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 Parent 1983, 4 4105 01.) is as follow:

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: 1.0SiO₂: (0.0167, 0.01, 0.0067)TiO₂: 0.18TPAOH: 18H₂O. 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 HNO₃ 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 H$_2$O$_2$ 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 H$_2$O$_2$ (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 H$_2$O$_2$ was determined by titration with 0.05 M Ce(SO$_4$)$_2$ solution.

The epoxidation of alkene with introduced acceptor

The epoxidation of alkene with H$_2$O$_2$ 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 H$_2$O$_2$ (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 H$_2$O$_2$

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 CH$_3$OH/H$_2$O$_2$/H$_2$O with different flow rates were fed to the reactor with a peristaltic pump (SURPASS 102S/R-20). The content of unreacted H$_2$O$_2$ liquid was determined by titration with 0.05 M Ce(SO$_4$)$_2$ 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 CuKα radiation and a nickel filter in the 2θ angle range of 5º to 35º at 35 kV and 25 mA. UV-Vis spectra were recorded on a Shimadzu UV-2400PC spectrophotometer using BaSO$_4$ 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 (Eₐ) of formed hydroperoxy intermediate Ti-O₅-O₆-Hₙ₆ (A) the system without ammonia introduced (B) the system with ammonia introduced. c(ammonia)=0.08%. Reaction condition: Eₐ was tested in a fixed-bed reactor. c(H₂O₂)= 2.2%, WHSV= 5.13 h⁻¹, TOS= 1 min.
<table>
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<th>No.</th>
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<th>MAT</th>
<th>Convention/%</th>
<th>Selectivity/%</th>
<th>Utilization/%</th>
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Reaction conditions: cat. Ti-MWW 0.05 g; solvent 10 mL; 1-hexene 10 mmol; H$_2$O$_2$ 10 mmol; ammonia; time 2 h; temp. 333 K.