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Enhancement of chemoselectivity in epoxidation reactions over TS-1 catalysts by alkali and alkaline metal ions

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Abstract

Alkali metal ions, when present during the synthesis of TS-1, lead to inactive oxidation catalysts. However, when added, in small amounts, to the reaction medium during the epoxidation of allyl alcohol or allyl chloride by H_2O_2 over TS-1, they increase the selectivity for the epoxide. To probe this phenomenon in detail, the influence of pH and alkali and alkaline earth ions on the structure and catalytic activities of the oxo-Ti species generated in H_2O_2. TS-1 and TiMCM-41 systems have been investigated using EPR and diffuse reflectance UV-Vis spectroscopies. In acidic and neutral pH, two types of superoxo-Ti species ($Ti(O_2^{\bullet-})$), A and B, are observed over TS-1. In the presence of alkali and alkaline metal ions or at high pH, Ti^{3+} ions and a new type of $Ti(O_2^{\bullet-})$ species, A' are observed. Only the B-type species, however, is observed on TiMCM-41. The A-type are more reactive than the B-type. Epoxide selectivities approaching 100% can be achieved by a proper control of the reaction medium.
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1. Introduction

Titanium silicalite-1 (TS-1) molecular sieves have been widely investigated for their unique catalytic properties in selective oxidation reactions with H_2O_2 as the oxidant [1–3]. It is well known that the presence of alkali metal ions such as Na^+ and K^+ *in the synthesis gel of TS-1* results in inactive catalysts for *n*-alkane oxidations [4–10]. Washing these catalysts with acids prior to catalytic activity evaluation could, however, restore their activity [5]. It was postulated [6] that the alkali metal ions present during the synthesis might prevent the incorporation of Ti in the silicalite framework. Clerici and Ingallina [10] reported that basic compounds added, in low concentrations, to TS-1 catalysts during epoxidation of olefins inhibit the ring opening of the epoxide due to solvolysis in methanol and improve the selectivity to the epoxide. Capel-Sanchez et al. [11] have confirmed the enhanced selectivity to epoxide when alkali ions are impregnated on TS-1 samples. They attributed this effect to the neutralization of the surface acidity of TS-1 by the alkali ions and the consequent inhibition of the

solvolysis reactions of the epoxide on the acid sites. It may, however, be recalled that the presence and type of acid sites on TS-1 has not been unambiguously confirmed so far [12].

We have, recently, investigated the structure of the reactive oxo-titanium species in TS-1, Ti-β, amorphous Ti–SiO₂ and TiMCM-41 generated on interaction with H_2O_2 [13–15]. Differences in selectivities of different titanosilicates in the epoxidation of olefins were successfully correlated with the type and concentration of the oxo-titanium species present during the reaction. In the present paper, we explore the influence of pH and added alkali ions on the oxo-titanium species. We find that the observed differences in selectivity in the presence of alkali ions can also arise from differences in the type and concentration of the various reactive oxo-titanium species generated in their presence, in addition to the neutralization of surface acidity of TS-1 by the alkali ions.

2. Experimental

2.1. Synthesis

TS-1 (Si/Ti = 33) and TiMCM-41 (Si/Ti = 52) were prepared and characterized as reported earlier [13].

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The alkali modified TS-1 and TiMCM-41 samples used in the spectroscopic studies were prepared as follows. TS-1 and TiMCM-41 (40 mg) were initially activated in air at 673 K. It was then suspended in 10 ml of CH_3OH and the pH was adjusted to a desired value using NaOH (for pH above 7) and oxalic acid (for pH of 4.5 and 5.5). The suspension was stirred for 10–30 min, and the solid catalyst was separated by centrifugation and air-dried.

TS-1 modified with other alkali and alkaline earth ions (pH 8) were prepared in a similar manner using the compounds Li_2CO_3, KOH, CsOH, NH_4OH, MgO, CaO and $Ba(OH)_2$.

2.2. Catalyst characterization

Crystallinity, phase purity and framework substitution of Ti in all the samples were confirmed by X-ray diffraction (Rigaku D MAX III VC), energy dispersive X-ray analysis (Kevax equipment attached to a JEOL JSM-5200) and FT-IR (Shimadzu 8201 FT-IR), diffuse reflectance UV-Vis (Shimadzu UV-2550) and EPR (Bruker EMX X-band; 100 kHz field modulation) spectroscopic techniques [13]. The Si/Ti ratios in TS-1 and TiMCM-41 were found to be 32 and 52, respectively. Alkali impregnation did not alter the crystallinity (XRD) and physicochemical (FT-IR and UV-Vis) characteristics of TS-1 or TiMCM-41. Prior to EPR measurements, the samples (in suprasil quartz tubes) were activated at 373 K, in air. Oxo-Ti species were generated by contacting TS-1, TiMCM-41 or modified titanosilicates (40 mg), completely soaked in 0.4 ml of CH_3OH, with 0.1 ml of aqueous H_2O_2 (46%).

3. Catalytic activity

Epoxidation of allyl alcohol, allyl chloride and styrene were carried out in a rotating hydrothermal synthesis reactor unit (Hiro Company, Japan, Model KH-02) maintained at a constant temperature of 333 K (FC-410 ADVANTEC Forced Convection Oven) and rotation speed of 30 rpm. The reactions were carried out at different pH conditions and in different solvents (CH_3OH, $CH_3OH + CH_3CN$ and CH_3COCH_3). In a 100 ml Teflon-lined steel autoclave, 100 mg of unmodified catalyst (TS-1 or TiMCM-41) was taken in the solvent (10 g). The pH of the slurry was, then, adjusted to a desired value using NaOH (for pH > 6.8) or oxalic acid (for pH < 6.8). The substrate (8.62 mmol) and aqueous H_2O_2 (50%, 0.9 ml) were then added. The autoclave was sealed, placed in the reactor and the reaction was carried out for 8 h. At the end of the reaction, the catalyst was separated by centrifugation. Liquid samples were analyzed by gas chromatography (CHROMPACK CP 9001; Hewlett Packard fused silica column—50 m long, 0.32 mm i.d., and 0.3 μm film thickness). Product identification was done using GC–MS (Shimadzu, QP-5000, DB-1 capillary column—30 m long, 0.25 mm i.d., and 0.25 μm film thickness). The pH of the reaction mixture was measured before and after H_2O_2 addition and also at the end of the reaction. These pH values are listed in Table 1. H_2O_2 was taken in excess (twofold) in the reaction. Only a part of it was consumed for the epoxidation reaction; some amount decomposed (to H_2O and O_2) and the rest remained, unreacted, in the reaction mixture. The unreacted amount of H_2O_2 at the end of the reaction was estimated by iodometric

Table 1
Epoxidation of allyl alcohol and chloride-influence of pH[a]

Run number	Catalyst	Substrate	pH			TOF[b]	Olefin conversion (mol%)	H_2O_2 efficiency (mol%)	Epoxide selectivity (mol%)
			Initial (before H_2O_2 addition)	After H_2O_2 addition	At the end of the reaction				
1	TS-1 (unmodified)	AA	6.5	3.5	4.2	18.6	93.5	100	88.5
2	TS-1 (Run 1, reused)	AA	6.8	3.5	4.5	18.4	92.7	100	93.0
1	TS-1	AA	4.5	3.5	4.2	18.9	95.3	100	86.8
2	TS-1	AA	5.5	3.5	4.2	18.7	94.4	100	87.4
3	TS-1	AA	7.0	5.5	5.8	17.7	89.2	95	92.8
4	TS-1	AA	8.0	5.7	5.9	16.0	80.7	87	100
5	TS-1	AA	9.0	5.9	6.2	7.1	35.6	46	100
6	TS-1	AA	10.0	8.5	8.0	4.4	22.2	21	100
7	TS-1 (Runs 3 and 4, reused)	AA	7.8	5.5	5.7	14.8	74.4	97	96.8
8	TS-1-Na(8)	AA	8.0	5.7	5.9	16.2	81.6	89	100
9	TS-1-Na(10)	AA	10.0	7.8	8.0	5.9	29.7	20	100
10	TiMCM-41	AA	6.8	–	–	2.1	10.4	–	100
11	TiMCM-41	AA	8.0	–	–	2.3	11.4	–	100
12	TS-1	AC	6.8	3.2	3.0	19.3	97.2	97	73.8
13	TS-1	AC	7.0	3.8	3.8	19.8	100	100	79.7
14	TS-1	AC	8.0	4.3	4.2	19.8	100	100	81.6

[a] Reaction conditions: catalyst (100 mg) + substrate (0.5 g) + CH_3OH (10 g) + H_2O_2 (50%, 0.9 ml); H_2O_2/allyl alcohol = 2.0; temperature = 333 K; run time = 8 h; AA: allyl alcohol; AC: allyl chloride.

[b] Moles of substrate converted per mole of Ti per hour.

titrations. H_2O_2 selectivity was determined based on the amount of H_2O_2 consumed in allyl alcohol or allyl chloride epoxidation (Table 1). A significant amount of formic acid formed over TiMCM-41 by the oxidation of methanol. It was, however, very low with TS-1 catalysts.

Epoxidation of allyl alcohol was carried out also in the presence of different alkali metal and alkaline compounds (Li_2CO_3, NaOH, KOH, CsOH, MgO, CaO, Ba(OH)$_2$ and NH_4OH) in a similar manner at pH 8.0.

4. Results and discussion

4.1. EPR and DRUV-Vis spectroscopies

Upon contacting H_2O_2, three types of $Ti(O_2^{\bullet-})$ species A–C were generated on TS-1 [13–15]. They were different 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 $g_x = 2.0023$; C-type: $g_z = 2.0220$, $g_y = 2.0090$ and $g_x = 2.0023$). A and B were more abundant than C [13–15]. A comparison of the EPR results with the EXAFS analysis [16] suggested that, while the A-type species probably originated from tetrapodally-coordinated Ti sites (Ti(OSi)$_4$), the B-type originated from tripodally-coordinated Ti sites ((HO)Ti(OSi)$_3$) [14,15]. TiMCM-41, in contrast to TS-1, generated, predominantly, the B-type species. Zhao et al. [17] and Bonoldi et al. [18] have also identified the A- and B-type species in TS-1 catalysts.

The present study reveals a new type of $Ti(O_2^{\bullet-})$ species, A′, in the presence of alkali metal ions (Fig. 1). In acidic and neutral pH, the A- and B-type $Ti(O_2^{\bullet-})$ species (curves a and b) were observed over TS-1. When the pH was raised to 7–9 (using NaOH), an additional species, A′, characterized by a signal at $g_z = 2.031$, was also detected (see curves b–d). Above pH 9, A′ was the predominant species (curves e and f). Integrated EPR signal intensity and, hence, the total concentration of the paramagnetic $Ti(O_2^{\bullet-})$ species, increased by about three times when the pH was changed from 4.5 to 10. At high pH, in addition to the A′ species, signals due to Ti^{3+} ions ($g_\perp = 1.986$ and $g_\parallel = 1.951$), were also detected (curves e and f). The addition of NaOH did not influence, significantly, the spectral features of TiMCM-41. The latter generated, mainly, the B-type species in the entire pH range. Ti^{3+} signals were also not detected in TiMCM-41. The EPR signal intensity was higher in TiMCM-41 than in TS-1 and it did not increase any further at high pH.

TS-1 samples showed a charge transfer band at 208 nm in the DRUV-Vis spectrum, characteristic of framework Ti species (Fig. 2, curve a). On contact with aqueous H_2O_2, this band shifted to 217 nm in neutral condition (curve b) and to 240 nm in basic conditions (curves c and d) due to solvent interactions with the framework Ti [19]. When contacted with H_2O_2, the TS-1 samples showed an additional, broad, asymmetric signal in the range 300–500 nm (curves c–d). We have
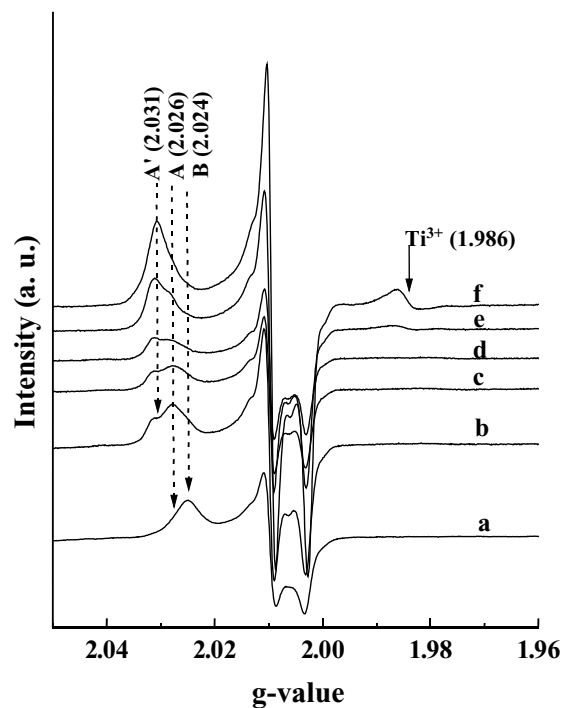

Fig. 1. EPR spectra of superoxo-Ti species in TS-1 + CH_3OH + H_2O_2 system at 90 K. Influence of pH: 6.8 (a), 7 (b), 8 (c), 9 (d), 10 (e), and 11 (f).

deconvoluted this into two bands I (330 nm) and II (395 nm) (Fig. 2, dotted curves) and attributed them to the charge transfer transitions associated with superoxo-Ti ($Ti(O_2^{\bullet-})$) and hydroperoxo/peroxo-Ti ($Ti(OOH)/Ti(O_2^{2-})$) species, respectively [14]. The relative concentration of superoxo-Ti (band I) increases at high pH (Fig. 2) in agreement with the EPR results discussed above. Reducing the pH to 7 regenerates curve b from curve d, ruling out the leaching of Ti from the framework under these conditions. Earlier, Zecchina et al. [20] had attributed similar spectral changes to the formation of η^1-hydroperoxo-Ti in neutral medium and η^2-anionic peroxo-Ti species under basic conditions.

The stability of the oxo-Ti species formed in neutral and basic conditions was determined by recording the DRUV-Vis spectra as a function of time (Fig. 3, panels I and II). As seen from panel I, the intensity of the charge transfer band in the neutral medium was invariant for about 1 h and then decreased with time. This band, under basic conditions (panel II) was, however, stable for about 1.5 h and then decreased with time. Hence, the oxo-Ti species formed under basic conditions are somewhat more stable than the ones formed in acidic/neutral conditions.

Fig. 4 shows the influence of other alkali metal and alkaline ions on the EPR spectra. Li^+ yielded mainly, the A′-type $Ti(O_2^{\bullet-})$ species. Both A′- and A-type species in different proportions were observed in the presence of K^+, Na^+, Cs^+ and NH_4^+ ions; the B-type species was dominant in the presence of Ba^{2+}. The total superoxo-Ti signal intensity was more in the presence of Li^+ than in the presence of NH_4^+, Na^+, K^+, Cs^+ and Ba^{2+}. In addition to
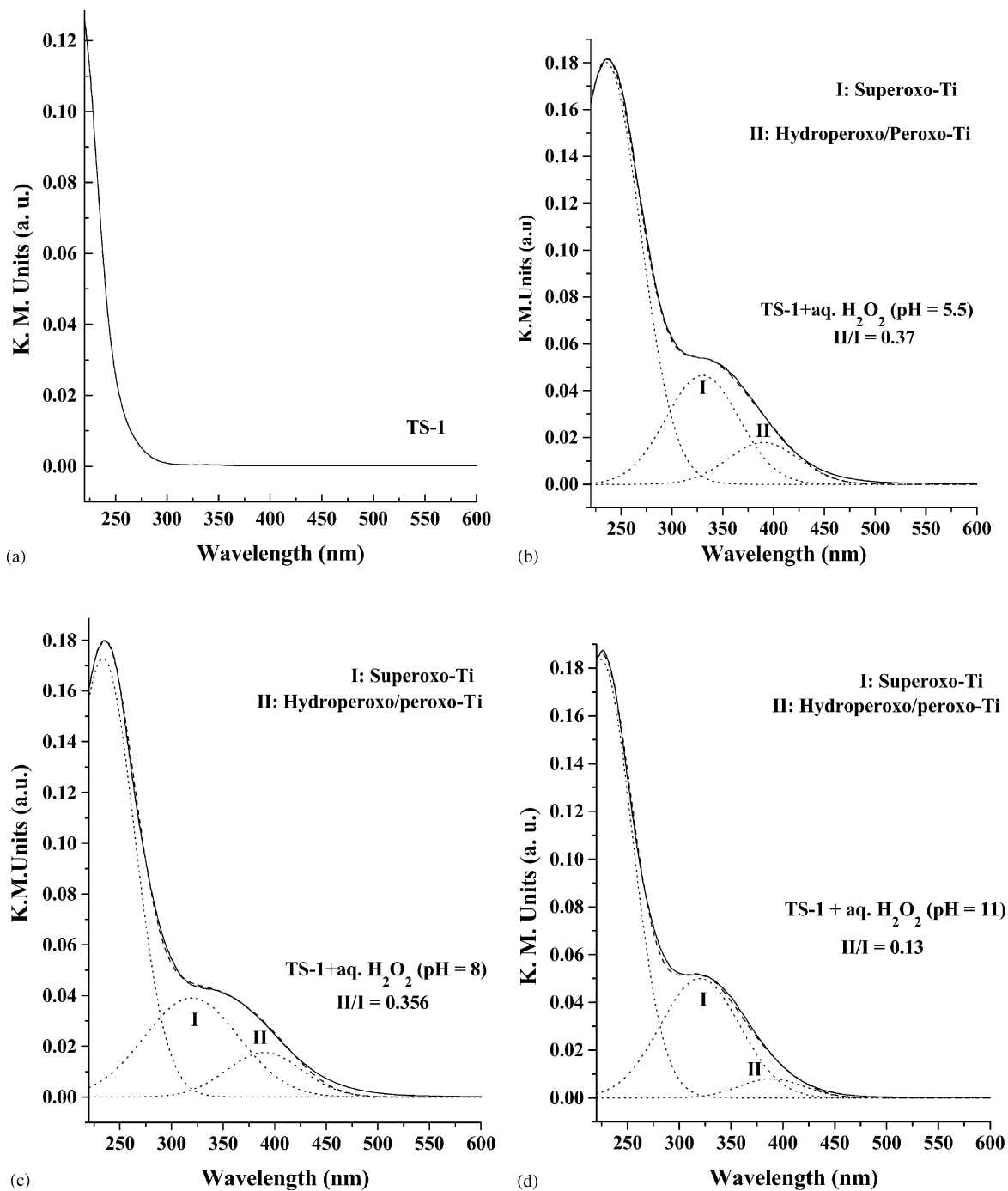
Fig. 2. Diffuse reflectance UV-Vis spectra of TS-1 (a) and TS-1 in CH_3OH reacted with aqueous H_2O_2 at different pH (b)–(d).

$Ti(O_2^{\bullet -})$, signals at 2.078, 2.065 and 2.057, corresponding to the superoxo-species of the alkali metal and alkaline earth ions and Ti^{3+} ions [21], were also observed.

Fig. 5 shows the EPR spectra of TS-1 samples at controlled experimental conditions and reveals the differences in the reactivities of oxo-Ti species A′, A and B. At neutral pH, on contact with allyl alcohol, the A-type species are consumed faster than the B-type (curves a and b). However, at pH 9.5, A′ species are consumed faster than the A-type

species (compare curves c and d). This indicates that the reactivity of the oxo-Ti species increases in the order: B < A < A′.

4.2. Catalytic activity—epoxidation of allyl alcohol, allyl chloride and styrene

Table 1 reports the effect of pH on the catalytic activities of TS-1 and TiMCM-41. Adjustment of pH was done
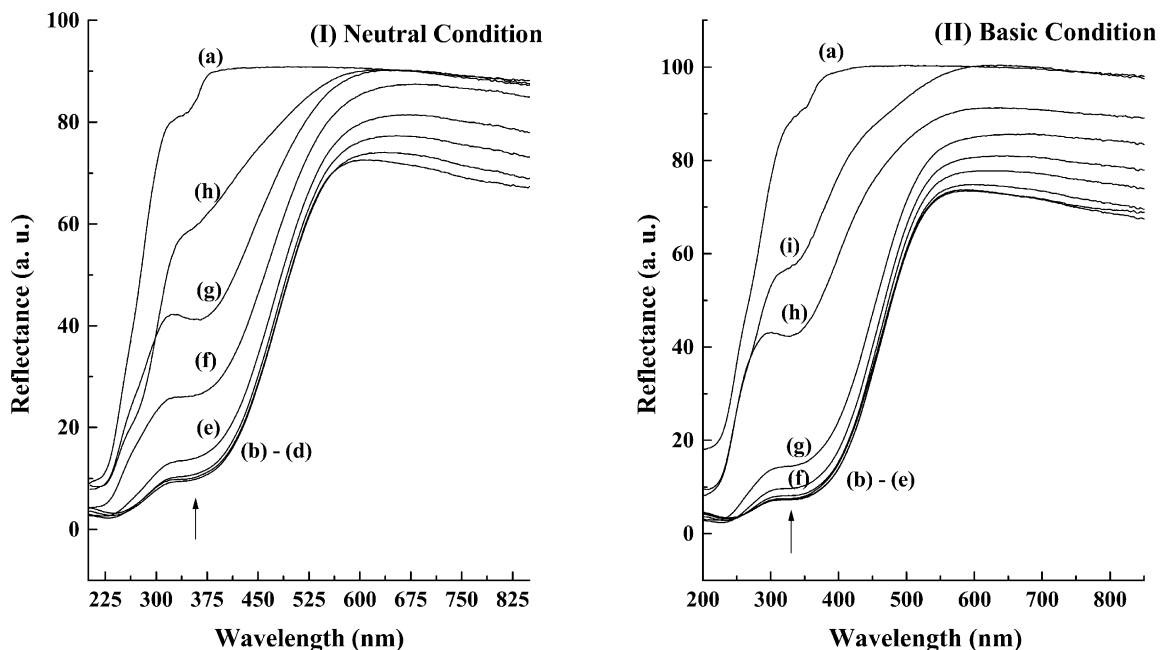
Fig. 3. Stability of oxo-titanium species generated on TS-1 in: (I) neutral condition (pH 6.8) and (II) basic condition (pH 10)—diffuse reflectance UV-Vis spectra: (I) (a) TS-1 + CH_3OH; (b) TS-1 + CH_3OH + H_2O_2, 0 h; (c) TS-1 + CH_3OH + H_2O_2, 0.5 h; (d) TS-1 + CH_3OH + H_2O_2, 1 h; (e) TS-1 + CH_3OH + H_2O_2, 1.5 h; (f) TS-1 + CH_3OH + H_2O_2, 2.5 h; (g) TS-1 + CH_3OH + H_2O_2, 4 h; (h) TS-1 + CH_3OH + H_2O_2, 24 h. (II) (a) TS-1 + CH_3OH + NaOH; (b) TS-1 + CH_3OH + NaOH + H_2O_2, 0 h; (c) TS-1 + CH_3OH + NaOH + H_2O_2, 0.5 h; (d) TS-1 + CH_3OH + NaOH + H_2O_2, 1 h; (e) TS-1 + CH_3OH + NaOH + H_2O_2, 1.5 h; (f) TS-1 + CH_3OH + NaOH + H_2O_2, 2 h; (g) TS-1 + CH_3OH + NaOH + H_2O_2, 2.5 h; (h) TS-1 + CH_3OH + NaOH + H_2O_2, 5.5 h; (i) TS-1 + CH_3OH + NaOH + H_2O_2, 24 h.

before H_2O_2 addition. As the H_2O_2 solutions were acidic, the pH of the reaction mixture decreased from the initially adjusted values after H_2O_2 addition (Table 1). Only a part of the H_2O_2 taken was consumed. The rest remained in the
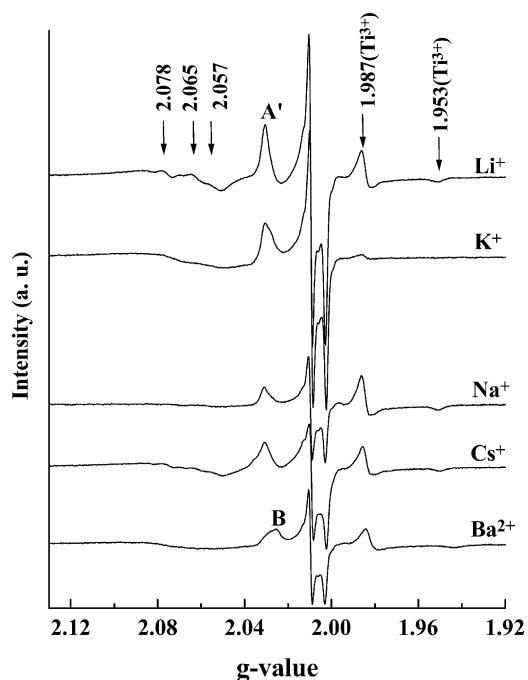

Fig. 4. EPR spectra of TS-1 (modified with alkali metal and alkali earth ions) + CH_3OH + H_2O_2 system (pH = 10.3 ± 0.3).
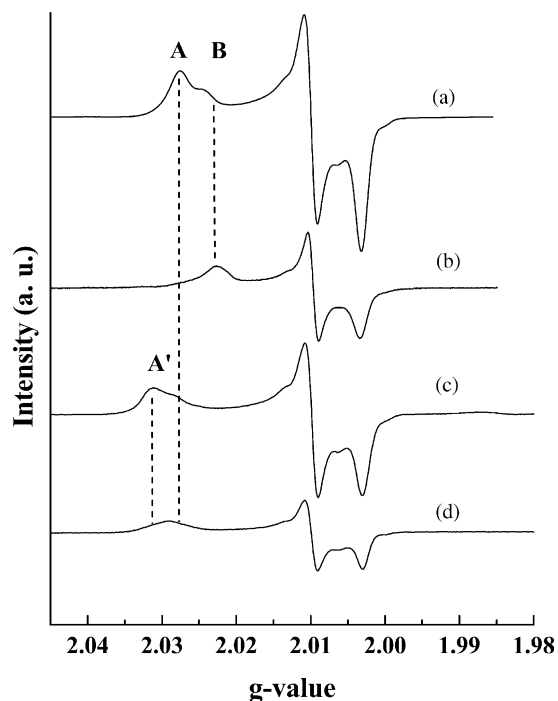

Fig. 5. EPR spectra revealing the reactivity of superoxo-Ti species in TS-1: (a) TS-1 + H_2O_2; (b) TS-1 + H_2O_2 + allyl alcohol; (c) TS-1 + H_2O_2 + CH_3OH + NaOH + H_2O_2 (pH 9); (d) TS-1 + H_2O_2 + CH_3OH + NaOH + H_2O_2 + allyl alcohol (pH 9).

reaction mixture. The pH of the solution at the end of the reaction was lower than the initially adjusted pH due to the presence of the unreacted H_2O_2. The changes in the catalytic activities are correlated with the initial, adjusted pH values. It may be noted that the point of departure to enhanced chemoselectivity is the actual pH after H_2O_2 addition, but not the initially adjusted values.

With an increase in pH, conversion of allyl alcohol in methanol decreased from 95.3% (at pH 3.5) to 22.2 mol% (at pH 8.5) (Run 3–8). However, the epoxide (glycidol) selectivity increased from 86.8 to 100 mol%. The amount of H_2O_2 present in the medium before and after the reaction, was estimated (by iodometric titration) and the H_2O_2 efficiency for epoxide formation was determined from the amount of H_2O_2 consumed. The H_2O_2 efficiency decreased markedly at high pH conditions. Most of the H_2O_2, probably decomposed into H_2O and O_2 at high pH.

To probe the location of the alkali ions, added during the reaction, the used catalyst samples after Runs 5 and 6 were recovered by centrifugation, combined, air-dried and then reused *without adding any additional alkali* (Run 9). The epoxide selectivity (96.8%), intermediate between Runs 5 and 6 (92.8 and 100%, respectively) indicates that, the Na^+ added during Runs 3 and 4 are still located on the surface and were not leached out from the solid catalyst into the medium during the reaction.

Next, we impregnated fresh samples of TS-1 with small amounts of alkali. TS-1-Na(8) and TS-1-Na(10) were thus prepared (initial pH 8 and 10, respectively, as described in Section 2). Catalytic runs with these catalysts (with no further alkali addition) exhibited activities similar to the TS-1 catalysts wherein the alkali was added in situ (compare Runs 10 and 11 with 6 and 7, respectively).

Table 2
Effect of alkali and alkaline ions on the epoxidation of allyl alcohol[a]

Run number	Alkali/alkaline earth ions	TOF[b]	Conversion (mol%)	Epoxide selectivity (mol%)
1	Li^+	2.4	11.9	100
2	NH_4^+	9.7	48.6	100
2	Na^+	17.0	85.8	91.7
3	K^+	18.7	94.4	79.1
4	Cs^+	19.8	100	76.7
5	Mg^{2+}	12.5	63.0	100
6	Ca^{2+}	18.8	94.7	88.5
7	Ba^{2+}	18.6	94.1	75.0

[a] Reaction conditions: catalyst (100 mg) + allyl alcohol (0.5 g) + CH_3OH (10 g) + H_2O_2 (50%, 0.9 ml); H_2O_2/allyl alcohol = 2.0; temperature = 333 K; run time = 8 h; pH 8.0.

[b] Moles of allyl alcohol converted per mole of Ti per hour.

TiMCM-41 exhibited lower activity compared to TS-1. Changes in pH did not affect conversions significantly (Runs 12 and 13). It may be recalled that TiMCM-41 generated only the B-type of superoxo-Ti species, which are less active than the A- and A′-type species generated on TS-1 catalysts.

The epoxidation of allyl alcohol was carried out at pH 8 in the presence of different alkali metal and alkaline earth compounds (Li_2CO_3, NaOH, KOH, CsOH, MgO, CaO and $Ba(OH)_2$) and NH_4OH (Table 2). Catalytic activity increased in the order: $Li^+ < NH_4^+ < Na^+ < K^+ < Cs^+$ and $Mg^2 < Ca^{2+} < Ba^{2+}$. Epoxide selectivity followed a reverse order; Cs^+ exhibited 100% allyl alcohol conversion, but with lower epoxide selectivity, only 76.7% (Table 2, Run 4).

The epoxidation of styrene was less selective over TS-1 catalysts compared to the epoxidation of allylic compounds. Significant amounts of methylated diols were obtained (Table 3). About 15% of benzaldehyde was also observed.

Table 3
Epoxidation of styrene over TS-1: influence of pH[a]

Run number	pH Initial (before H_2O_2 addition)	At the end of the reaction	Conversion (mol%)	Styrene oxide	Methylated diol	Diol	Benzaldehyde	Phenyl acetaldehyde	Others
Solvent: CH_3OH									
1	6.8	4.0	39.9	35.9	46.0	1.1	13.8	0.3	2.9
2	7.0	4.0	42.3	35.0	45.5	0.8	15.1	0.5	3.1
3	8.0	4.0	35.2	40.9	40.7	1.1	15.5	0.3	1.5
4	9.0	4.5	27.3	45.0	37.4	0.8	16.8	0.0	0.0
5	11.0	5.5	4.4	66.6	5.9	0.0	18.3	9.2	0.0
Solvent: $CH_3OH + CH_3CN$ (1:1)									
6	7.0	4.0	26.3	29.4	21.8	3.1	35.0	9.2	1.5
7	8.0	4.0	26.1	28.5	20.6	2.3	36.0	11.8	0.8
8	9.0	4.0	28.4	31.8	19.1	2.9	34.7	10.0	1.5
9	10.0	4.5	27.6	32.1	14.1	2.3	40.0	11.2	0.3
Solvent: CH_3CN									
10	6.4	4.0	25.2	20.2	1.0	3.9	65.3	9.1	0.5
Solvent: CH_3COCH_3									
11	6.0	3.5	25.4	61.4	0.7	2.6	31.9	3.4	0.0

[a] Reaction conditions: TS-1 (100 mg) + styrene (0.898 g) + solvent (10 g) + H_2O_2 (50%; 0.9 ml); H_2O_2/styrene = 2; temperature = 333 K; run time = 8 h.
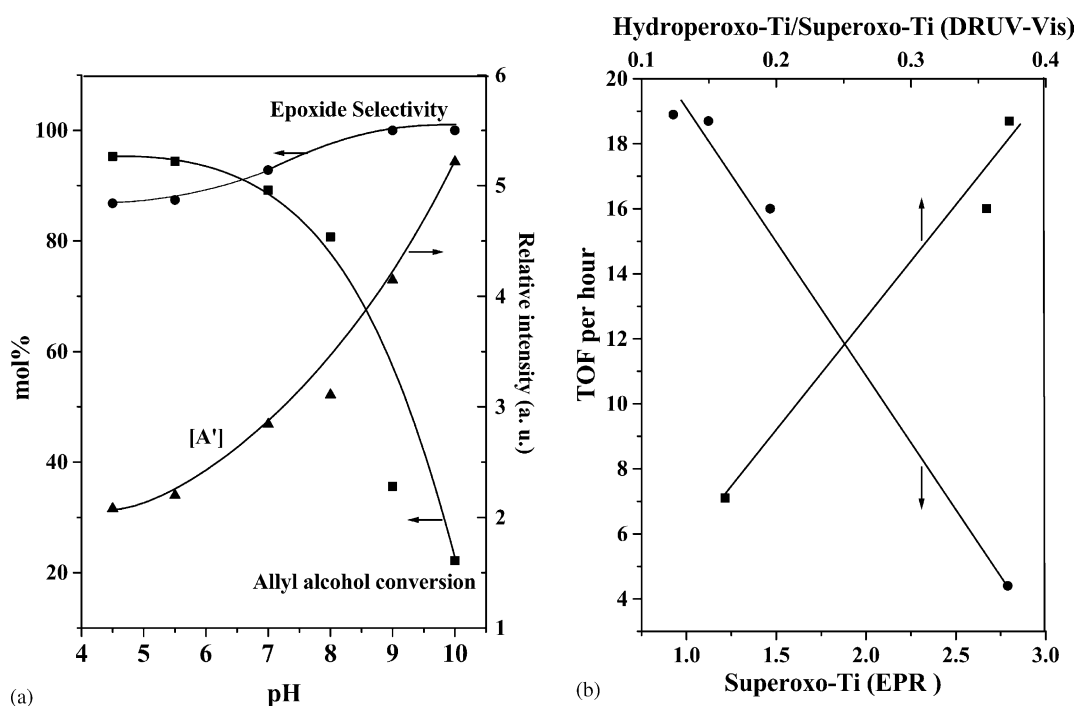
Fig. 6. (a) Variation of allyl alcohol conversion, epoxide selectivity and relative A′ signal intensity as a function of pH; (b) variation of catalytic activity (TOF per hour) as a function of supero-Ti (total EPR signal intensity) and hydroperoxo-Ti/superoxo-Ti (from DRUV-Vis).

Conversion of styrene decreased and styrene oxide selectivity increased marginally at high initial pH values. The solvent has a significant influence on the reactivity (conversion) and product selectivity. In CH_3OH+CH_3CN (1:1 v/v), CH_3CN or CH_3COCH_3, methylated diol was suppressed but benzaldehyde formed in significant amounts.

A comparison of the spectroscopic results with the catalytic activity data reveals that while specific activity in allyl alcohol conversion (turnover frequency per hour) decreases with increasing *paramagnetic*, *superoxo-Ti species* (Fig. 6a and b), it increases linearly with the *hydroperoxo/peroxo content* (estimated from DRUV-Vis spectra) (Fig. 6b). The present study, in agreement with our earlier results [13–15] and that of others [1,2], suggests that the diamagnetic hydroperoxo/peroxo-Ti species are, probably, responsible for the selective epoxidation activity. Selectivity for the epoxide increased with the relative A′ signal intensity (estimated from EPR spectra) (Fig. 6a). Similar correlations between total EPR signal intensity (superoxo-Ti concentration) vs. allyl alcohol conversion and relative A′ signal intensity vs. epoxide selectivity were also observed when the alkali metal ion was changed from Cs^+ to K^+, Na^+ and Li^+ (Fig. 7). A′ species were generated also when TS-1 was impregnated with Pd^{2+} ions and exposed to $(H_2 + O_2)$ [14] or when urea–H_2O_2 adduct was used in the place of aqueous H_2O_2 [15].

Over TS-1, the only primary product is the epoxide. In methanol the epoxide may be opened by the solvent forming a monomethylglycol. This ring opening is possibly favored and catalyzed by the acidic sites of TS-1. The added bases neutralize (deactivate) the acid site of TS-1 and thereby,

enhance the chemoselectivity. When the unmodified TS-1 catalyst was reused (see Run 2, Table 1), we observed an improved epoxide selectivity (from 88.5 to 93 mol%), but the product was not exclusively epoxide as was observed in
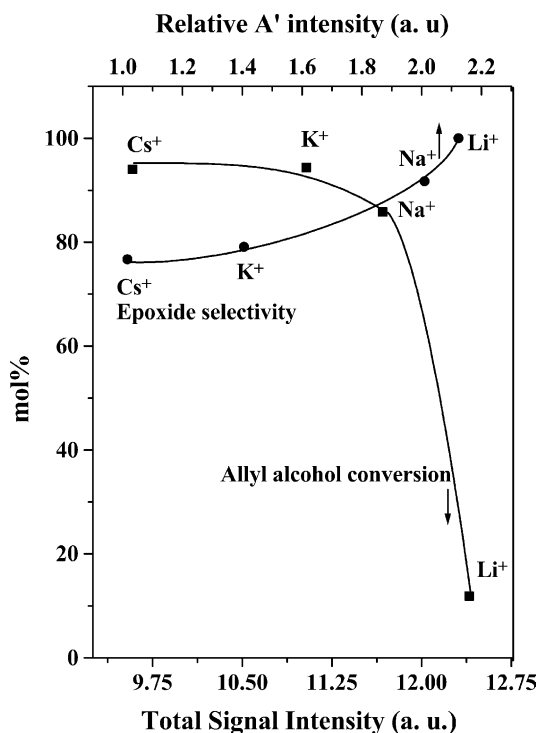

Fig. 7. Variations of allyl alcohol conversion with the total EPR signal intensity and epoxide selectivity with the relative A′ signal intensity.

the case of Na$^+$-modified TS-1 catalyst (initial pH 8, Run 6). It is likely, that the strong Brönsted acid sites that were present in the unmodified TS-1 catalyst are deactivated in the first run or by alkali ion modification. It appears that the deactivation of acid sites as well as the modified Ti sites are responsible for the enhanced chemoselectivity in epoxidation reactions.

5. Conclusions

Reactive oxo-Ti species in TS-1 and TiMCM-41, generated by interactions with H_2O_2 at different pH values were investigated by EPR and DRUV-Vis spectroscopies. Alkali addition enhanced epoxide selectivity. A new type of superoxo-Ti species, A$'$ and Ti^{3+} ions were detected under basic conditions by EPR spectroscopy. Epoxide conversion (turnover frequency per hour) decreased with increasing *paramagnetic, superoxo-Ti species*, it increased linearly with the *hydroperoxo/peroxo content* (estimated from DRUV-Vis spectra). Neutralization of acid sites on TS-1 by alkali addition and formation of modified Ti sites are the possible reasons for the enhanced selectivity.

References

[1] B. Notari, Adv. Catal. 41 (1996) 253, and the references therein.

[2] G.N. Vayssilov, Catal. Rev. Sci. Eng. 39 (1997) 209, and the references therein.

[3] M.G. Clerici, in: R.A. Sheldon, H. Van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley/VCH, Weinheim, 2001, p. 538.

[4] C.B. Khouw, C.B. Dartt, J.A. Labinger, M.E. Davis, J. Catal. 149 (1994) 195.

[5] C.B. Khouw, M.E. Davis, J. Catal. 151 (1995) 77.

[6] G. Bellussi, V. Fattore, Stud. Surf. Sci. Catal. 69 (1991) 79.

[7] M.G. Clerici, Appl. Catal. 68 (1991) 249.

[8] M.G. Clerici, G. Bellussi, U. Romano, J. Catal. 129 (1991) 159.

[9] G. Bellussi, A. Carati, M.G. Clerici, G. Maddinelli, R. Millini, J. Catal. 133 (1992) 220.

[10] M.G. Clerici, P. Ingallina, J. Catal. 140 (1993) 71.

[11] M.C. Capel-Sanchez, J.M. Campos-Martin, J.L.G. Fierro, Appl. Catal. A 246 (2003) 69.

[12] T. Armaroli, F. Milella, B. Notari, R.J. Willey, G. Busca, Top. Catal. 15 (2001) 63.

[13] K. Chaudhari, D. Srinivas, P. Ratnasamy, J. Catal. 203 (2001) 25.

[14] V.N. Shetti, P. Manikandan, D. Srinivas, P. Ratnasamy, J. Catal. 216 (2003) 461.

[15] D. Srinivas, P. Manikandan, S.C. Laha, R. Kumar, P. Ratnasamy, J. Catal. 217 (2003) 160.

[16] D. Gleeson, G. Sankar, R.A. Catlow, J.M. Thomas, G. Spano, S. Bordiga, A. Zecchina, C. Lamberti, Phys. Chem. Chem. Phys. 2 (2000) 4812.

[17] Q. Zhao, X.-H. Bao, Y. Wang, L.-W. Lin, G. Li, X.-W. Guo, X.-S. Wang, J. Mol. Catal. A 157 (2000) 265.

[18] L. Bonoldi, C. Busetto, A. Congiu, G. Marra, G. Ranghino, M. Salvalaggio, G. Spanó, E. Giamello, Spectrochim. Acta A 58 (2002) 1143.

[19] F. Geobaldo, S. Bordiga, A. Zecchina, E. Giamello, G. Leofanti, G. Petrini, Catal. Lett. 16 (1992) 109.

[20] A. Zecchina, S. Bordiga, C. Lamberti, G. Ricchiardi, D. Scarano, G. Petrini, G. Leofanti, M. Mantegazza, Catal. Today 32 (1996) 97.

[21] A. Tuel, Y. Ben Taârit, Appl. Catal. A 110 (1994) 137.