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Highly Selective Epoxidation of Olefinic Compounds over TS-1 and TS-2 Redox Molecular Sieves Using Anhydrous Urea–Hydrogen Peroxide as Oxidizing Agent

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Highly selective epoxidation of different olefinic compounds was carried out using urea–hydrogen peroxide adduct (UHP) as the oxidizing agent in the presence of TS-1 and TS-2 as redox catalysts. A considerable increase in the epoxide selectivity was observed for different unsaturated compounds, such as allylic (allyl alcohol, allyl chloride, allyl bromide, and methylallyl chloride), open-chain, and cyclic (1-hexene and cyclohexene) and aromatic (styrene and allylbenzene) olefinic compounds, when UHP and U + HP (urea and aqueous H_2O_2 added separately for the *in situ* formation of UHP) were used as oxidants instead of aqueous H_2O_2. The controlled release of anhydrous H_2O_2 from UHP is the main reason for enhanced epoxide selectivity. Direct spectroscopic evidences for the formation of different Ti-superoxo complexes by the solid–solid interaction between TS-1/TS-2 and urea–hydrogen peroxide adduct were obtained from the characteristic continuous absorption band in the UV–vis region (300–500 nm) and the anisotropic EPR spectra for the superoxide radical attached to Ti(IV) centers on TS-1 and TS-2.

Key Words: **epoxidation; olefin; urea–hydrogen peroxide; TS-1; TS-2; diffuse reflectance UV–vis; EPR.**

INTRODUCTION

Epoxides, very important chemicals in synthetic organic chemistry as well as in industry, are largely used for the synthesis of key intermediates and in many important organic transformation reactions. Most important, these chemicals are widely used in industry for manufacturing various types of important products, ranging from perfumery chemicals to polymeric materials. So, the selective synthesis of various epoxides by an environmentally friendly process using solid recyclable molecular sieve materials as catalysts is very important to applied chemistry.

Among all the microporous metallosilicate molecular sieves, titanium-containing silica-based materials, particularly TS-1 and TS-2, are extensively studied in liquid-phase selective oxidation reactions using aqueous hydrogen peroxide as the oxidant (1–6). Although, the TS-1 as well as TS-2 catalysts are quite suitable for various types of selective oxidation reactions using aqueous H_2O_2 (HP) as oxidant, in the epoxidation of various olefinic compounds the epoxide selectivity is reduced due to the formation of isomerized and/or cleaved secondary products, as the oxirane ring is quite prone to acid-catalyzed isomerization and hydrolysis in the presence of water (coming from aqueous H_2O_2) (7, 8). The presence of protic solvents with a high degree of polarity (e.g., water) generates acidity on active Ti-centers in titanium–silicate molecular sieves, leading to the formation of corresponding isomerized and hydrolyzed secondary products particularly for epoxidation reactions. These types of phenomena are observed not only for TS-1 and TS-2 (9) but also for other silica-based Ti-containing catalysts, e.g., Ti-β (10), Ti–MCM-41 (11), and so forth.

In order to circumvent this problem an anhydrous source of hydrogen peroxide, namely urea–hydrogen peroxide adduct (UHP), which slowly releases anhydrous H_2O_2 into solution (12), has been successfully employed for the epoxidation of substituted allylic alcohols (13) and styrene (14) in the presence of TS-1 as redox catalyst, producing excellent epoxide yields. Since UHP releases *anhydrous* H_2O_2, it may provide interesting information on the nature of the active sites in TS-1 and TS-2 using diffuse reflectance UV–vis and EPR techniques, which have been already reported using aqueous hydrogen peroxide (15, 16).

In our earlier work using a TS-1/UHP system, the epoxidation of styrene was carried out, giving quite high selectivity for styrene oxide (14). Now, in this work, we report on detailed and systematic studies of the epoxidation of a variety of olefinic compounds using TS-1 and TS-2 as the solid redox catalysts and HP, U+HP (urea and aqueous H_2O_2 added separately for the *in situ* formation of UHP), and UHP as the oxidizing agents. Different structural properties of TS-1/UHP and TS-2/UHP systems using diffuse

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reflectance UV–vis and EPR spectroscopy are also described and compared with those exhibited by the TS-2/HP system.

EXPERIMENTAL

Synthesis of TS-1 and TS-2

Titanium–silicate molecular sieves, TS-1 and TS-2, were prepared by employing the concept of promoter-induced synthesis of zeolitic materials (17, 18). In the synthesis of both TS-1 and TS-2, tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate (TBOT), and orthophosphoric acid (H_3PO_4) were used as the silica source, titanium source, and promoter, respectively. Tetrapropylammonium hydroxide (TPAOH) was used as the templating agent for the synthesis of the TS-1 sample. The final molar gel composition for the TS-1 sample was 1 TEOS : 0.5 TPAOH : 0.033 TBOT : 0.067 H_3PO_4 : 25 H_2O, as described earlier (18).

The TS-2 sample was also prepared similarly using tetrabutylammonium hydroxide (TBAOH, 40 wt% aqueous solution) as the organic templating agent (19). The final molar gel composition for the TS-2 sample was 1 TEOS : 0.35 TBAOH : 0.033 TBOT : 0.067 H_3PO_4 : 25 H_2O.

Characterization Techniques

The TS-1 and TS-2 samples were characterized by powder X-ray diffraction (XRD), diffuse reflectance UV–vis spectroscopy, FTIR spectroscopy, energy-dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), and electron paramagnetic resonance (EPR) spectroscopy.

X-ray diffractograms of the calcined samples were recorded on a Rigaku D MAX III VC and Rigaku Miniflex diffractometers using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) over $2\theta = 5$–50° and a scan speed of 4°/min. Diffuse reflectance UV–vis spectra of the solid samples were recorded on a Shimadzu UV-2101 PC spectrophotometer equipped with a diffuse reflectance attachment using $BaSO_4$ as the reference. FTIR spectra of the samples were recorded on a Shimadzu FTIR-8201 PC (in Nujol on a KBr disk). The chemical composition of the calcined samples was determined by EDX analyses using Kevex equipment attached to a Jeol JSM-5200 scanning microscope. The SEM micrographs of the calcined samples were obtained in a Leica Stereoscan 440. The EPR spectra were recorded on a Bruker EMX spectrometer operating at X-band frequency and 100-kHz field modulation. The EPR spectra of TS-1 and TS-2 samples were recorded at 77 K for aqueous hydrogen peroxide (HP)-treated samples (using liquid N_2) and at room temperature (298 K) for solid urea–hydrogen peroxide (UHP)-treated samples, respectively.

Catalytic Reactions

The epoxidation of different olefins was carried out in a glass batch reactor (50-ml capacity). In a typical reaction, a solution of 20 mmol of olefinic substrate in solvent was added slowly to the mixture of catalyst (20 wt% of the substrate) and 5 mmol of urea–hydrogen peroxide (UHP) 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 × 0.2 mm × 0.2 μm thickness) and Agilent 6890 series GC system (Supelco β-Dex 110, 10% permethylated β-cyclodextrin, 30 m × 0.25 mm × 0.25 μm film thickness). Selected samples were also analyzed by GCIR (Perkin–Elmer, GC-IR 2000) and GCMS (Shimadzu, GCMS-QP 2000A).

RESULTS AND DISCUSSION

Characterization of TS-1 and TS-2

The XRD patterns of the calcined samples are characteristic of MFI and MEL topologies for TS-1 and TS-2, respectively. The absorption maxima at ca. 210 nm in the diffuse reflectance UV–vis spectra and the characteristic band at ca. 960 cm^{-1} in the IR spectra clearly indicate the incorporation of Ti in the framework of TS-1 and TS-2. The absence of any bands at ca. 260 and 330 nm in the UV–vis spectra indicate that hexa-coordinated Ti in the extraframework and anatase form of TiO_2 are not present in the TS-1 and TS-2 samples. The average particle size of the crystallites determined by scanning electron microscopy is in the range between 100 and 200 nm. The Si/Ti molar ratios in the solids were 32 and 33, as determined by chemical analysis (EDX) for the TS-1 and TS-2 samples, respectively.

Figure 1 depicts the diffuse reflectance UV–vis spectra of TS-1 (Fig. 1A) and TS-2 (Fig. 1B) samples in the presence of water, aqueous H_2O_2 (HP), and solid urea–hydrogen peroxide (UHP). Intense absorption bands at 210 nm (curves a and f in Figs. 1A and 1B, respectively) are obtained in the spectra for calcined TS-1 and TS-2 samples. However, the mixtures of TS-1/TS-2 and urea–hydrogen peroxide (UHP) show two absorption bands (curves b and g), a sharp absorption band at 210 nm, as well as a continuous absorption band in the region of 300–500 nm. The presence of a continuous absorption band (300–500 nm) indicates the formation of different Ti-superoxo complexes by the solid–solid interaction between catalyst and UHP. The hydrated TS-1 and TS-2 samples in the presence of adsorbed water show a shift in the absorption maxima from 210 to 230 nm and some absorption in the region of 250–350 nm (curves c and h) due to the ligand-to-metal charge transfer involving isolated penta-/hexa-coordinated Ti atoms, where one or two water molecules form part of the metal coordination sphere. Curves d and e (Fig. 1A), representing TS-1/UHP/acetone and TS-1/HP, as well as curves i and j (Fig. 1B), representing TS-2/UHP/acetone and TS-2/HP samples, exhibit similar types of absorptions (a strong absorption at 210–215 nm and a continuous absorption in the 300–500 nm) in the UV–vis

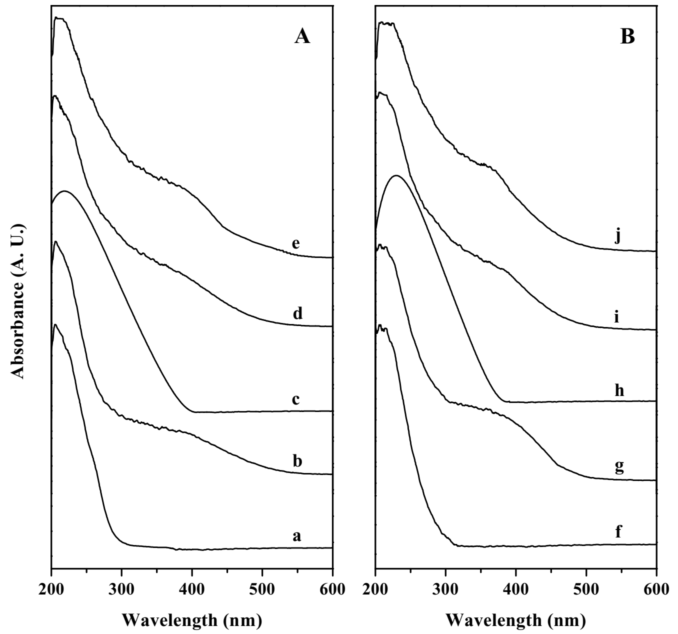

FIG. 1. Comparison of diffuse reflectance UV–vis spectra of different TS-1 (A) and TS-2 (B) samples: calcined TS-1 and TS-2 (curves a and f), TS-1/TS-2 + UHP (curves b and g), TS-1/TS-2 + H_2O (curves c and h), TS-1/TS-2 + UHP + acetone (curves d and i), and TS-1/TS-2 + aqueous H_2O_2 (curves e and j).

region. It is interesting that curves d and i also show some absorbance in the 250- to 350-nm region, assigned to solvent molecules coordinated to Ti centers, which has not been observed in the solvent free systems (curves b and g).

Figure 2 compares the EPR spectra of TS-1/UHP (A), TS-2/UHP (B), and TS-2/HP (C). A total of five EPR signals (four from different Ti-superoxo species (a, b, c, and d) and one from free superoxo radicals weakly attached to lattice silicon atoms (e)) were observed in the EPR spectrum of the TS-1/UHP system (curve A), resulting from the solid–solid interaction between TS-1 and UHP, indicating the existence of different Ti^{4+} sites in the original TS-1 (20) and/or generated during reaction with anhydrous H_2O_2 coming from UHP (14). It is pertinent to mention here that in our earlier work on the TS-1/UHP system, we recognized a total of four distinct EPR signals (three different Ti-superoxo species (b, c, and d) and one free superoxo radicals weakly attached to lattice silicon atoms (e)), and the quite weak EPR signal at $g = 2.030$ was not taken into consideration mainly due to a somewhat high signal-to-noise ratio. However, after detailed analysis of TS-1/UHP (curve A) and TS-2/UHP (curve B) systems under enhanced intensity, we could observe species a in both cases. The overall EPR spectrum of TS-2/UHP system (curve B) is similar to that of the TS-1/UHP system (curve A). As was expected, in the case of the TS-2/HP system, where aqueous H_2O_2 (instead of anhydrous H_2O_2 (UHP) in the case of the TS-2/UHP system) is used, the different EPR signals originating from nonequivalent Ti environments seemed to loose their inequality, leading to the observation of two broad signals (curve C). This result (curve C) also corroborates the above explanation in view of the earlier results obtained for the TS-1/HP system (14, 16).

Epoxidation of Allyl Alcohol, Allyl Chloride, Allyl Bromide, and Methylallyl Chloride

It is interesting to compare the oxidation behavior of TS-1 and TS-2 with different sources of hydrogen peroxide as oxidant. Since H_2O has a strong affinity for coordinating with the tetra-coordinated Ti species and generate acid centers, it is of great importance from the catalytic point of view to make the reaction system more hydrophobic using anhydrous oxidants to reduce isomerization and hydrolysis of the desired product, particularly for the epoxidation reactions.

Table 1 shows the effect on the activity and selectivity for the epoxidation of different allylic substrates using TS-1 as solid redox catalyst and different H_2O_2 sources as oxidants. The results given in Table 1 clearly show that

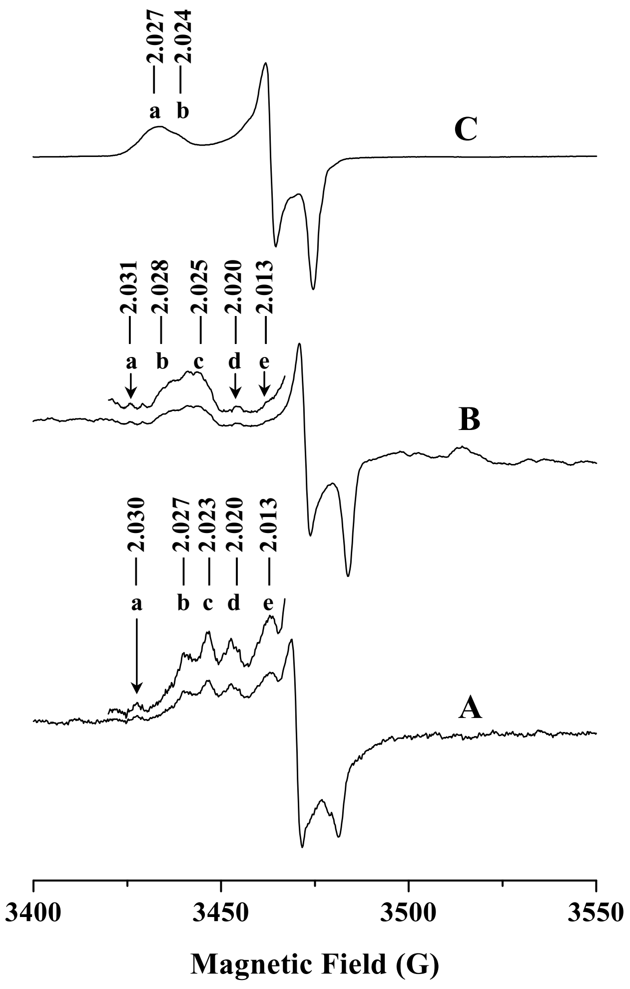

FIG. 2. EPR spectra of TS-1 + UHP (A), TS-2 + UHP (B), and TS-2 + aqueous H_2O_2 (C).

TABLE 1

Effect of Different Oxidants on Epoxidation of Allyl Alcohol, Allyl Chloride, Allyl Bromide, and Methylallyl Chloride over TS-1[a]

Substrate	Oxidant[b]	Conversion (mol%)[c]	TON[d]	Product distribution (mol%) Epoxide	Diol[e]
Allyl alcohol	HP	66	56.8	84	11[f]
	U + HP	72	62.0	90	10
	UHP	74	63.7	98	2
Allyl chloride	HP	95	62.1	87	13
	U + HP	95	62.1	92	8
	UHP	96	62.7	97	3
Allyl bromide	HP	94	38.8	87	13
	U + HP	95	39.3	94	7
	UHP	97	40.1	98	2
Methylallyl chloride	HP	64	35.3	76	24
	U + HP	71	39.2	92	8
	UHP	74	40.9	94	6

[a] Reaction conditions: substrate, oxidant (mol/mol) = 2.0; solvent, methanol; substrate, methanol (wt/wt) = 3.0; reaction time (h) = 8; catalyst wt = 20 wt% of the substrate; $T = 313$ K.

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

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

[d] Turnover number (TON), moles of H_2O_2 converted for producing epoxide + secondary products per mole of Ti.

[e] Mostly the corresponding diols, including some high-boiling products.

[f] Remaining 5 mol% is acrolein.

the epoxide selectivity exhibited by three oxidants decreases in the order UHP > U + HP > HP. It is observed that the conversion as well as the selectivity for the three allylic substrates increases in the order allyl alcohol < allyl chloride < allyl bromide. This is mainly due to the decrease in the electronegative character of the three electron withdrawing groups (OH > Cl > Br) present in the three allylic substrates (21) and therefore the C=C double bond becomes much more localized and also accessible for the epoxidation, which accounts for the increasing trend in the conversion. Similarly, the increase in the selectivity stands for the increased hydrophobic character of the allylic molecules. However, the higher activity of allyl chloride vis-à-vis methylallyl chloride, also observed earlier using aqueous H_2O_2, in contrast to the homogeneous systems (21, 22) is probably a manifestation of the reactant shape selectivity exhibited by TS-1 in retarding the diffusion of bulkier methylallyl chloride vis-à-vis allyl chloride to the active Ti centers located inside the channel system.

Epoxidation of 1-Hexene and Cyclohexene

Effect of different oxidants (HP, U + HP, and UHP) on the epoxidation of 1-hexene and cyclohexene is demonstrated in Table 2. In the case of TS-1 and TS-2 molecular sieves used as catalysts for the cyclohexene epoxidation (Table 2), it is clear that if one takes into account the pore diameters and hydrophobic character of the TS-1 and TS-2 catalysts, one should expect somewhat similar intrinsic activity and selectivity for the epoxide in both cases, as is observed experimentally. It is observed that the selectivity of both 1,2-epoxyhexane and cyclohexene oxide is very low in aqueous hydrogen peroxide in comparison with the allylic substrates (Tables 1 and 2). This difference may be attributed to increasing diffusional constraints for relatively bulky molecules (e.g., 1-hexene and cyclohexene). Further, diffusion of bulkier epoxides slower than that of substrates from the Ti sites of TS-1 and TS-2, which develop acidic character in the presence of water (9), may result in consecutive hydrolysis of epoxides to the corresponding diols due to increased residence time of the former on the active sites. It may be emphasized that TS-1 (and TS-2 also)

TABLE 2

Effect of Different Oxidants on Epoxidation of 1-Hexene and Cyclohexene over TS-1 and TS-2[a]

Substrate	Catalyst	Oxidant	Conversion (mol%)	TON	Product distribution (mol%)[b] EP	OL	ONE	DIOLS
1-Hexene	TS-1	HP	35	10.4	29	—	—	71
		U + HP	42	12.5	94	—	—	6
		UHP	47	14.0	98	—	—	2
Cyclohexene	TS-1	HP	38	11.6	21	2	8	69
		U + HP	41	12.5	96	—	—	4
		UHP	45	13.7	99	—	—	1
	TS-2	HP	40	12.1	26	2	10	62
		U + HP	42	12.7	94	—	—	6
		UHP	44	13.3	98	—	—	2

[a] Reaction conditions: substrate, oxidant (mol/mol) = 4.0; solvent, methanol; substrate, methanol (wt/wt) = 1.0; reaction time (h) = 12; catalyst wt = 20 wt% of the substrate; $T = 313$ K. See also Table 1.

[b] EP, 1,2-Epoxyhexane and cyclohexene oxide; OL, cyclohexeneol; ONE, cyclohexenone; DIOLS, 1,2-hexanediol and mixture of *cis*/*trans*-1,2-cyclohexanediols.

TABLE 3

Effect of Different Oxidants on Epoxidation of Styrene and Allylbenzene over TS-1 and TS-2[a]

Substrate	Catalyst	Oxidant	Conversion (mol%)	TON	Product distribution (mol%)[b] EP	PAD	BD	DIOLS
Styrene	TS-1[c]	HP	56	13.4	5	44	29	22
		U + HP	65	15.6	81	8	7	4
		UHP	71	17.0	87	5	7	1
	TS-2	HP	57	14.1	7	42	28	23
		U + HP	62	15.8	80	8	8	4
		UHP	67	17.3	85	6	7	2
Allylbenzene	TS-1	HP	60	12.7	58	—	—	42
		U + HP	68	14.4	95	—	—	5
		UHP	70	14.8	98	—	—	2

[a] Reaction conditions: Substrate, oxidant (mol/mol) = 4.0; solvent, acetone; substrate, acetone (wt/wt) = 1.0; reaction time (h) = 12; catalyst wt = 20 wt% of the substrate; $T = 313$ K. See also Table 1.

[b] EP, Epoxy allylbenzene and styrene oxide; PAD, phenylacetaldehyde; BD, benzaldehyde; DIOLS, 3-phenyl-1,2-propanediol and styrene diol, including some high-boiling products.

[c] Data taken from Table 1 of Ref. (14).

exhibits weak Brønsted acid sites due to coordination of water with "≡Ti–O–O–H" forming a five-membered ring (9, 14). In the case of smaller allylic substrates, such diffusional limitation is expected to be very low, and therefore, the desorption of the product (epoxide) from the active Ti sites will be faster; hence, the cleavage of the oxirane ring is very low, leading to high epoxide selectivity even in the case of HP. The low conversion for both the substrates may also be attributed to diffusional restriction of comparatively bulky molecules (6), which may face increased diffusional resistance through the pores of MFI and MEL structures.

In the presence of aqueous H_2O_2, allylic oxidation of cyclohexene (~10 mol%) occurs at the α-carbon of the C=C double bond to produce undesired cyclohexenol, which then further oxidizes to more stable cyclohexenone via a radical-type mechanism. However, in U + HP and UHP systems, neither cyclohexenol nor cyclohexenone were produced in detectable quantities, mainly due to the anhydrous nature of the oxidizing agents. As expected, it was observed that the 1-hexene and cyclohexene conversion as well as the selectivity for epoxides increases as the hydrogen peroxide becomes more and more anhydrous in nature (HP < U + HP < UHP).

Epoxidation of Styrene and Allylbenzene

Table 3 demonstrates the epoxidation of styrene using TS-1 and TS-2 as catalysts. It is observed that the styrene conversion and the selectivity for styrene oxide increases in the order HP < U + HP < UHP, for TS-1 and TS-2, respectively. It has been noticed that a considerable amount of benzaldehyde (29 mol%) is also produced during styrene epoxidation using aqueous H_2O_2 as the oxidizing agent and TS-1/TS-2 as the redox catalysts (8, 14). Probably, the cleavage of a highly reactive benzylic C=C double bond in styrene is capable of producing benzaldehyde via a radical type of transformation, which is not feasible in the epoxidation for other olefins (allylic, isolated, etc.) with a nonbenzylic C=C double bond. It seems that a similar type of active species stabilized in the presence of aqueous H_2O_2 (HP) is also responsible for allylic oxidation in cyclohexene and for small conversion of allyl alcohol to acrolein. In the case of U + HP (where urea–hydrogen peroxide adduct is prepared *in situ*) and UHP systems, anhydrous H_2O_2 is released into the solution in a controlled manner and therefore excess oxidizing agent is not present in the reaction system, which in turn minimizes the formation of benzaldehyde. If this is so, one could expect to control the formation of benzaldehyde by adding aqueous H_2O_2 very slowly over the period of time (8 h) through a mechanical syringe pump. Indeed, the result obtained shows a considerable decrease in the formation of benzaldehyde (15 mol%). However, the selectivity of styrene oxide (8 mol%) is merely increased because of its isomerization into phenylacetaldehyde (57 mol%) in the presence of highly polar water. Although statistically acetophenone is also expected to be produced due to isomerization of styrene oxide, very high regioselectivity toward the formation of phenylacetaldehyde may be explained on the basis of stabilization of benzylic carbinium ion formed during rearrangement. Very high epoxide selectivity for allylbenzene (having an allylic C=C double bond) in comparison with styrene (having a benzylic C=C double bond) is obtained using UHP. These results (Table 3) also corroborate the above explanation in view of the results obtained for different epoxidation reactions.

CONCLUSIONS

A highly selective heterogeneous catalytic method for the synthesis of epoxides from their corresponding olefins has been demonstrated using anhydrous urea–hydrogen peroxide adduct as the oxidizing agent in the presence of microporous molecular sieve materials (TS-1 and TS-2). Urea present in UHP or added separately in aqueous hydrogen peroxide (U + HP) acts not only as a dehydrating agent but also as a buffer for the system, which minimizes further acid-catalyzed isomerization and hydrolysis of the desired epoxide. The formation of benzaldehyde by C=C double bond cleavage of styrene is minimized by using anhydrous oxidizing agents (U + HP and UHP) and also by adding aqueous H_2O_2 very slowly through a mechanical syringe pump. The lower activity of methylallyl chloride relative to that of allyl chloride observed in the present study is due to the reactant shape selectivity of TS-1.

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