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Enhanced catalytic activity of titanosilicates controlled by hydrogen-bonding interactions[†]

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A typical volcano-shaped curve has been found in heterogeneous catalytic systems containing titanosilicates for the first time. A new reactive intermediate with double H-bonds is proposed. Systematic results clearly evidence another H-bond formed between the high-electronegativity atom of the H-bond acceptor and the H_{end} atom of Ti–O_x–O_g–H_{end}.

Titanium-containing silicates (such as TS-1, Ti-MWW), increasingly recognized as heterogeneous catalysts, have widely exhibited excellent catalytic properties in selective oxidation reactions using H_2O_2 as a mild oxidant.¹⁻⁴ Great efforts have been devoted to investigate the active sites and reactive intermediates of epoxidation over titanosilicates.⁵⁻⁹ It is fairly well accepted that the Ti– O_{α} – O_{β} – H_{end} species (I) (Scheme 1) which is generated by the interaction of the Ti(rv) framework, H_2O_2 and the solvent during catalytic reactions is the reactive intermediate.^{10–14} In the case of epoxidation, the C==C double bond in alkenes is expected to interact with more electrophilic O_{α} as the active oxygen-donating species.¹⁴ Moreover, the stability of the intermediate answers why titanosilicates are active catalysts in epoxidation with H_2O_2 .¹⁵

It is well-known that the stability of the intermediate $Ti-O_{\alpha}-O_{\beta}-H_{end}$ species is operated through hydrogen-bonding interactions with



Scheme 1 Structural scheme of the proposed intermediate Ti species. (I) Conventional system and (II) hydrogen-bond acceptor-introduced system. ROH included H₂O and alcohol.

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† Electronic supplementary information (ESI) available: Synthesis, characterization methods and supplementary figures. See DOI: 10.1039/c3cc43372b the solvent, silanol, or other agents.^{9,10,14,16–19} The O_β atom of Ti–O_α–O_β–H_{end} is usually recognized as the hydrogen bond acceptor to bond with the extra H atom of the solvent or terminal silanol groups to further stabilize reactive intermediates (Scheme 1(I)).^{10,17–19} The H_{end} atom of Ti–O_α–O_β–H_{end} intermediates was reported as the hydrogen bond donor to bond with the oxygen of the adjacent Si–OH moiety by cleavage of the Ti–O–Si linkage as well.¹⁴ Thus, based on the Ti–O_α–O_β–H_{end} species (I), if another hydrogen bond is further constructed between the H_{end} atom and the extra introduced acceptor (*e.g.* NH₃), a new reactive intermediate (II) (Scheme 1) will be formed. This intermediate shows more suitable stability which is beneficial to its catalytic activity. However, little is known about its applications to enhance the catalytic ability over titanosilicate/H₂O₂ catalytic systems. Does the hydrogen bond really exist in the reactive intermediates?

In this communication, to demonstrate the hydrogen-bonding interactions, we examined the catalytic activity of the extra introduced hydrogen bond acceptor (*e.g.* NH_3) over TS-1 (Si/Ti = 61) using 1-hexene epoxidation with H_2O_2 as a representative probe reaction (Fig. 1).

Fig. 1 shows a typical volcano-shaped curve for the conversion of 1-hexene and H2O2 with an increasing amount of NH3, and the relatively highest increase is almost 50%. To our knowledge this is the first report on catalytic oxidation systems containing titanosilicates. As we know that one of the most fundamental concepts in heterogeneous catalysis is the volcano curve, wherein an important problem in connection with volcano curves is which fundamental parameters the catalytic activity depends on.^{20,21} In this case, the amount of NH3 was found to be the fundamental parameter, suggesting an interaction between NH₃ and the catalyst. Certainly, the selectivity of 1,2-epoxyhexane increased to about 100% with an increasing amount of NH3 and too much NH3 caused the decline of the activity on the right side of the curves, just like the reports found in the literature.²²⁻²⁴ This is because NH3 as an alkali could neutralize the weak acidity of TS-1 further to deter the ring-opening reaction for high epoxide selectivity, while it also restrained the activity of the catalyst due to poisoning some active sites.²²⁻²⁴ Thus, we conjectured that NH3 with a lone electron pair of N atoms could bind slightly stronger with titanosilicate in the coordination



Fig. 1 Effect of ammonia on the catalytic performance of TS-1. Reaction conditions: cat. TS-1 (Si/Ti = 61) 0.05 g; CH₃OH 10 mL; 1-hexene 10 mmol, H₂O₂ 10 mmol; ammonia; time 2 h; temp. 333 K. (a) Convention (1-hexene), (b) convention (H₂O₂), (c) utilization (H₂O₂) and (d) selectivity (epoxide).

complex *via* hydrogen bonding rather than coordination mechanisms according to estimated adsorption energies.¹⁶ So NH₃ was supposed to act as the hydrogen bond acceptor to bond with the H_{end} atom of the Ti– O_{α} – O_{β} –H_{end} intermediate (I) further to form a new Ti– O_{α} – O_{β} –H_{end} intermediate (II) as expected.

The characteristics of hydrogen-bonding interactions are their specificity and saturability. It is surprising that the conversion of 1-hexene and H_2O_2 linearly increased on the left side of the curves, similar to the results due to the cation– π interactions reported previously.²⁵ The convention increased to the highest level when the molar ratio of NH₃ to the active Ti(rv) sites of the TS-1 catalyst (MAT) was close to 1 in the reaction system. This showed that a lower amount of NH₃ mainly interacted with the intermediate. So to a larger extent that is in good agreement with the saturability of the hydrogen-bonding interaction.

To test this possibility of the hydrogen-bonding interactions, we further carried out 1-hexene epoxidation over TS-1 zeolite with different amounts of Ti (Si/Ti molar ratios of 138, 105, 61) (Fig. S1, ESI[†]). As expected, the catalytic activity of all TS-1 with different Si/Ti molar ratios also showed volcano curves (Fig. S2, ESI[†]). Moreover, the conversion of 1-hexene increased to the highest level with the MAT of 1. It means that NH₃ really played the role of the hydrogen bond acceptor.

The high-electronegativity atoms (such as N, O, F) containing lone electron pairs usually act as hydrogen bond acceptors. Different ammonium salts with functional groups containing oxygen (e.g., CO₃²⁻, SO₄²⁻, CH₃COO⁻) as hydrogen bond acceptors were also investigated in 1-hexene epoxidation over TS-1 (Table 1). As good as NH₃, the acceptors could enhance the activity of TS-1 to various degrees with the MAT of 1, while they had no obvious influence on the utilization of H2O2 (Table 1, no. 2-4). Ammonium salts in solution existed in ionic states, a small amount of molecular NH₃ could form from the hydrolyzed NH₄⁺, which may be enough to neutralize the weak acidity of TS-1 but not enough to decompose H₂O₂ like NH₃ as an acceptor (Table 1, no. 1). The effect of NH₄Cl or NH₄F with no free high-electronegativity atom as the acceptor (Table 1, no. 5, 6) on TS-1 proved this point. The activity could be enhanced, although 1-hexene conversion only reached 36.9%, lower than that with NH₃ and other acceptors, which may be due to that the amount of NH3 formed in this system was not enough. In addition, organic CH₃CH₂CH₂NH₂ could also provide a

 Table 1
 Catalytic properties of TS-1 in epoxidation of 1-hexene with H₂O₂^a

No.	H-bond	Convention/%		Selectitvity/%	Utilization/%
	acceptor	1-Hexene	H_2O_2	1,2-Epoxyhexane	H_2O_2
1	NH ₃ ·H ₂ O	46.6	58.0	98.4	80.4
2	$(NH_4)_2CO_3$	46.4	51.8	100	89.3
3	$(NH_4)_2SO_4$	45.4	53.2	98.4	85.4
4	CH ₃ COONH ₄	45.7	56.2	98.6	81.3
5	NH ₄ Cl	36.9	44.5	95.0	82.8
6	NH ₄ F	35.5	42.7	100	83.1
7	(CH ₃ CH ₂) ₂ NH	36.0	41.7	100	86.4
8	CH ₃ CH ₂ CH ₂ NH ₂	42.1	50.2	100	83.9
9		30.5	35.5	89.2	85.9

lone electron pair to form species II. However, 1-hexene conversion only increased to 36.0% when $(CH_3CH_2)_2NH$ was used as the acceptor (Table 1, no. 7, 8). This was due to the electronegativity of the N atom in $(CH_3CH_2)_2NH$, with the electrophilic ethyl group being weaker than that of NH₃.

Solvent effects are a very important factor to investigate the mechanism of alkene oxidation.13,18,24,26 Besides the role of solvents in homogenizing the liquid phase, it is widely accepted that the fivemembered ring was formed by coordination of ROH with Ti(IV) and the hydrogen bond to the Ti-peroxo complex (I) (Scheme 1).¹³ These results showed that the conversion of 1-hexene and H2O2 in alcohol solvent decreased in the order of MeOH > IPA > t-BuOH (Table 2, no. 1, 3, 5), in accord with previous reports.¹³ When an appropriate amount of NH3 as expected to act as an acceptor was introduced, 1-hexene and H₂O₂ conversion increased evidently to a certain extent (Table 2, no. 2, 4, 6). The relative increase of 1-hexene conversion decreased from 52.8% to 30.9%. The relative magnitude of increase was in the order of MeOH > IPA > t-BuOH, too. The observations indicated that NH3 surely acted as the hydrogen bond acceptor to bond with the Hend atom of the Ti-Oa-OB-Hend intermediate (I) further to form a new $Ti-O_{\alpha}-O_{\beta}-H_{end}$ intermediate (II), and the intermediate (II) is more stable and suitable to contribute its catalytic activity.

The above results clearly demonstrated that a new hydrogen bond was constructed between the high electronegativity atom of the acceptor and the H_{end} atom of $Ti-O_{\alpha}-O_{\beta}-H_{end}$, and the stability of the new reactive intermediate (II) seems to depend on the type of hydrogen bond acceptor, and to decide the influence of the catalytic activity.

In order to confirm the new intermediate (II) formed in the catalytic system, many hydrocarbon epoxidation reactions on

 $\label{eq:Table 2} \mbox{ Catalytic properties of TS-1 in epoxidation of 1-hexene with H_2O_2 in different solvents^a$}$

			Convention/%		Selectivity/06	Utilization/%
					Selectivity/70	Othization/ 70
No.	Solvent	MAT	1-Hexene	H_2O_2	1,2-Epoxyhexane	H_2O_2
1	CH ₃ OH	0	30.5	35.5	89.2	85.9
2		1	46.6	58.0	98.4	80.4
3	IPA	0	19.7	31.2	90.7	63.1
4		1	29.2	47.2	100	61.9
5	t-BuOH	0	16.2	18.4	95.7	88.0
6		1	21.2	31.2	100	68.0

^a Reaction conditions: solvent 10 mL; for others see Fig. 1.

Table 3 Catalytic properties of different substrates with H₂O₂ on TS-1^a

			Convention/%		Selecitivity/%	Utilization/%	
No.	Substrate	MAT	Alkene	H_2O_2	Oxide	H_2O_2	
1	Allyl chloride	0	93.0	99.0	92.7	93.9	
2		1	93.8	99.8	95.4	94.0	
3	1-Octene	0	24.3	30.2	71.4	80.5	
4		1	31.0	39.5	94.6	78.5	
5	1-Heptene	0	31.7	32.2	84.6	98.4	
6		1	44.0	45.5	95.7	96.7	
7	Cyclopentene	0	65.0	_	8.74	_	
8	•	1	86.4	_	90.3	_	
^{<i>a</i>} Reaction conditions: substrate 10 mmol, for others see Fig. 1.							

TS-1 are studied in Table 3. The desired results showed that not only the selectivity of the epoxide product increased but also the obvious enhancement in conversion of alkene was obtained in favor of the hydrogen-bond interactions.

Based on the specific effect of hydrogen bond acceptors on catalytic oxidation over TS-1, they can also be applied on Ti-MWW. Table S1 (ESI⁺) displays the effect of appropriate amount of NH3 on the catalytic activity of Ti-MWW. The conversion of 1-hexene and H₂O₂ in the NH₃-introduced system is higher than that without NH3. Acetonitrile was accepted as a suitable solvent for Ti-MWW in epoxidation of 1-hexene due to the five-membered ring of the hydrogen bonded intermediate with H₂O in acetonitrile which is more intrinsically active than the species with ROH in methanol,²⁴ and the catalytic activity in acetonitrile is much higher than in methanol (Table S1, no. 1, 2, ESI[†]). In fact, the N atom of acetonitrile could interact with the H atom of Ti-OH or Si-OH which acts as the acid site of zeolite,^{13,24} so acetonitrile also can act as the hydrogen bond acceptor. However, compared with NH₃, the formed reactive intermediates had lower stability, which resulted in higher activity when NH₃ was introduced (Table S1, no. 4, ESI⁺). It is worth mentioning that the activity of Ti-MWW was extremely higher than that without NH₃ when methanol was used as the solvent (Table S1, no. 1, 3, ESI⁺). These showed the same function of NH₃ obtained from TS-1. It implied that the new intermediate (II) with double hydrogen bonds surely formed in this catalytic system, where the extra H atom of methanol (or H₂O) acted as the hydrogen bond donor to bond with the O_{β} atom of Ti- O_{α} - O_{β} - H_{end} and the N atom of NH₃ acted as the hydrogen bond acceptor to bond with the H_{end} atom of Ti- O_{α} - O_{β} - H_{end} .

The apparent activation energy of $\text{Ti}-O_{\alpha}-O_{\beta}-H_{end}$ formed over TS-1 was studied to explain the catalytic phenomenon.^{17,27-29} The apparent activation energy of the system with an appropriate amount of introduced NH₃ is about 19.9 kJ mol⁻¹, much lower than that without NH₃ introduced (31.9 kJ mol⁻¹) (Fig. S3, ESI[†]). This explained that it was easier to form the new reactive intermediate (II) with the help of another hydrogen bond formed between Ti-O_{α}-O_{β}-H_{end} and the acceptor (*e.g.* NH₃) when the hydrogen bond acceptor (*e.g.* NH₃) was introduced into the titanosilicate catalytic oxidation system. That is the intrinsic reason for obvious catalytic epoxidation enhancement of titanosilicates. In summary, we conclude that a new intermediate (II) with double hydrogen bonds is formed in a catalytic oxidation system over titanosilicates by introducing a hydrogen bond acceptor. The catalytic activity of titanosilicates is enhanced significantly as a resulting of the new intermediate with suitable stability due to the new hydrogen bond formed. This study demonstrates that utilization of hydrogen bond interactions provides a method for achieving high catalytic efficiency in catalytic oxidation reactions over titanosilicates. We expect that the insight obtained in this study can be further extended to make clear the solvent effects in titanosilicate catalytic oxidation systems which have not been understood completely to date.^{10,13,24}

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