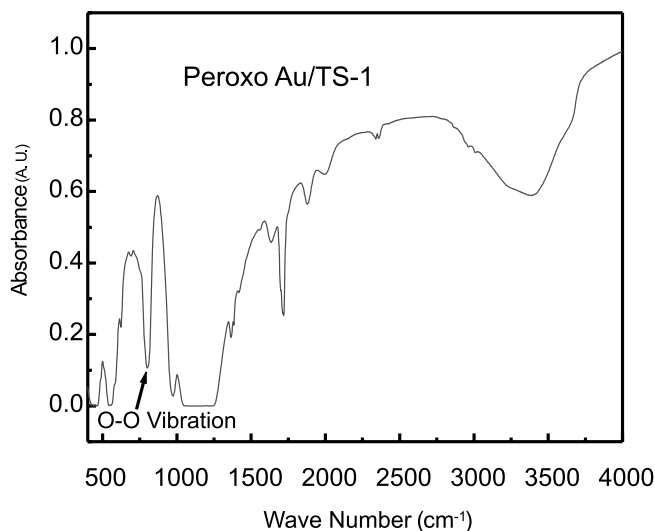

Figure 6. FTIR spectrum of Peroxo Au/TS-1

in Figure 6. The band at 800 cm^{-1} indicates the presence of O-O vibrations for Ti / Au peroxo complex[15]. Further evidence for the formation of peroxo species was provided by the DR-UV record reproduced in Figure 7. The peaks which appeared at 450 nm can be ascribed to peroxo moiety. A further confirmation of the peroxo species was obtained from the Raman record of (1)Au-TS-1 treated with hydrogen peroxide and (2) in situ Raman record of styrene mixed with Au-TS-1 treated with hydrogen peroxide and is reproduced in Figure 8. The record was made
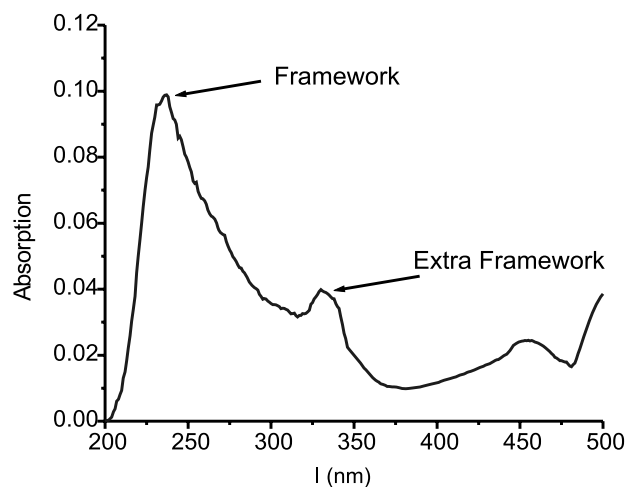

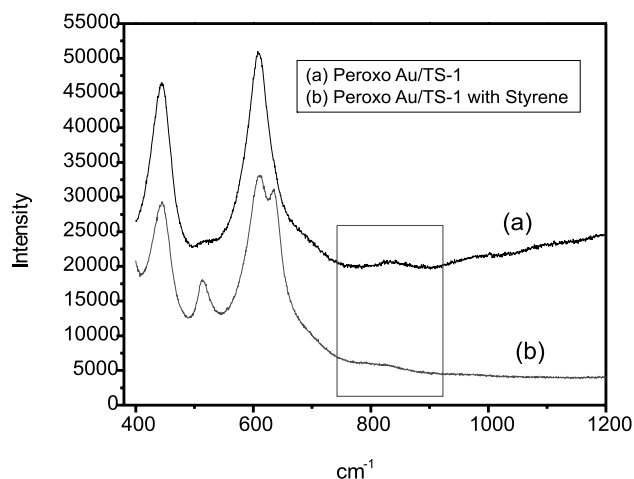**Figure 7.** Dr-UV-VIS spectrum of peroxo Au/TS-1

Figure 8. Raman Spectra of Au/TS-1 and Au/TS-1 after the interaction of Styrene

on a Labram HR800 microRaman spectrometer using Labspec software at UGC-DAE-CSR centre at Indore. The decrease in the intensity of peroxo band at 830 cm^{-1} confirmed the involvement of peroxo group during reaction

For the confirmation of the presence of extra framework ions, we recorded DR UV-VIS spectra of peroxo Au-TS-1 and is reproduced in Figure 7. The bands appeared at 236 and 330 nm can be assigned to the framework and extra frame work Ti sites[16]. These bands appear in TS-1 at 220 and 300 nm, respectively. The shifting of the band in Au/TS-1 compounds can be attributed to the interaction of Au clusters with Ti sites. A quantitative estimation of the ratio of frame work metal to extra-frame work metal was made by measuring the performance of the catalyst and performance of the catalyst after exchanging extra-frame work ions with sodium chloride. The ratio of the conversions of styrene with the two catalysts was found to be 50.0 / 96.41. The reduction in the yield can be attributed to the partial removal of extra-frame work metal.

Attempts have been made in the past to identify the active sites in TS-1 materials. The first direct evidence that Ti atoms are not equally distributed in the 12 crystallographically independent T sites of the MFI framework is reported by Lamberti et al[17] on the basis of neutron diffraction data. According to these authors T6, T7, and T11 are the most populated sites and weak evidence that Ti may be hosted in T10. Ti occupancy can be excluded for sites T1, T2, T4, T5, T9, and T12. The occupancy of the remaining sites is doubtful. Since defective silicalite has been shown to exhibit the same preferential sites (T6, T7, T11, and T10) for Si vacancies, it may be suggested that the incorporation mechanism of the Ti atoms in the MFI framework occurs via the insertion of titanium in the defective sites. The preferentially substituted T6, T7, T11, and T10 are shown in Figure 9.

The evidence of the defect-promoted reactivity for the epoxidation of propylene in titanosilicate (TS-1) catalyst has been proposed by Wells et al[18]. Their Density functional theory study of hydroperoxy (OOH) intermediates
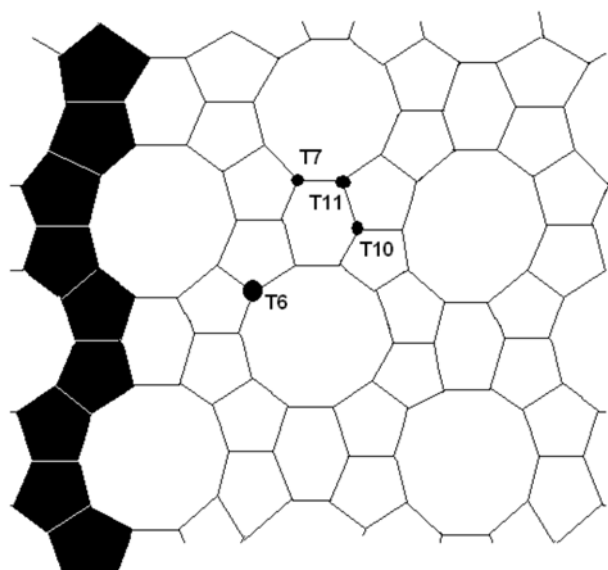
Figure 9. Schematic representation of the MFI orthorhombic structure, viewed along the [010] direction. Preferentially substituted T6, T7, T11, and T10 are shown by black spheres

on various model titanosilicalite (TS-1) Ti centers explores how microstructural aspects of Ti sites affect propylene epoxidation reactivity and shows that the Ti sites located adjacent to Si vacancies in the TS-1 lattice are more reactive than the fully coordinated Ti sites, which do not react at all. It has been shown that propylene epoxidation near a Si-vacancy occurs through a sequential pathway where H_2O_2 first forms a hydroperoxy intermediate Ti-OOH and then reacts with propylene by proximal oxygen abstraction. The abstraction step is greatly facilitated through a simultaneous hydride transfer involving neighboring terminal silanol groups arising from the Si vacancy. The transition state for this step exhibits 6-fold oxygen coordination on Ti, and is concluded that the less constrained environment of Ti adjacent to a vacancy accounts for greater transition state stability by allowing relaxation to a more octahedral geometry. A hybrid quantum mechanics / molecular mechanics (QM/MM) calculation for simulation of the adsorption of Au_n (n=1 – 5) clusters inside the TS-1 and S-1 pores has been reported by Joshi et al[19]. They predict stronger binding of all clusters near Ti sites in Titanium substituted frameworks compared to adsorption near Silicon sites and that cluster binding is stronger near the lattice-metal vacancies compared to the fully coordinated non-defect sites. They predict that there is enough room for an attack of H_2O_2 on the titanium defect sites even with Au1-4 adsorbed- a result that supports the possibility of H_2O_2 spillover from the Au cluster to the adjacent Titanium defect sites either by adsorption of H_2O_2 on Au or formation Au peroxo compound[20], thus increasing the local concentration of hydrogen peroxide at the defect Ti site.

On the basis of their NMR studies some authors[21 – 23] suggested the presence of Broensted acidic sites in titanium silicate which partially isomerize styrene oxide to phenylacetaldehyde. In order to confirm this view we performed several reactions under alkaline pH and the results are presented in Table 3. It can be seen that the increase in pH does not change the conversion of styrene, however, it increases the conversion to styrene oxide and decreases conversion to benzaldehyde. These results ruled out the presence of Broensted acidic sites in the catalyst. It seems, even if a few acidic sites are present in TS-1, they are replaced by gold in Au-TS-1.

Based on the present kinetic investigation and defect structures proposed by Wells et al. and Joshi et al. a tentative mechanism for the epoxidation of styrene is presented in scheme 2.The details of a typical Au3 cluster having isosceles triangular geometry adsorbed on the T6-Ti-defect site of the TS-1 lattice is shown in the inset of scheme 2.

CONCLUSIONS

Epoxidation of styrene to styrene oxide was studied by using Au doped TS-1 as catalyst and hydrogen peroxide as oxidant. Styrene is converted almost completely to styrene oxide with hydrogen oxide selectivity more than 96%, at almost ambient temperature. It was found that the product selectivity and the rate of reaction are greatly influenced by the concentration of styrene and hydrogen peroxide. Kinetic studies reveal that the mechanism of the reaction is of the "Redox" type. The rate equation derived,

Table 3. The effect of pH on the epoxidation of styrene over Au/TS-1.
Reaction Conditions:
Temperature: 333K, Catalyst Concentration: 10 W%, Duration of the reaction: 4 h

S. No.	pH	Styrene conversion (wt %)	Product Distribution		
			Styrene (wt %)	Styrene Oxide (wt %)	Others (wt %)
1.	8	95.80	4.20	53.18	42.62
2.	10	95.30	4.70	63.14	32.16
3.	12	95.90	4.10	73.66	22.24
4.	13	95.93	4.07	85.14	10.79
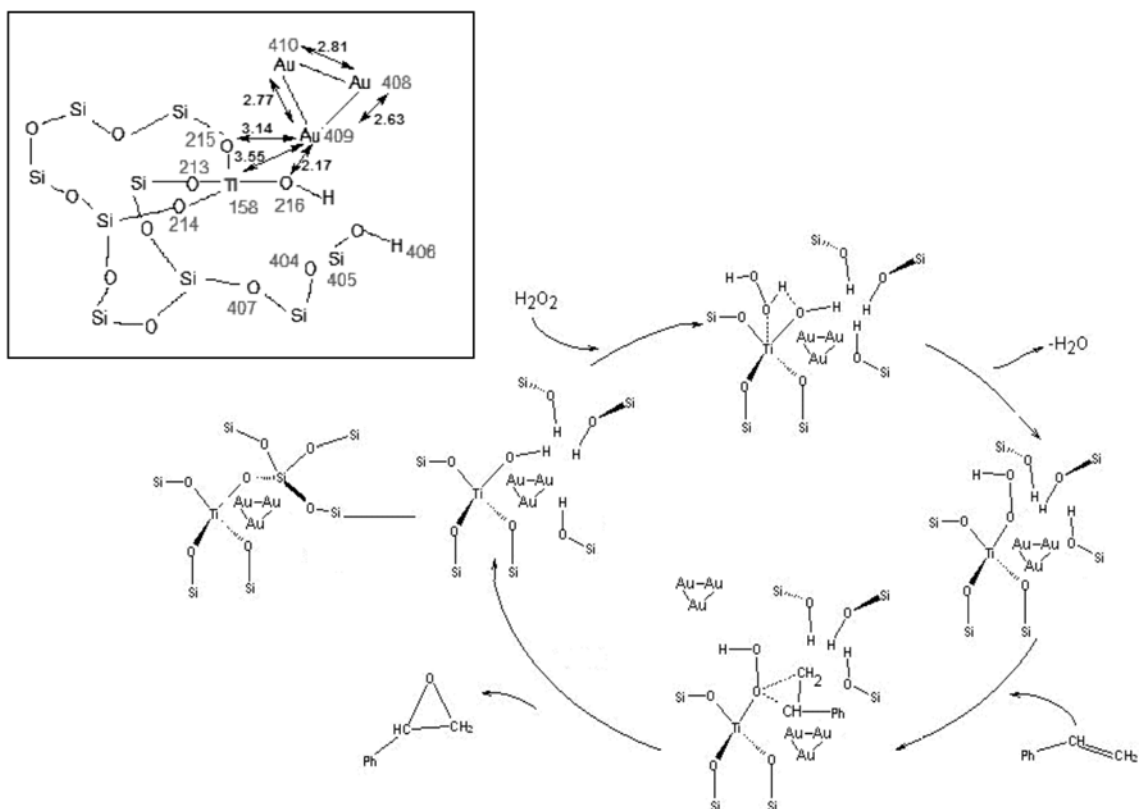
Scheoe 2. A possible mechanism of epoxidation of styrene. Inset shows the details of a typical Au3 cluster having isosceles triangular geometry adsorbed on the T6-Ti-defect site of the TS-1 lattice

assuming a steady state, involving a two stage oxidation-reduction process, presented the data most satisfactorily for the conversion of styrene to styrene oxide.

Nomenclature

H= hydrocarbon (styrene), S= surface
O= oxidants (hydrogen peroxide), P_O = concentration of oxidant,
P_H = concentration of hydrocarbon, S_{OX} = oxidized surface,
S_{red} = reduced surface, k_1, k_2 and k_3 = rate constants in the redox model
TS = transition state, HP= hydrogen peroxide.

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