Selective Epoxidation of Styrene to Styrene Oxide over TS-1 Using Urea–Hydrogen Peroxide as Oxidizing Agent

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The use of anhydrous urea–hydrogen peroxide adduct as an oxidizing agent in the epoxidation of styrene catalyzed by a titanium–silicate (TS-1) molecular sieve resulted in very high selectivity (~85%) for styrene oxide. When aqueous hydrogen peroxide (H_2O_2) was used for styrene epoxidation, the styrene oxide selectivity was very poor (5–10%) mainly due to its isomerization into phenylacetaldehyde. The formation of different types of Ti–superoxo complexes was also observed by the solid–solid interaction with anhydrous urea–hydrogen peroxide and TS-1. It was confirmed by the characteristic continuous absorption band in the UV-Vis region (300–500 nm) and also by an intense and anisotropic EPR spectrum for the superoxide radical ion stabilized on Ti (IV) centers of TS-1 samples. © 2001 Academic Press

Key Words: epoxidation; styrene; styrene oxide; urea–hydrogen peroxide; TS-1; UV-Vis; EPR.

INTRODUCTION

Epoxidation of olefins or substituted olefins is a very important and sometimes a necessary step in a number of important organic transformation reactions. Epoxides are industrially important bulk chemicals. These materials are largely used for the synthesis of several perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs, sweeteners, etc. Therefore the synthesis of an epoxide by an easier method and a low cost route is of great interest to researchers working in this field.

The epoxidation of alkenes using titanium–silicate (TS-1) as a solid catalyst and aqueous hydrogen peroxide as oxidant has been studied extensively (1–4). However, in some cases the use of aqueous hydrogen peroxide decreases the selectivity of the desired epoxide due to isomerization and hydrolysis of the epoxide and also the formation of other cleaved products. The presence of highly polar water in the system usually makes a difference by facilitating isomerization and hydrolysis of the desired product.

One of the most interesting cases is the epoxidation of styrene. The epoxidation of styrene was studied in detail using TS-1 as a catalyst and aqueous hydrogen peroxide as the oxidizing agent (5, 6) but the selectivity of desired styrene oxide was poor (ca. 5–15%). Hence, it was thought that instead of aqueous hydrogen peroxide, anhydrous urea–hydrogen peroxide (UHP) can be used as the oxidizing agent for the epoxidation of styrene in the presence of TS-1 as catalyst for increased selectivity for epoxide. The use of UHP in the chemo- and diastereoselective epoxidation of allylic alcohols catalyzed by TS-1 (7) produced good epoxide yields. A major advantage of UHP lies in its potential for releasing anhydrous H_2O_2 into solution in a controlled manner (8).

It is also important to understand and establish the different structural properties of TS-1 for its remarkable activity toward oxidation reactions (9). The formation of different Ti–superoxo compounds was observed in the UV-Vis spectra of TS-1 mixed with aqueous H_2O_2 (10). However, in most of the cases, these different Ti–superoxo compounds are indistinguishable from one to another mainly due to the presence of water coming from aqueous H_2O_2. Earlier EPR results of TS-1 and aqueous H_2O_2 also show a broad spectrum but the existence of different Ti^{4+} species in TS-1 is not clear (11). This motivated us to use anhydrous solid urea–hydrogen peroxide adduct as the source of H_2O_2 in which the absence of water molecules will not increase and/or equalize the coordination number of different Ti species during the formation of Ti–superoxo compounds.

In this work, we describe and discuss direct spectroscopic evidence to establish the existence of different Ti species in TS-1. We also report detailed studies of the epoxidation of styrene using TS-1 as a solid efficient catalyst and anhydrous urea–hydrogen peroxide as an oxidizing agent. The results obtained under the most favorable conditions using UHP as oxidizing agent are compared with those obtained with aqueous H_2O_2 under the same reaction conditions.

EXPERIMENTAL

Synthesis

The catalyst TS-1 was synthesized employing the concept of promoter-induced synthesis of zeolite materials (12, 13).

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In a typical preparation, 20.8 g tetraethyl orthosilicate (TEOS) was added to 50.8 g tetrapropylammonium hydroxide (TPAOH, 20% aqueous solution) under vigorous stirring for 2 h. Then 1.13 g tetrabutyl orthotitanate (TBOT) dissolved in 5.7 g dry isopropanol (IPA) was added slowly to the above clear solution of TPA–silicate under vigorous stirring. Stirring was continued for another 30 min and then a solution of 0.77 g H_3PO_4 in 4.4 ml water was added very slowly under vigorous stirring, which was continued for another hour. The initial molar gel composition of the reaction mixture was 1 TEOS : 0.5 TPAOH : 0.033 TBOT : 0.067 H_3PO_4 : 25 H_2O. The crystallization of the sample was carried out in a stainless-steel autoclave at 433 K for 6 h under agitation (60–65 rpm). After crystallization the solid product was collected by centrifugation, washed thoroughly first with deionized water and then with dilute acid solution (containing 2 wt% H_2SO_4 and 5 wt% H_2O_2), washed again with deionized water, dried at 393 K for 4 h, and calcined at 813 K in air for 12 h.

Characterization Techniques

The TS-1 sample was mainly characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance UV-Vis spectroscopy, FTIR spectroscopy, energy dispersive X-ray analysis (EDX), and electron paramagnetic resonance (EPR) spectroscopy.

The X-ray diffractogram of the sample was recorded on a Rigaku D MAX III VC, Ni-filtered Cu K_α radiation ($\lambda = 1.5404$ Å). The SEM micrographs of the calcined samples were obtained in a Leica Stereoscan 440. The diffuse reflectance UV-Vis spectrum in the 200–600 nm range was recorded with a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment using $BaSO_4$ as a reference and the FTIR spectrum in the 400–1300 cm^{-1} range was recorded on a Shimadzu FTIR-8201 PC (in Nujol on KBr disc technique), respectively. The metal contents of the calcined samples were determined by EDX analysis with Kevex equipment attached to a Jeol JSM-5200 scanning microscope. The EPR spectra of the samples were recorded on a Bruker EMX spectrometer operating at X-band frequency and 100 kHz field modulation.

Catalytic Tests

The epoxidation of styrene was carried out in a batch reaction. In a typical reaction, 2.08 g styrene (20 mmol) and 2.08 g acetone were added slowly to the mixture of catalyst (0.416 g, 20 wt% of the styrene) and urea–hydrogen peroxide (0.47 g, 5 mmol) and the reaction mixture was heated to 313 K under stirring. After the completion of the reaction, the organic layer was collected by centrifugation and analyzed using a Shimadzu 17A series gas chromatograph (HP 101 methyl silicone fluid, 50 m long 0.2 mm i.d. with 0.2 μm thickness of coated film), GCIR (Perkin Elmer, GC-IR 2000), and GCMS (Shimadzu, GCMS-QP 2000A).

RESULTS AND DISCUSSION

Catalyst Characterization

The XRD pattern (characteristic of MFI topology), diffuse reflectance UV-Vis spectrum (sharp absorption at 210 nm), framework region IR spectrum (band at 960 cm^{-1}), etc., characteristic of a titanium silicate molecular sieve, clearly indicate the incorporation of Ti in the framework and the absence of any extra framework TiO_2 species. The scanning electron micrograph of TS-1 sample synthesized using H_3PO_4 as a promoter exhibits small crystallites (100–200 nm). The Si/Ti molar ratio in the solid was 32 as determined by EDX analysis.

Figure 1 depicts the UV-Vis spectra of TS-1 samples. Curve A (TS-1) exhibits a sharp absorption at ca. 210 nm. When TS-1 sample was mixed with UHP (TS-1/UHP), two absorption bands (curve B) were obtained. One is a sharp absorption at 210 nm as observed in pure TS-1 and another is a continuous absorption band in the UV-Vis region from 300 to 500 nm, which is due to the formation of different Ti–superoxo complexes formed by the solid–solid interaction between TS-1 and UHP. A similar type of curve C was also obtained when TS-1 was mixed with aqueous hydrogen peroxide (HP), except some absorption in the 250–300 nm range, which is due to the coordinated water molecules on Ti centers coming from aqueous hydrogen peroxide (10).
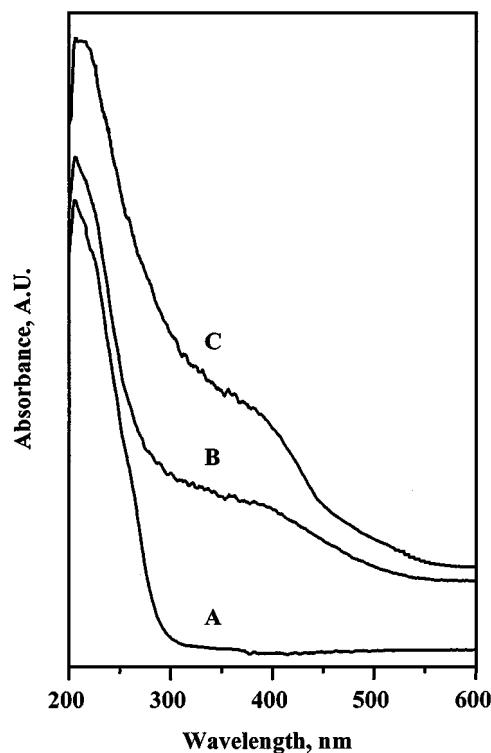

FIG. 1. Diffuse reflectance UV-Vis spectra of TS-1 (A), TS-1 + UHP (B), and TS-1 + aqueous H_2O_2 (C).
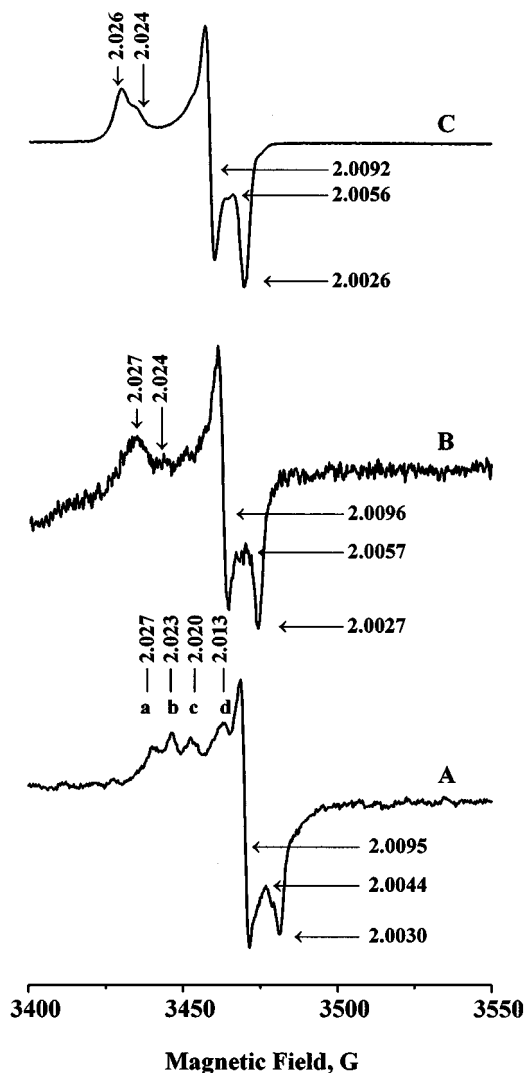
FIG. 2. EPR spectra of TS-1 + UHP (A), TS-1 + UHP + Acetone (B), and TS-1 + aqueous H_2O_2 (C).

Figure 2 (curve A) depicts the anisotropic EPR spectra of TS-1/UHP sample due to the interaction between TS-1 and UHP ($\nu = 9.7589$ GHz, 298 K), which represents direct spectroscopic evidence for the existence of different Ti–superoxo species. The presence of three different Ti–superoxo species (a, b, and c) in curve A indicates the existence of different Ti^{4+} sites in the original TS-1 (9) and/or generated during reactions with UHP whereas free superoxo radicals weakly attached to lattice silicon represent species "d". Curve B is obtained when acetone (solvent) was added to the mixture of TS-1 and UHP ($\nu = 9.4565$ GHz, 77 K). Whereas, curve C resulted from the mixture of TS-1 and aqueous H_2O_2 ($\nu = 9.4439$ GHz, 77 K). In both curves B and C, the dominant Ti–superoxo species is "a" which represents that other coordination sites of Ti are occupied by solvent molecules (acetone and water, respectively, for curves B and C). However, solvent

molecules cannot fill vacant coordination sites of Ti in the case of curve A. The g values of the three curves are in good agreement with those reported in the literature for the superoxide radical ion stabilized on Ti (IV) centers of both supported and bulk titanium dioxide (14).

Epoxidation of Styrene

The effect of different sources of the oxidizing agent (H_2O_2) on the styrene conversion (mol%) and product selectivity (mol%) is given in Table 1, for comparative purpose. It is observed that the styrene conversion as well as the selectivity for the desired epoxide increases when instead of aqueous hydrogen peroxide urea–hydrogen peroxide is used. In the case of U + HP system, where urea and aqueous hydrogen peroxide solution (45 wt%) were added separately, both the conversion and the selectivity of the desired epoxide were found to be slightly lower compared to the solid UHP system and significantly higher in comparison to the aqueous hydrogen peroxide system. Probably, the urea acts not only as a dehydrating agent but also as a buffer for the system, which prevents further isomerization and hydrolysis of the desired epoxide.

The graphic profile (Fig. 3A) of temperature dependence on styrene epoxidation shows that in the case of both U + HP and UHP systems, the styrene conversion first increases (273–313 K), reaches a maximum level at 313 K, and then decreases with an increase in temperature (313–353 K). In the case of the HP system, although initially the reaction was slow, the maximum conversion was higher compared to that in the case of U + HP and UHP systems at higher temperatures (>313 K). Further there was no decrease in the conversion. At higher

TABLE 1

Effect of Different Oxidants on the Epoxidation of Styrene over TS-1[a]

Oxidant[b]	Styrene conversion, mol%[c]	TOF,[d] h⁻¹	Product distribution, mol%[e]			
			Styrene oxide	Ph–CH$_2$–CHO	Ph–CHO	Others[f]
HP	56	1.1	5	44	29	22
U + HP	65	1.3	81	8	7	4
UHP	71	1.4	87	5	7	1

[a] Reaction conditions: Catalyst wt = 0.416 g (20 wt% of the styrene); $T = 313$ K; styrene : oxidant (mol/mol) = 4.0; solvent = acetone; styrene : acetone (wt/wt) = 1.0; reaction time (h) = 12.

[b] HP, hydrogen peroxide (45 wt%); U + HP, urea and hydrogen peroxide mixture (1 : 1, mole ratio); UHP, urea hydrogen peroxide adduct.

[c] (Styrene conversion/theoretically possible styrene conversion) × 100.

[d] Turnover frequency (TOF) = moles of H_2O_2 converted for producing styrene oxide + secondary products per mole of Ti per hour.

[e] Ph–CH$_2$–CHO, phenylacetaldehyde; Ph–CHO, benzaldehyde.

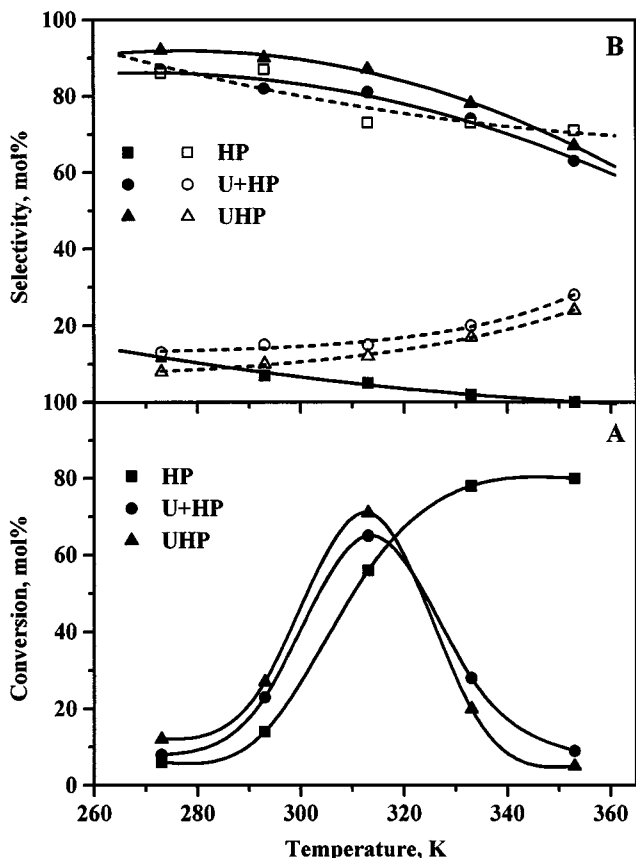[f] High boiling products including diols, benzoic acid, and some unidentified compounds.

FIG. 3. Effect of reaction temperature on the epoxidation of styrene. Reaction conditions: catalyst TS-1 (20 wt% with respect to styrene); styrene : H$_2$O$_2$ (mol/mol) = 4.0; styrene : acetone (wt/wt) = 1.0; reaction time = 12 h. (A) Comparison of styrene conversion with different H$_2$O$_2$ sources: (■) HP, (●) U + HP, and (▲) UHP. (B) Comparison of selectivities for styrene oxide (solid symbol) and benzaldehyde + phenylacetaldehyde (open symbol) with different H$_2$O$_2$ sources: (■ □) HP, (● ○) U + HP, and (▲ △) UHP.

temperatures (>313 K), the stability of solid urea–hydrogen peroxide adduct decreases. Therefore, the decomposition of hydrogen peroxide becomes more competitive than the desired epoxidation. However, in the case of HP system, in which aqueous hydrogen peroxide is stabilized by hydrogen bonding, the decomposition of hydrogen peroxide is rather low particularly at higher temperatures (>313 K). In that case, the styrene conversion increases with increasing temperature. The selectivity of styrene oxide and benzaldehyde + phenylacetaldehyde is plotted in Fig. 3B, for all the three systems. In all cases, upon increasing the temperature from 273 to 353 K, the selectivity of undesired secondary products increases at the expense of styrene oxide. However, at all reaction temperatures, the styrene oxide selectivity was quite high in the case of UHP and U + HP (70–90%), while in the case of the HP system, the same was very low (5–10%).

In the Fig. 4A, styrene conversion is plotted as a function of reaction time at 313 K. In all three systems, HP,

U + HP, and UHP, the reaction proceeds in a similar fashion with time in the order UHP > U + HP > HP. The reaction is fast at the beginning, since the total amount of oxidant was added in one lot at the beginning of the reaction. The conversion for the reaction reaches a maximum level at ca. 12 h. However, as the hydrogen peroxide added becomes more and more anhydrous in nature (HP < U + HP < UHP), the conversion level increases. Figure 4B depicts the selectivities of styrene oxide and benzaldehyde + phenylacetaldehyde plotted against reaction time for the three different systems.

The effect of styrene/UHP mole ratio on the styrene conversion and the product selectivity is shown in Fig. 5. The styrene conversion increases with the increase in styrene/UHP mole ratio mainly due to increased H$_2$O$_2$ utilization for styrene oxidation. However, the selectivity of styrene oxide increases very slowly over the range. It is also
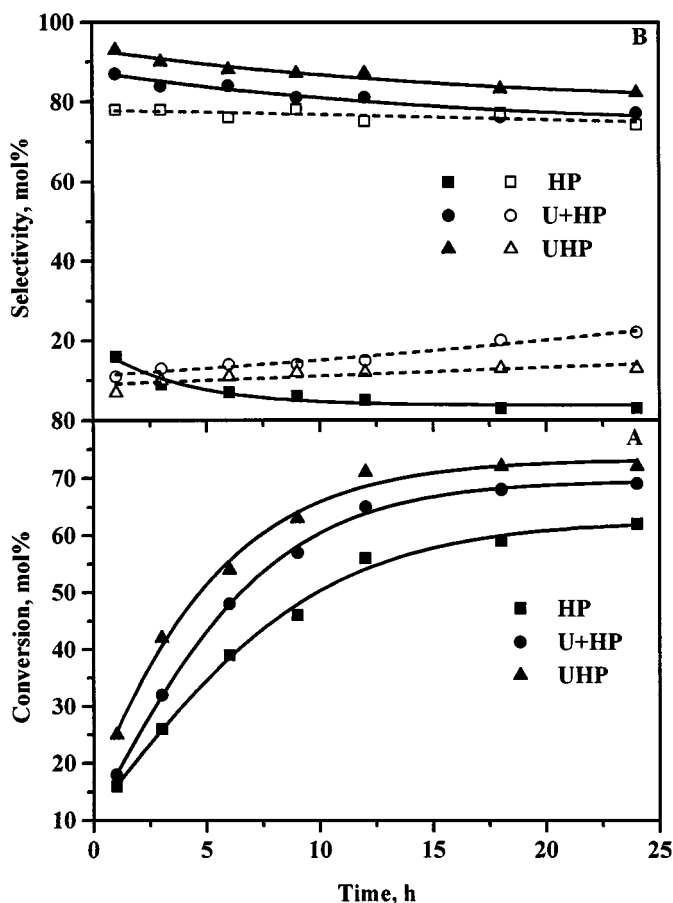

FIG. 4. Effect of reaction time on the epoxidation of styrene. Reaction conditions: temperature = 313 K; catalyst TS-1 (20 wt% with respect to styrene); styrene : H$_2$O$_2$ (mol/mol) = 4.0; styrene : acetone (wt/wt) = 1.0. (A) Comparison of styrene conversion with different H$_2$O$_2$ sources: (■) HP, (●) U + HP, and (▲) UHP. (B) Comparison of selectivities for styrene oxide (solid symbol) and benzaldehyde + phenylacetaldehyde (open symbol) with different H$_2$O$_2$ sources: (■ □) HP, (● ○) U + HP, and (▲ △) UHP.
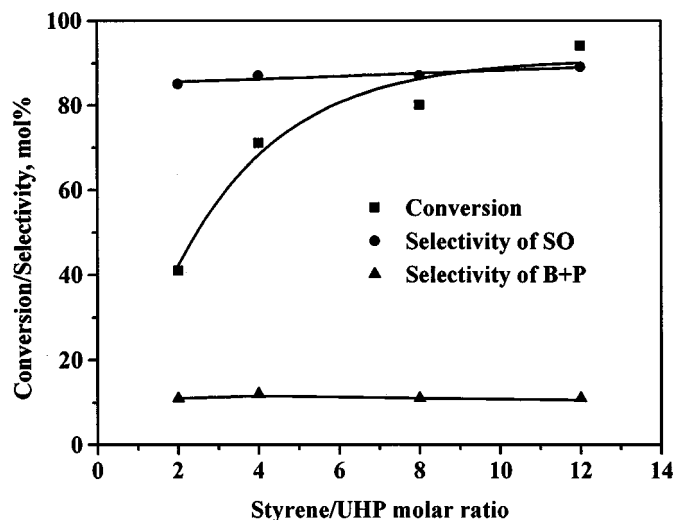
FIG. 5. Effect of styrene to H_2O_2 molar ratios on the epoxidation of styrene. Reaction conditions: temperature = 313 K; catalyst TS-1 (20 wt% with respect to styrene); styrene : acetone (wt/wt) = 1.0; reaction time = 12 h. (■) Styrene conversion, (●) styrene oxide (SO) selectivity, and (▲) benzaldehyde + phenylacetaldehyde (B + P) selectivity.
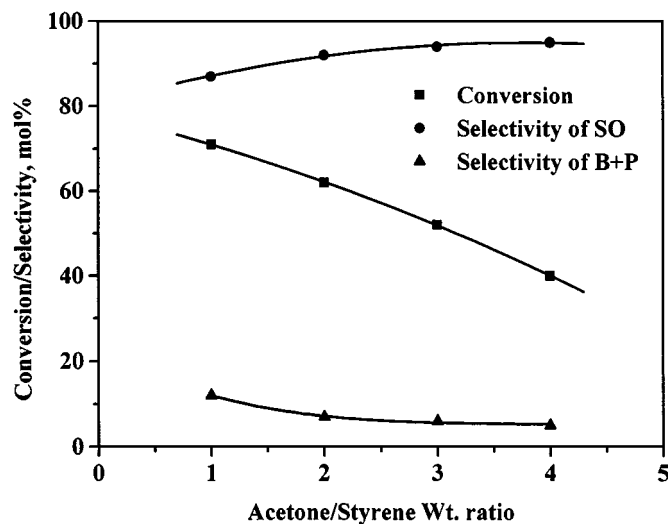

FIG. 6. Effect of acetone to styrene weight ratios on the epoxidation of styrene. Reaction conditions: temperature = 313 K; catalyst TS-1 (20 wt% with respect to styrene); styrene : H_2O_2 (mol/mol) = 4.0; reaction time = 12 h. (■) Styrene conversion, (●) styrene oxide (SO) selectivity, and (▲) benzaldehyde + phenylacetaldehyde (B + P) selectivity.

observed that the concentrations of phenylacetaldehyde + benzaldehyde remain unchanged with the increase of the styrene/UHP molar ratio.

Table 2 displays the effect of solvent on styrene epoxidation over the TS-1/UHP system. As expected, in aprotic solvents like acetone and acetonitrile, the product selectivity is higher than in protic solvent like methanol. In methanol, the concentrations of undesired secondary products (phenylacetaldehyde, benzaldehyde, and styrene diol) are higher compared to those of acetone and acetonitrile. Still, the selectivity of the desired styrene oxide (~72%) is quite high in methanol due to anhydrous reaction conditions.

Figure 6 illustrates the effect of acetone concentration on styrene conversion and styrene oxide selectivity. Upon increasing the acetone/styrene wt ratio, the selectivity of styrene oxide increases, at the expense of secondary products, indicating that at lower dilutions secondary reactions

are facilitated. However, styrene conversion decreases with increases in acetone/styrene wt ratios. Here, it is pertinent to note that although the substrate to catalyst ratio was the same in these experiments, catalyst concentrations with respect to total reaction volume were changed considerably.

Figure 7 depicts the effect of catalyst concentration on styrene epoxidation. It is observed that an increase in the catalyst concentration (with respect to styrene) resulted in an increase in the styrene conversion initially before
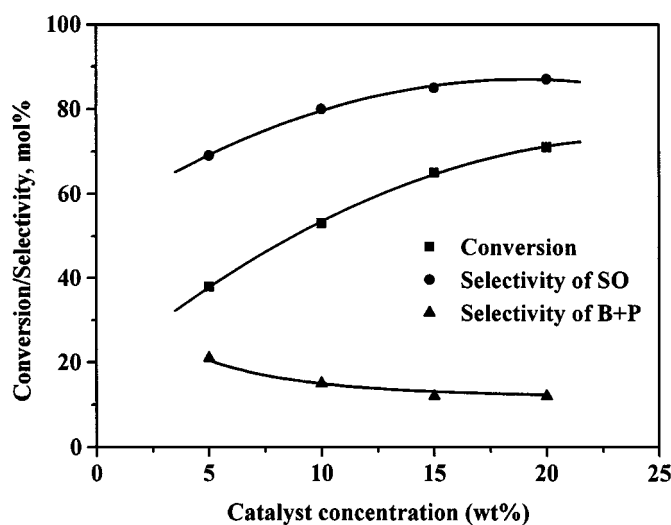
TABLE 2

Effect of Solvent on Epoxidation of Styrene with UHP over TS-1[a, b]

Solvent	Styrene conversion, mol%	TOF, h^{-1}	Product distribution, mol%			
			Styrene oxide	Ph–CH₂–CHO	Ph–CHO	Others
Acetone	71	1.4	87	5	7	1
Acetonitrile	51	1.0	82	7	6	5
Methanol	54	1.1	72	11	9	8

[a] Reaction conditions: Catalyst wt = 0.416 g; T = 313 K; styrene : UHP (mol/mol) = 4.0; styrene : solvent (wt/wt) = 1.0; reaction time = 12 h.

[b] Also see Table 1.

FIG. 7. Effect of catalyst concentration on the epoxidation of styrene. Reaction conditions: temperature = 313 K; styrene : H_2O_2 (mol/mol) = 4.0; styrene : acetone (wt/wt) = 1.0; reaction time = 12 h. (■) Styrene conversion, (●) styrene oxide (SO) selectivity, and (▲) benzaldehyde + phenylacetaldehyde (B + P) selectivity.

leveling off at ca. 70 ± 5 mol%. Styrene oxide selectivity also increases with increases in catalyst concentration before reaching a limiting value of 85 ± 5 mol%. As expected, at low catalyst concentrations, the concentration of Ti–superoxo complex is low and therefore secondary reactions are facilitated. With the increase in the catalyst concentration, the concentration of Ti–superoxo complex also increases which facilitates the formation of desired styrene oxide inside the zeolitic pore.

The addition of urea has a significant effect on the selectivity of the epoxide. This motivated us to carry out the epoxidation of styrene with aqueous H_2O_2 in the presence of varying amounts of urea separately added to the reaction mixture. The results obtained are plotted as a function of the urea/hydrogen peroxide molar ratio in Fig. 8. The styrene conversion first increases steadily, and then it reaches a limiting value of 65 ± 2 mol%, when the urea/hydrogen peroxide molar ratio becomes ≥ 1. The selectivity of styrene oxide increases considerably from 5 mol% (urea/$H_2O_2 = 0.0$) to 61 mol% (urea/$H_2O_2 = 0.25$) by the addition of a small amount of urea which indicates the importance of its presence in the reaction mixture. Further increase in the urea/H_2O_2 molar ratio also increases the styrene oxide selectivity before leveling off at ca. 82 ± 3 mol%. On the contrary, the selectivity of undesired benzaldehyde + phenylacetaldehyde decreases drastically by the addition of a small amount of urea and reaches a limiting value of 15 ± 3 mol%, when the urea/hydrogen peroxide molar ratio becomes ≥ 1.

It has been reported that TS-1 develops acid centers in the presence of H_2O_2 in alcoholic or aqueous solutions (15, 16).
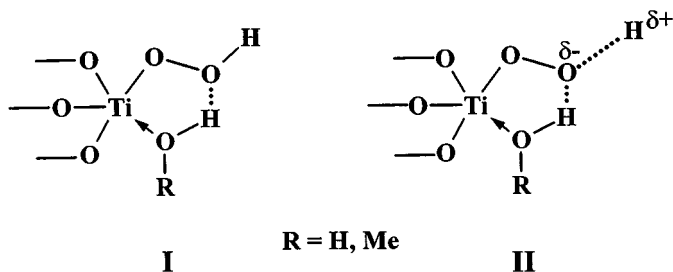
SCHEME 1. Different cyclic Ti species active for epoxidation reactions.

The Ti–OOH species, formed by the interaction between framework Ti atom and H_2O_2 molecule, is able to form a stable five-membered cyclic structure with a donor hydroxyl moiety coordinated on titanium (species I) as shown in Scheme 1. The enhanced acid strength may be generated in charge-separated species (species II) due to greater hydrogen bonding. The acid centers (species I and II) are able to catalyze the epoxide ring opening. When aqueous H_2O_2 (HP) is used as oxidant for styrene epoxidation, the selectivity of the desired epoxide was very poor ($\sim$5 mol%) mainly because of its isomerization to phenylacetaldehyde, catalyzed by the acid centers generated on TS-1. However, in the case of the U + HP system, the selectivity of styrene oxide increases considerably ($\sim$80 mol%). This is mainly due to the presence of urea, which acts as a dehydrating agent as well as buffer for the system and thereby reduces the acid-catalyzed isomerization of styrene oxide as was seen in Fig. 8. Expectedly, maximum selectivity of styrene oxide ($\sim$85 mol%) is achieved in the case of the UHP system because of the absence of water in the reaction mixture. Still, the formation of water molecules in the vicinity of active Ti centers due to consumption of H_2O_2 during the epoxidation reaction causes some epoxide ring opening leading to isomerized product. In methanol, the selectivity of styrene oxide is less compared to that in other solvents also because of the same acid-catalyzed isomerization of the epoxide.

The difference between curve B and curve C in the UV-Vis spectra (Fig. 1) is that curve C absorbs in the 250–300 nm region which is due to the coordination of water (solvent) molecules with Ti centers coming from aqueous H_2O_2 or solvent (10). However, in the case of UHP no such absorption was observed (curve B). Most interestingly, curves B and C in the EPR spectra (Fig. 2) are very similar and contain mostly solvent-coordinated Ti–superoxo complexes (species 'a'), which are also shown in Scheme 1 (species "I"). But since acetone being an aprotic solvent is not able to generate acid centers on Ti species, the selectivity of styrene oxide is very high compared to that in aqueous H_2O_2. In the case of methanol such species will also lower the styrene oxide selectivity. The existence of different Ti–superoxo species as evidenced by the diffuse reflectance UV-Vis spectra and EPR spectra and
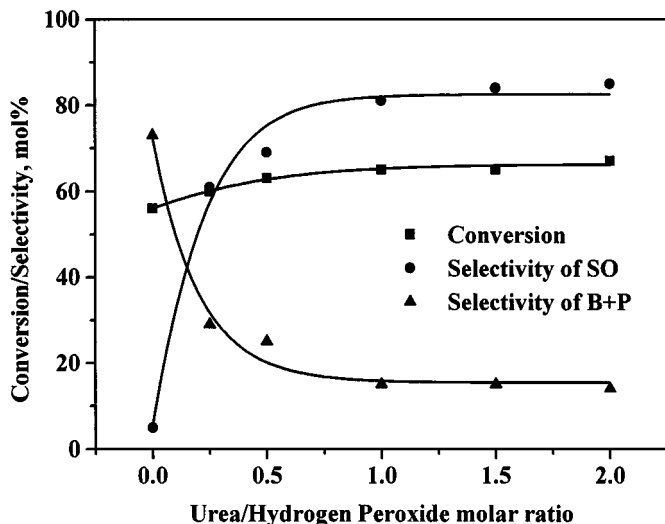

FIG. 8. Effect of urea to H_2O_2 molar ratios on the epoxidation of styrene. Reaction conditions: temperature = 313 K; catalyst TS-1 (20 wt% with respect to styrene); styrene : H_2O_2 (mol/mol) = 4.0; styrene : acetone (wt/wt) = 1.0; reaction time = 12 h. (■) Styrene conversion, (●) styrene oxide (SO) selectivity, and (▲) benzaldehyde + phenylacetaldehyde (B + P) selectivity.

the variation of different reaction parameters explain why anhydrous urea–hydrogen peroxide is highly selective for the epoxidation of styrene.

CONCLUSIONS

A significant increase in the conversion and a very high selectivity of the desired styrene oxide was achieved when in comparison to aqueous hydrogen peroxide, urea–hydrogen peroxide was used as oxidant for the epoxidation of styrene. In the case of U + HP system, both the conversion and most importantly the selectivity of the desired styrene oxide were significantly higher in comparison to the aqueous hydrogen peroxide system.

When aqueous hydrogen peroxide was used as an oxidant for styrene epoxidation, the presence of highly polar water in the reaction system facilitates acid-catalyzed isomerization and hydrolysis of styrene oxide. Probably, it also catalyzes the cleavage of C=C bond of styrene to produce benzaldehyde via radical transformation. The presence of urea is very important in the reaction medium. It acts not only as a dehydrating agent but also as a buffer for the system.

ACKNOWLEDGMENTS

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