# **Ti-Oxo Radicals and Product Selectivity in Olefin Oxidations over Titanosilicate Molecular Sieves**

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Dedicated to Prof. Dr. Helmut Knözinger on the occasion of his 70<sup>th</sup> birthday

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# Titanosilicates / Molecular Sieves / Titanium-Oxo Radicals / Reactive Oxygen Species / Oxidations / Product Selectivity / EPR-Spin Trap Experiments / Cyclic Voltammetry of Titanosilicates

The O–O bond of Ti-oxo species (Ti-peroxo, Ti-hydroperoxo or Ti-superoxo) generated on titanosilicate molecular sieves contacted with  $H_2O_2$  cleaves either heterolytically or homolytically. While the former type of O–O cleavage (generating non-radical reactive oxygen intermediates) leads to selective epoxide products, the latter (generating reactive oxygen radical intermediates,  $O_2^{-\bullet}$  and HOO•) results in non-selective, allylic oxidation products in cyclohexene oxidation. These radicals were detected using EPR spin trapping techniques; 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as the spin trap. Radical quenchers like hydroquinone suppressed their concentration and enhanced epoxide selectivity.

# **1. Introduction**

The enormous interest in titanosilicate molecular sieves is due to their remarkable catalytic activity in oxidation reactions using the environmentally benign aqueous  $H_2O_2$  as the oxidant [1–3]. In the dehydrated state, the surface of a well-prepared titanosilicate molecular sieve like TS-1, is known [4–8] to contain mainly two types of Ti<sup>4+</sup> ions (1) those wherein the Ti<sup>4+</sup> ions are 4-fold coordinated with lattice (–OSi) groups, Ti(OSi)<sub>4</sub>, in near tetrahedral symmetry, called the tetrapodal Ti ions, and (2) those wherein they are tripodally coordinated to the surface, Ti(OSi)<sub>3</sub>(OH), an extra-lattice OH group forming

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the fourth ligand. The tetrapodal species dominates in TS-1, TS-2 and Ti-beta while the tripodals are more prevalent in Ti-MCM-41 and other mesoporous materials [4–8]. On interaction with  $H_2O_2$ ,  $(H_2 + O_2)$  or alkyl hydroperoxides (ROOH), the Ti ions expand their coordination number to 5 or 6 and form Ti-hydroperoxo/peroxo [9–16] and superoxo [17–24] complexes, which catalyze the oxidation reactions. What is the influence of the nature and mode of cleavage of the O-O bond (in the oxo-Ti species) on product selectivity? In many oxidations catalyzed by titanosilicates it has been noted [1-3] that product selectivity depends on a variety of factors including the type of crystalline structure (TS-1, Ti-beta, Ti-MCM-41), solvent, temperature and oxidant  $(H_2O_2, alkyl hydroperoxide, (H_2 + O_2), urea-H_2O_2 etc.)$ . For example, in olefin oxidations, both epoxidation and allylic oxidations occur, their relative importance varying with the factors mentioned above [1]. In the present paper, an attempt is made to explore the relationship between (1) the structure of the Ti-oxo complex, (2) the mode of cleavage of the O-O bond in Ti-oxo species and (3) product selectivity in olefin epoxidation reactions over different titanosilicate molecular sieves. The redox behavior of Ti in TS-1 and Ti-MCM-41 is investigated by cyclic voltammetric (CV) measurements. The stability of the oxo-Ti species is investigated by UV-visible and EPR spectroscopic studies. The O-centered radical species such as HO<sup>•</sup>, HOO<sup>•</sup> and O<sub>2</sub><sup>-•</sup> generated by homolytic O–O cleavage are very short lived  $(10^{-9} \text{ s for HO}^{\bullet})$ , for example). We have used the EPR-spin trapping method to detect such free radicals. The O-centered radicals are reacted with a spin trap, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), to generate relatively long-lived nitroxide free radicals (spin adducts), easily detected by EPR spectroscopy. The spectral features and the spin Hamiltonian parameters (superhyperfine coupling constant) are highly sensitive to the type of radical adduct (DMPO-OH, DMPO-O<sub>2</sub>) and DMPO-OOH). Changes in radical concentrations in different solvents and in the presence of known radical scavengers, like hydroquinone, were also studied. Product selectivities in cyclohexene and styrene oxidations are found to be influenced by the concentration of such radicals.

# 2. Experimental

# 2.1 Materials and characterization

TS-1, Ti-MCM-41, Ti-SBA-15 and ETS-10 were prepared and characterized as reported earlier [22, 25]. TS-1: Si/Ti = 33 (XRF); BET surface area  $\approx 400 \text{ m}^2/\text{g}$ ; FT-IR characteristic band at 964 cm<sup>-1</sup>; cuboidal morphology; particle size = 0.3 µm (SEM); Ti-MCM-41: Si/Ti = 46 (XRF); BET surface area = 960 m<sup>2</sup>/g; FT-IR characteristic band at 968 cm<sup>-1</sup>; average pore diameter = 3 nm; pore volume = 0.9 cm<sup>3</sup>; Ti-SBA-15: Si/Ti = 30 (XRF); BET surface area = 790 m<sup>2</sup>/g, pore volume = 1.7 cm<sup>3</sup> and average pore diameter = 8.3 nm, pore volume = 1.7 cm<sup>3</sup>. EPR spectra were recorded on a Bruker EMX spectrometer operating at *X*-band ( $\nu \approx 9.45$  GHz) frequency and 100 kHz field modulation [22]. EPR spectral simulations were done using the Bruker Simfonia software package. Spectral intensity calculations (by double interaction method) and other manipulations were done using the WINEPR package.

Cyclic voltammetric measurements were performed using a CHI 660 A (USA) electrochemical instrument. A conventional three-electrode cell assembly was used. Saturated Ag/AgCl as reference and Pt as auxiliary electrodes were used for this purpose. Zeolite-modified graphite electrode was used as working electrode. In the preparation of this electrode, powder samples of zeolite and graphite were mixed together by gentle grinding in a weight ratio of 60:40. It was then made into a pellet (diameter = 10 mm and thickness  $\sim 1$  mm) and fixed to a polished silver wire. Silver paint was diluted with iso-amyl acetate and a small drop of it was used for making electrical contact between the pellet and wire. It was dried under an IR lamp for 30 min. An adhesive, Araldite gum was applied to hold the pellet and the wire covering the silver paint. The modified electrode was kept for 16 h for drying before it was used in the experiment. 0.1 M KNO<sub>3</sub> solutions were used as electrolyte. Prior to the CV experiments, dissolved oxygen in the electrolyte solution was removed by purging with argon for 30 min. The CV scans were made in the potential range +1 to -1 V with a scan rate of  $50 \, \text{mV/s}$ .

# 2.2 EPR-spin trapping and sample preparation

In this technique, the lifetime of radicals is prolonged (from ~  $10^{-9}$  s to ~ 30 s, for HO<sup>•</sup> radicals, for example) by forming spin adducts with spin traps such as nitrones or nitroso compounds. We have used 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, Aldrich Co.) as the spin trap. In a typical sample preparation procedure, to DMPO solution in water (0.5 mmol; 0.2 ml), 0.5 ml of solvent (DMSO, CH<sub>3</sub>CN or C<sub>2</sub>H<sub>5</sub>OH) was added and the pH was adjusted to 7.4 using 0.1 M phosphate buffer (K<sub>2</sub>HPO<sub>4</sub> + KH<sub>2</sub>PO<sub>4</sub>). Separately, TS-1 (8 mg) was treated with dilute H<sub>2</sub>O<sub>2</sub> (30% aqueous H<sub>2</sub>O<sub>2</sub> was diluted by 10 times; 0.5 ml), warmed for 5 min at 333 K and then centrifused. The spin trap solution prepared as above at 298 K was added to the centrifugate. It was immediately taken in an EPR quartz flat cell and its EPR measured at 298 K.

# 2.3 Reaction procedures and product analysis

*Epoxidation of cyclohexene.* 0.1 g of titanosilicate (TS-1, Ti-MCM-41, Ti-SBA-15 or ETS-10), 0.82 g of cyclohexene, 5 ml of solvent were taken in a glass flask fitted with a water-cooled condenser and placed in a constant temperature (333 K) oil bath.  $H_2O_2$  ([cyclohexene]/[ $H_2O_2$ ] = 3 mol/mol) was

added drop-wise over a period of 10 min and then the reaction was carried out for 4 h. The products were analyzed by gas chromatography (CHROMPACK CP9001; 50 m-long  $\times$  0.32 mm-i.d.  $\times$  0.3 µm thick Hewlett-Packard fused silica capillary column) and identified by GC-MS (Shimadzu QP-5000; 30 m-long  $\times$  0.25 mm-i.d.  $\times$  0.25 mm-thick capillary DB-1 column).

*Epoxidation of styrene.* In a 100 ml Teflon-lined steel autoclave, 0.1 g of TS-1, 10 g of solvent, 8.63 mmol of styrene and 17.2 mmol of  $H_2O_2$  (aqueous) were taken and the reaction was conducted at 333 K in a rotating hydrothermal synthesis reactor (rotation speed = 30 rpm) for 8 h. The products were analyzed by gas chromatography/mass spectrometry.

Certain oxidations were conducted in the presence of radical scavengers such as mannitol, catechol, thiourea, sodium acetate, sodium salicylate, *p*-benzoquinone, hydroquinone and sodium formate. In those experiments a known quantity of the radical scavenger (0-0.018 mmol) was added to the reaction mixture and the reaction conducted in a similar manner.

# 3. Results and discussion

# 3.1 Structure and redox behavior of Ti<sup>4+</sup> ions

The titanosilicate samples, TS-1, Ti-MCM-41 and Ti-SBA-15, show an intense UV band at 200–230 nm corresponding to a charge transfer transition from  $O^{2-}$  to Ti<sup>4+</sup>. This band was attributed [1–3] to dispersed-Ti ions in a psuedo-tetrahedral coordination. Spectral deconvolution studies revealed that this band comprises of two bands with maximum at 206 and 228 nm corresponding to tetrapodal Ti species, Ti(OSi)<sub>4</sub> and tripodal Ti species, Ti(OSi)<sub>3</sub>(OH), respectively. Intensity of the 206 nm band was more in the case of TS-1. Ti-MCM-41 and Ti-SBA-15 contained mainly the band at 228 nm corresponding to the tripodal Ti species were drawn earlier [26] from the EPR investigations. The two Ti species differed in their reducibility in H<sub>2</sub>, with the tripodal Ti<sup>4+</sup> being more easily reducible than the tetrapodal Ti<sup>4+</sup> ions [26].

Cyclic voltammetry (CV) is a highly sensitive technique for detecting changes in the oxidation state and/or redox potential of ions. TS-1 showed two reduction peaks, A and B (corresponding to  $Ti^{4+} + e^- \rightarrow Ti^{3+}$ ) at -0.51 and -0.27 V (Fig. 1a), with the former being more intense than the latter redox peak. They represent  $Ti^{4+}$  ions in two different structural environments and, hence, with different reduction potentials. Ti-MCM-41 exhibited (Fig. 1b) four reduction peaks (A, B, C and D) at -0.52, -0.21, -0.22 and -0.05 V, respectively, with intensities A:B:C:D = 1:33:33:33, respectively. The reduction peak A by analogy to TS-1, arises from a tetrapodal Ti while B arises from the tripodal Ti; C and D, originate, perhaps, from penta- and hexa-coordinated defect open structures, respectively. The less negative reduction potential of the tripodal Ti (reduction



**Fig. 1.** Cyclic voltammographs of TS-1, Ti-MCM-41 and TS-1 contacted with aqueous  $H_2O_2$ . Peaks A–D correspond to different types of Ti species in TS-1 and Ti-MCM-41.

peak B) compared to the tetrapodal species (reduction peak A) indicates that the former could be reduced more easily. This observation is in agreement with our earlier EPR studies [26] wherein the tripodal  $Ti^{4+}$  could be reduced with dry  $H_2$  at 673 K while the tetrapodal Ti were reduced only above 823 K.

Upon contacting TS-1 with  $H_2O_2$ , a new reduction peak was observed at -0.69 V (Fig. 1c). The original reduction peaks of TS-1 disappeared completely. The new peak is attributed to the reduction of  $Ti(O_2^{-\bullet})$  to  $Ti(O_2^{2-})$ . Molecular oxygen and free superoxide ion are reduced only beyond -0.9 V. Superoxide ions bound to Ti are, hence, more easily reduced than free superoxide ions.



Fig. 2. EPR spectra (at 80 K) of superoxo-Ti on titanosilicates contacted with aqueous  $H_2O_2$ . Dotted line indicates the  $g_z$  component signal of superoxo species A and B.

#### 3.2 Oxo-Ti species and reactivity

On contact with aqueous H<sub>2</sub>O<sub>2</sub>, TS-1 generated different types of Ti-oxo species (hydroperoxo, peroxo- and superoxo-Ti) [20, 22–24]. These oxo species showed a characteristic charge transfer band in the DRUV-visible spectrum in the region 300–500 nm [22, 23]. While the peroxo- and hydroperoxo-Ti were diamagnetic, the superoxo-Ti species were paramagnetic and exhibited characteristic rhombic-type EPR spectrum. Two types of superoxo-Ti species A and B were identified on TS-1 [20, 22–24]. They differed mainly in their  $g_z$  parameter;  $g_x$  and  $g_y$  values being identical (A-type:  $g_z = 2.0260$ ,  $g_y = 2.0090$  and  $g_x = 2.0023$ ; B-type:  $g_z = 2.0235$ ,  $g_y = 2.0090$  and  $g_x = 2.0023$ ). Their concentration decreased in the order: A > B. Ti-MCM-41 and Ti-SBA-15 contained mainly the B-type superoxo-Ti species (Fig. 2). By analogy, the A and B-type superoxo species are attributed to originate from the tetrapodal Ti structures (showing the UV band at 206 nm) and the tripodal Ti structures (showing the UV band at 228 nm), respectively.

In situ EPR studies provided evidence for the participation of these oxo-Ti species in epoxidation reactions (Fig. 3). In allyl alcohol epoxidation, the oxo-Ti species (A-type) generated from the tetrapodal Ti were consumed faster than those (B-type) generated from the tripodal Ti (Fig. 3a). Participation of A and B-type species was also observed in the epoxidations of cyclohexene and styrene (Fig. 3b,c). In the latter two cases, organic C-centered radicals (multiplet pattern indicated by asterisk; see the 2<sup>nd</sup> derivative plots; g = 2.0022) were also detected. Such organic radicals were not observed in allyl alcohol



**Fig. 3.** Reactivity of Ti-oxo species on TS-1 +  $H_2O_2$  system in substrate oxidation. Reactions were conducted at 333 K for a known period of time (0–25 min) and spectra recorded at 80 K. Asterisk (\*) indicates signals due to substrate-based radicals. These could be seen more clearly in the 2<sup>nd</sup> derivative plots.

epoxidations (Fig. 3a). The rate of consumption of the A and B-type species varied with the type of substrate. In the oxidation of cyclohexene, the A-type species were consumed  $4.6 \times 10^2$  times faster (estimated from the EPR signal intensity as a function of time) than the B-type species. In the case of styrene,

Catalyst	Cyclohexene	TOF	Product	selecti	vity (mol%)	(Epoxide + diol)
	conv. mol%	$(\mathbf{h}^{-1})^{\mathbf{b}}$	Epoxide	Diol	Allylic (-ol + -one)	selectivity, %
TS-1 Ti-MCM-41 Ti-SBA-15 ETS-10	18.6 32.4 52.5 12.3	10 17 25 1	55.6 12.9 12.0 8.5	28.7 60.3 62.0 64.6	15.7 26.8 26.0 26.9	84.3 73.2 74.0 73.1

Table 1. Influence of Ti structure: oxidation of cyclohexene with aqueous H<sub>2</sub>O<sub>2</sub><sup>a</sup>.

<sup>a</sup> Reaction conditions: catalyst, 0.1 g; cyclohexene, 0.82 g (10 mmol);  $H_2O_2$  (30% aqueous), 3.33 mmol; CH<sub>3</sub>CN, 5 ml; temperature, 333 K; reaction time, 4 h. <sup>b</sup> Turnover frequency (TOF,  $h^{-1}$ ) = moles of cyclohexene converted (experimental) per mole of Ti per hour.

the A species were consumed  $0.63 \times 10^2$  times faster than B. In allyl alcohol epoxidation, the A type species were consumed twice faster. The higher reactivity of the A type oxo-Ti species can be correlated with the reversible reduction–oxidation behavior of the corresponding Ti ions (Fig. 1). In cyclic voltammographs, a reversible redox couple was observed only for the A-type species. The B-type species showed only a reduction peak, the corresponding oxidation peak could not be detected. Hence, the facile reduction and oxidation behavior of the tetrapodal-Ti species, A type, is responsible for their superior activity. The irreversible redox behavior of the tripodal Ti leads to weak activity.

# 3.3 Catalytic activity and selectivity

Oxidation of olefins containing allylic hydrogens can give rise to (1) epoxides, (2) allylic oxidation products (alcohol or ketone) or (3) cleavage of the double bond. In addition, the epoxide can undergo further acid-catalyzed isomerization (for example, styrene oxide to phenyl acetaldehyde) or hydration to diol (ethylene oxide to ethylene glycol).

#### 3.3.1 Oxidation of cyclohexene

The product distribution in cyclohexene oxidation (Scheme 1) over different titanosilicate catalysts is listed in Table 1. Olefin conversion is higher over the mesoporous material Ti-MCM-41 and Ti-SBA-15 due to the greater ease of diffusion of reactant molecules in their pores. However, the epoxide is favored only over TS-1. The large amount of diols formed over the mesoporous material and ETS-10 is due to their relatively greater acidity and consequent hydration of the epoxide to the diols. In the absence of solvents, cyclohexene conversion is significantly lower; -enol and -enone (from allylic oxidation) are the major products (Table 2). There is no epoxide/diol formation. The

conversions are also higher in the presence of aprotic solvents. Selectivity to epoxidation products (epoxide + diol) is however, higher in alcohol solvents. A similar trend is observed in acetonitrile–methanol (Table 2).



Scheme 1. Oxidation of cyclohexene.

#### 3.3.2 Oxidation of styrene

Styrene oxide, phenyl acetaldehyde, benzaldehyde and benzoic acid were the products in styrene oxidation (Table 3). Secondary reactions of styrene oxide also yielded the diol and methylated diol products. A significant influence of solvent on the reactivity and product selectivity is noted in this case also (Table 3).

#### 3.4 Oxo radicals – EPR-spin trap studies

In view of the observation of Ti-oxo radicals on contact of TS-1 with H<sub>2</sub>O<sub>2</sub> the role of radicals, if any, in the oxidation mechanism of TS-1, was investigated through EPR-spin trapping experiments with DMPO. Upon reaction with various O-centered radicals (like HO•, HOO• or O<sub>2</sub>-•, generated through homolytic O–O cleavage), DMPO forms paramagnetic adduct complexes, which show characteristic EPR spectra differing significantly in their superhyperfine coupling constants ( $a_N$  and  $a_H$ ) (Fig. 4). The superoxo and hydroperoxo-DMPO adducts (B) show similar EPR spectral patterns. The hydroxo-DMPO adduct (A), on the other hand, shows a completely different pattern (Fig. 4) (A: DMPO–OH: g = 2.0063,  $a_N = 14.9$  G,  $a_H^{\beta} = 14.9$  G. B: DMPO–OOH/O<sub>2</sub>-•: g = 2.0063;  $a_N = 14.2$  G,  $a_H^{\beta} = 11.2$  G;  $a_H^{\gamma} = 1.25$  G). The EPR spectrum of DMPO on contact with (H<sub>2</sub>O<sub>2</sub> + TS-1) can, hence, be used to differentiate the oxo radicals formed in the H<sub>2</sub>O<sub>2</sub>–TS-1 system.

DMPO alone did not exhibit any EPR spectrum; radicals were also not detected in the absence of TS-1; the self-decomposition of  $H_2O_2$  into O-centered radical species was negligible in the absence of TS-1. Contact of  $H_2O_2$  with TS-1 gave rise to the EPR spectrum of DMPO typical of  $O_2^{-\bullet}$ /HOO• radical

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Solvent	Cyclohexene	TOF	Prod	luct select	tivity (mc	1%)	(Epoxide + diol)
	conv. mol%	$(h^{-1})$	Epoxide	Diol	-enol	-enone	selectivity, %
No solvent	1.5	0.8	0	0	14.7	85.3	0
Acetonitrile	18.6	10.0	55.6	28.7	5.7	10.0	84.3
Acetone	19.2	9.6	5.9	69.3	9.7	15.1	75.2
Tertbutanol	11.7	6.0	24.2	53.2	5.8	16.8	77.4
Methanol	14.7	7.6	0	88.7	0	11.3	88.7
Ethanol	9.6	5.1	0.2	90.6	0	9.2	90.8
Iso-propanol	9.6	4.9	2.3	88.7	0.2	8.8	91.0
Solvent mixture							
Acetonitrile : Methanol							
(vol:vol)							
66:34	16.8	8.6	24.4	58.3	4.1	13.2	82.4
50:50	16.5	8.5	18.1	64.3	4.6	13.0	82.7
34:66	15.3	7.9	7.6	79.9	2.7	9.8	87.5
25:75	15.0	7.7	4.1	85.9	1.5	8.5	88.0
<sup>a</sup> Reaction conditions: (3.33 mmol); solvent, 5 <sup>b</sup> Turnover frequency (T	catalyst, 0.1 g; $(ml; temperatu OF, h^{-1}) = mo$	; cycloh re, 333 ] les of cy	exene, 0.82 K; reaction clohexene c	2 g (10 m time, 41 onverted	mol); H a; cycloh (experim	$_{2}O_{2}$ (30% exene/H <sub>2</sub> C ental) per 1	aqueous), $0.268 \text{ g}$ $0_2 \text{ (mol/mol)} = 3.$ nole of Ti per hour.

adducts (compare Figs. 4 and 5). No radicals were observed in ethanol. The concentration of  $O_2^{-\bullet}/HOO^{\bullet}$  radicals (estimated using a weak-pitch standard supplied by Bruker) decreased in the following order: water–DMSO ( $3.3 \times 10^{13}$  spins) > water–CH<sub>3</sub>CN ( $1.2 \times 10^{13}$  spins) > water alone ( $1.0 \times 10^{13}$  spins) > water–C<sub>2</sub>H<sub>5</sub>OH ( $7.5 \times 10^{11}$  spins). Solvents influence the identity of the radicals formed from H<sub>2</sub>O<sub>2</sub> ( $O_2^{-\bullet}/HOO^{\bullet}$  vs. HO<sup>•</sup>, for example). Keeping in mind that higher epoxidation selectivities were observed in alcoholic solvents (Table 2), wherein the concentration of such O-centered radicals was minimal, an influence of such radicals on the formation of allylic oxidation products (enol and enone) in cyclohexene oxidation reactions may be inferred.

Solvent	Styrene conv.	TOF		Pro	duct selo	sctivity (mol%)			(Styrene oxide +
	mol%	$(h^{-1})$	Styrene oxide	Methylated diol	Diol	Phenyl acetaldehyde	Benz- aldehyde	Others	diols + phenyl acetaldehyde) selectivity, %
Methanol	39.9	8.9	35.9	46.0	1.1	0.3	13.8	2.9	83.3
Acetone	25.4	5.7	61.4	0.7	2.6	3.4	31.9	0.0	68.1
Methanol + Acetonitrile $(1:1 v/v)$	26.3	5.9	29.4	21.8	3.1	9.2	35.0	1.5	63.5
Reaction conditions: ca 8 h. Reaction was carrie	talyst, 0.1 g; styr ed out in glass re	ene, 8.65 actor.	3 mmol; sty	$rene/H_2O_2 =$	0.5 (mc	l/mol); solven	t, 10 g; tem	perature, 33	3 K; reaction time,

Table 3. Influence of solvent: oxidation of styrene with aqueous  $H_2O_2$  over TS-1.



Fig. 4. Reaction of DMPO with O-centered radicals and the EPR spectra of the corresponding radical adducts.



Fig. 5. EPR spectra (at 298 K; normalized intensity) of DMPO-oxygen centered radical adducts in TS-1 + H<sub>2</sub>O<sub>2</sub> system – influence of solvents.



Fig. 6. EPR spectra (at 298 K) of  $(TS-1 + H_2O_2)$  contacted with DMPO, hydroquinone and DMPO + hydroquinone.

#### 3.5 Reactions in presence of radical scavengers

Radical-mediated reactions are suppressed in the presence of radical scavengers. We have carried out the epoxidation tests in the presence of various radical scavengers. In the presence of a spin trap (DMPO), characteristic signals due to  $O_2^{-\bullet}$ /HOO<sup>•</sup> radical adducts are seen (Fig. 6). When a radical scavenger, hydroquinone, was added to this reaction mixture, the EPR pattern of DMPO-oxo radical was not seen. Instead, the quintet line pattern (indicated by asterisks; Fig. 6) due to the formation of semiquinone radicals was detected; the hydroquinone had preferentially reacted with the O-centered radicals and formed the semiquinone. When both hydroquinone and DMPO were added simultaneously to the reaction slurry, hydroquinone reacted faster and quenched the radicals even before DMPO, the spin trap, could form the spin adducts. In this case, only the signals due to the semiquinone were observed.

Table 4 presents the influence of hydroquinone, on product selectivities in the oxidation of cyclohexene and styrene over TS-1. In the absence of hydroquinone, oxidation occurs at both olefinic and allylic carbons (Scheme 1). Upon hydroquinone addition, the selectivity for epoxide increased to 100%. Allylic products were suppressed indicating that radical intermediates are probably involved in their formation. In the case of diols, poisoning of the acid sites responsible for the hydration of the epoxide to diols by hydroquinone is

Epoxidation of cyclohexene <sup>a</sup>									
Hydroquinone	Cyclohexene		Product selectivity (mol%)						
(mmol)	conv. mol%	Epoxide	Diol	Allylic oxidation (	-ol + -one)				
Nil 0.018	18.6 15.3	55.6 100	28.7 0.0	15.7 0.0					
		Epoxidatio	on of styrene <sup>b</sup>						
Hydroquinone	Styrene		Produc	et selectivity					
(mmol)	conversion (mol%)	Styrene oxide	Phenyl acetaldehyde	Benzaldehyde	Benzolic acid				
0 0.009 0.018 0.027	16.4 11.5 7.9 8.0	37.8 45.5 59.0 62.4	12.2 12.9 12.8 13.2	49.3 39.8 27.2 23.3	0.7 1.8 1.0 1.1				

**Table 4.** Influence of hydroquinone addition on the epoxidation of cyclohexene andstyrene over TS-1.

<sup>a</sup> Reaction conditions for epoxidation of cyclohexene: catalyst, 100 mg; cyclohexene, 10 mmol; HQ, 0 or 0.018 mmol;  $H_2O_2$  (30% aqueous), 3.33 mmol;  $CH_3CN$ , 5 ml; temperature, 333 K; reaction time, 4 h. <sup>b</sup> Reaction conditions for epoxidation of styrene: TS-1, 100 mg; styrene, 8.63 mmol;  $H_2O_2$  (30%, aqueous), 17.2 mmol;  $CH_3CN$ , 10 g; temperature, 333 K; reaction time, 8 h. Reaction was carried out in a rotating steel autoclave (Hiro Company, Japan model KH 02; 30 rpm).

probably a reason for their absence in the products. A similar trend is also seen in the oxidation of styrene. Table 5 shows the influence of various radical scavengers on the product selectivity in cyclohexene oxidation. The selectivity for the epoxidation products increased with different radical scavengers in the order: mannitol < catechol < thiourea < sodium acetate < sodium salicylate < *para*-benzoquinone < sodium formate < hydroquinone.

# 4. Conclusions

Various Ti-oxo radical species are generated on reaction of  $H_2O_2$  with titanosilicate molecular sieves. The role of such radicals in the oxidation mechanism of TS-1 has been investigated using EPR-spin traps, like 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and radical scavengers like hydroquinone. The EPR spectra of DMPO on contact with  $H_2O_2$ -TS-1 indicate that  $O_2^{-\bullet}$  and OOH<sup>•</sup> radicals are predominant. Their concentrations vary with the solvent. The oxo radicals influence product selectivity in olefin epoxidation reactions. Addition of radical scavengers, like hydroquinone, suppresses the concentration of such radicals, and significantly enhances the selectivity for the epoxide

Radical scavenger Cyclohexene		Pro	duct se	Epoxide + Diol		
	conversion, %	Epoxide	Diol	-enol	-enone	selectivity, %
None	18.6	55.6	28.7	5.7	10.0	84.1
Mannitol	14.1	57.9	17.2	11.5	13.4	75.1
Catechol	14.4	62.5	20.1	11.0	6.4	82.6
Thiourea	9.9	43.9	42.3	6.7	7.1	86.2
Sodium acetate	26.4	73.1	14.8	2.3	9.8	87.9
Sodium salicylate	29.1	53.1	38.0	2.9	6.0	91.1
<i>p</i> -Benzoquinone	11.4	84.5	0	12.0	3.5	84.5
Hydroquinone	15.3	100	0	0	0	100
Sodium formate	26.1	94.3	3.8	0.3	1.6	98.1

Table 5. Oxidation of cyclohexene in the presence of radical scavengers.

Reaction conditions: catalyst (TS-1; 100 mg), cyclohexene (0.82 g), aq.  $H_2O_2$  (30%, 0.268 g), acetonitrile (5 ml), radical scavenger (0.018 mmol in 0.1 ml water), temperature (333 K), reaction time (4 h); cyclohexene/ $H_2O_2 = 3$  (mol/mol).

at the expense of the allylic oxidation products. A novel method to control product selectivity in oxidations over titanosilicate molecular sieves is demonstrated.

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