

Electronic Supplementary Information

Enhanced Catalytic Activity on Titanosilicates Controlled by Hydrogen-Bonding Interactions

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Experimental

1. Material Synthesis

Synthesis of TS-1

A typical synthesis of TS-1 (named TS-1(Si/Ti)) in conventional method (M. Taramasso, G. Perego, B. Notari, US Patent 1983, 4 4105 01.) is as follows:

A mixture of TEOS and TBOT was added dropwise into TPAOH solution under stirring at room temperature. After hydrolyzing at 323 K for 30 min and removing alcohols by evaporation at 353 K, a clear sol was obtained having the following molar composition: 1.0SiO_2 : $(0.0167, 0.01, 0.0067)\text{TiO}_2$: 0.18TPAOH : $18\text{H}_2\text{O}$. Then it was transferred into a Teflon-lined stainless-steel autoclave and crystallized at 443 K for 2 days. After that, the product was recovered by filtration, washed with distilled water, dried at 363 K overnight, and finally calcined at 823 K for 6 h. The real Si/Ti ratio of TS-1 tested by ICP was 61, 105, 138, respectively.

Synthesis of Ti-MWW

Ti-MWW was prepared by treating hydrothermally synthesized lamellar precursors with a 2 M HNO_3 solution following previous procedures (P. Wu, T.

Tatsumi, T. Komatsu and T. Yashima, *J. Phys. Chem. B*, 2001, 105, 2897.). And the final Si/Ti ratio was 42.

2. Catalytic Reactions

The epoxidation of alkene without acceptor

The epoxidation of alkene with H₂O₂ was carried out in a 50 mL round-bottomed flask equipped with a reflux condenser. It was mixed with 50 mg of catalyst, 10 mL of solvent (methanol), 10 mmol of alkene and 10 mmol H₂O₂ (30 wt% aqueous solution) under vigorous stirring at 333 K for 2 h. The product of the reaction was analyzed on an Agilent GC-7890A gas chromatograph equipped with a D-WAX capillary column (30 m×0.25 mm) and an FID detector using cyclohexanone as an internal standard. The amount of residual H₂O₂ was determined by titration with 0.05 M Ce(SO₄)₂ solution.

The epoxidation of alkene with introduced acceptor

The epoxidation of alkene with H₂O₂ was carried out in a 50 mL round-bottomed flask equipped with a reflux condenser. It was mixed with 50 mg of catalyst, 10 mL of solvent (methanol), 10 mmol of alkene, 10 mmol H₂O₂ (30 wt% aqueous solution) and moderate ammonia or other hydrogen bond acceptors(0.4 mol/L aqueous solution) under vigorous stirring at 333 K for 2 h. The product of the reaction was analyzed as same as above.

The decomposition of H₂O₂

The reaction in fixed-bed reactor: 0.5 g TS-1 was added into a columniform PTFE reactor (L=100 mm, d=4.4 mm), then the two ends of reactor was filled with quartz

fiber. The reaction temperature was controlled by a thermostatic circulating water bath. The mixed solutions of CH₃OH/H₂O₂/H₂O with different flow rates were fed to the reactor with a peristaltic pump (SURPASS 102S/R-20). The content of unreacted H₂O₂ liquid was determined by titration with 0.05 M Ce(SO₄)₂ solution. Then, the activation energy was calculated using Arrhenius equation ($k=A\exp(-E_a/RT)$).

3. Characterization Methods

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV diffractometer using CuK α radiation and a nickel filter in the 2 θ angle range of 5° to 35° at 35 kV and 25 mA. UV-Vis spectra were recorded on a Shimadzu UV-2400PC spectrophotometer using BaSO₄ plate as a reference. Inductively coupled plasma (ICP) atomic emission spectroscopy was performed on a Thermo IRIS Intrepid II XSP atomic emission spectrometer.

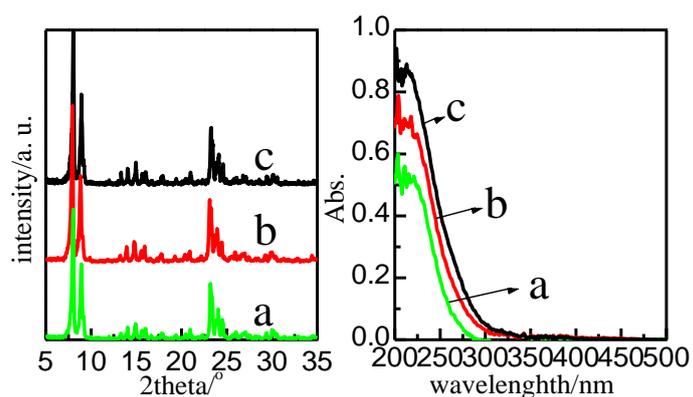


Fig. S1 XRD patterns and UV-Vis spectrum of TS-1 samples. (a) TS-1(138), (b) TS-1(105), (c) TS-1(61)

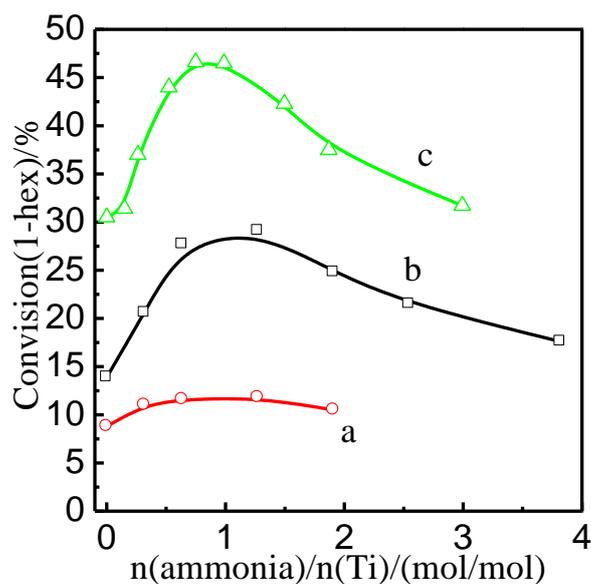


Fig. S2 Effect of ammonia on the catalytic performance of TS-1. (a) TS-1(138), (b) TS-1(105), (c) TS-1(61)

Reaction conditions: cat., 0.05 g; CH₃OH, 10 mL; 1-hexene 10 mmol; H₂O₂, 10 mmol; ammonia; time 2 hours; temp., 333 K.

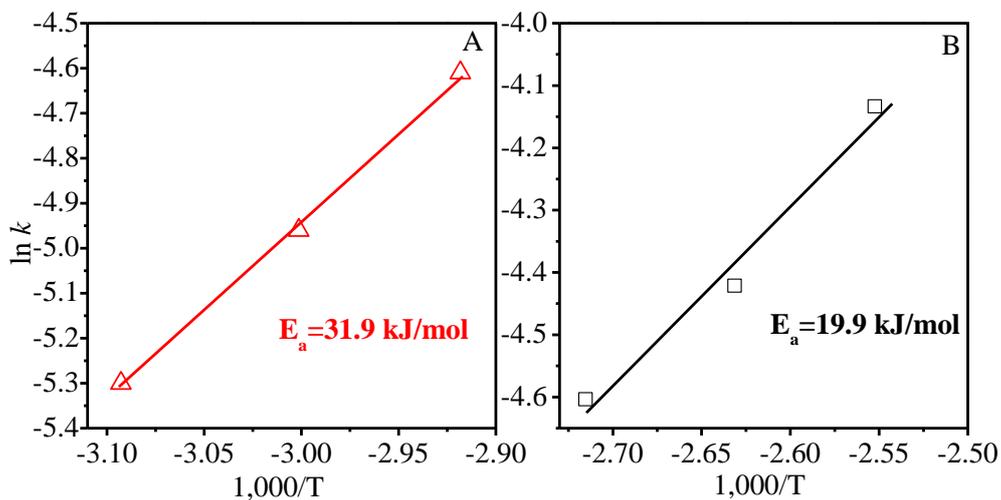


Fig. S3 The activation energy (E_a) of formed hydroperoxy intermediate $Ti-O_\alpha-O_\beta-H_{end}$ (A) the system without ammonia introduced (B) the system with ammonia introduced. $c(\text{ammonia})=0.08\%$. Reaction condition: E_a was tested in a fixed-bed reactor. $c(H_2O_2)=2.2\%$, $WHSV=5.13\text{ h}^{-1}$, $TOS=1\text{ min}$.

Table S1 Catalytic properties of Ti-MWW in epoxidation of 1-hexene with H₂O₂.

No.	solvent	MAT	Convention/%		Selevitivity/%	Utilization/%
			1-hexene	H ₂ O ₂	1, 2-epoxyhexane	H ₂ O ₂
1	CH ₃ OH	0	12.4	12.7	82.8	97.8
2	CH ₃ CN	0	45.2	47.8	100	94.6
3	CH ₃ OH	1	34.2	41.4	100	82.8
4	CH ₃ CN	1	59.3	70.0	100	84.7

Reaction conditions: cat. Ti-MWW 0.05 g; solvent 10 mL; 1-hexene 10 mmol; H₂O₂ 10 mmol; ammonia; time 2 h; temp. 333 K.