

Electronic Supplementary Information

Fluorine-Planted Titanosilicate with Enhanced Catalytic Activity in Alkene Epoxidation with Hydrogen Peroxide

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Experimental

1. Material Synthesis and Post Treatment.

Synthesis of Ti-MWW precursor: Following previous procedures (P. Wu, T. Tatsumi, T. Komatsu and T. Yashima, *J. Phys. Chem. B*, 2001, **105**, 2897). Ti-MWW precursor was hydrothermally synthesized from fumed silica (Cab-o-sil M5), tetrabutyl orthotitanate (TBOT) (95%), boric acid (99.5%) as a crystallization supporting agent, piperidine (PI) (98%,) as a structure-directing agent and deionized water. The gels with the molar compositions of 1.0 SiO₂ : (0.01- 0.05) TiO₂ : 1.4 PI : 0.67 B₂O₃ : 19 H₂O were crystallized under rotation (100 rpm) at 443 K for 7 days. After cooling, the solid product was filtered off and washed with deionized water to pH <9. The product was then dried at 323 K for 1 day.

Preparation of Ti-MWW: An acid treatment with 2 M HNO₃ solution was carried on the Ti-MWW precursor at 373 K for 20 h at a solid-to-liquid ratio of 1 g to 50 mL. This treatment would remove selectively the extraframework Ti species. The acid-treated sample was then calcined at 823 K for 6 h to burn off any residual organic species, giving rise to Ti-MWW samples.

Preparation of Fluorine-Planted Titanosilicate F-Ti-MWW: Similar to above acid treatment, the Ti-MWW precursor was treated with 2 M HNO₃ solution in the presence of NH₄F at Si/F of 26. The treatment was carried out at 373 K for 5 h and at a solid-to-liquid ratio of 1 g to 30 mL. The treated materials were further calcined at 823 K for 6 h, giving rise to F-Ti-MWW samples.

Re-MWW: The treatment was carried out at the molar ratio of 1.0 PI: 1.0 Ti-MWW: 10 H₂O 10 at 443 K for 1 days. The resulting solid was washed with deionized water, gathered by filtration, and subsequently dried at 373 K overnight. The organic species occluded were burned off in air at 803 K for 6 h.

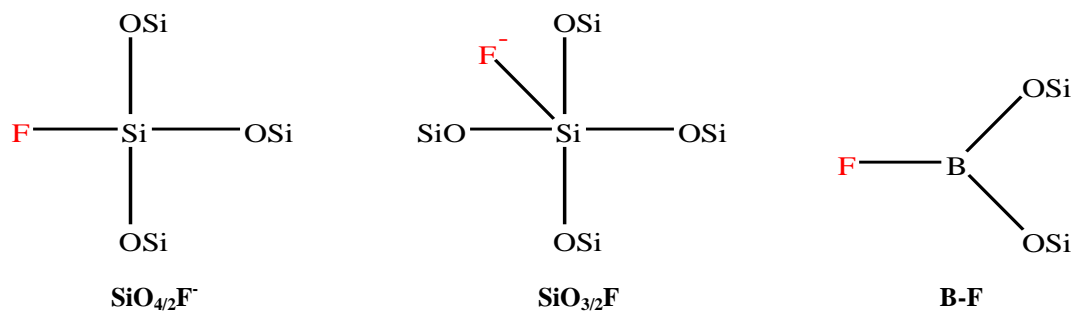
Ti-MWW-K: An treatment with KCl (Si/K=8) solution was carried on the Ti-MWW products at 333 K for 5 h at a solid-to-liquid ratio of 1 g to 100 mL, and dried at 353 K for 4 h.

F-Ti-MWW-K: An treatment with KCl (Si/K=8) solution was carried on the F-Ti-MWW products at 333 K for 5 h at a solid-to-liquid ratio of 1 g to 100 mL, and dried at 353 K for 4 h.

2. Characterization Methods

The catalysts were characterized by various techniques. X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer (35 kV and 25 mA) using Cu K α radiation ($\lambda=1.5405 \text{ \AA}$). UV-Vis spectra were recorded on a UV-2400PC spectrophotometer (Shimadzu). N₂ adsorption was carried out at 77 K on a BELSORP-MAX instrument after outgassing the samples for 10 h under vacuum at 573 K. The amount of Si, Ti was quantified by inductively coupled plasma (ICP) on a

Thermo IRIS Intrepid II XSP atomic emission spectrometer after dissolving the samples in HF solution. X-ray photoelectron spectroscopy (XPS) analyses were performed on a Kratos Axis Ultra spectrometer (Kratos Analytical, U.K.) equipped with a monochromatized aluminum X-ray source. The angle between the normal to the sample surface and the electrostatic lens axis was 0°. The analyzed area was $\sim 700 \mu\text{m} \times 300 \mu\text{m}$. The constant pass energy of the hemispherical analyzer was set at 40 eV. ^{19}F MAS experiments were performed on a Varian Infinity plus 300 WB NMR spectrometer with a 4mm H/F-X probe. A standard solid Hahn echo was employed with a recycle delay of 4s, while the value of echo delay (approximately 71.4 μs) was synchronized to the sample spinning rate of 14 kHz. The chemical shift reference was trifluoro acetic acid (CF_3COOH , -76.55 ppm). The ^{29}Si MAS NMR spectra were recorded on a VARIAN VNMRS 400 WB multinuclear solid-state magnetic resonance spectrometer. IR spectra were collected on a Nicolet NEXUS-FTIR-670 spectrometer at room temperature. A self-supported wafer (50 mg and Φ 2 cm) was set in a quartz IR cell sealed with CaF_2 windows, where it was evacuated at 673 K for 2 h before the pyridine adsorption. The adsorption was carried out by exposing the wafer to a pyridine vapor (1.3 kPa) at room temperature for 0.5 h. The pyridine was then removed by evacuation for 1 h at 323 K, 373 K, 423 K and 523 K, respectively.



Scheme S1 The F species attached to the framework in different states.

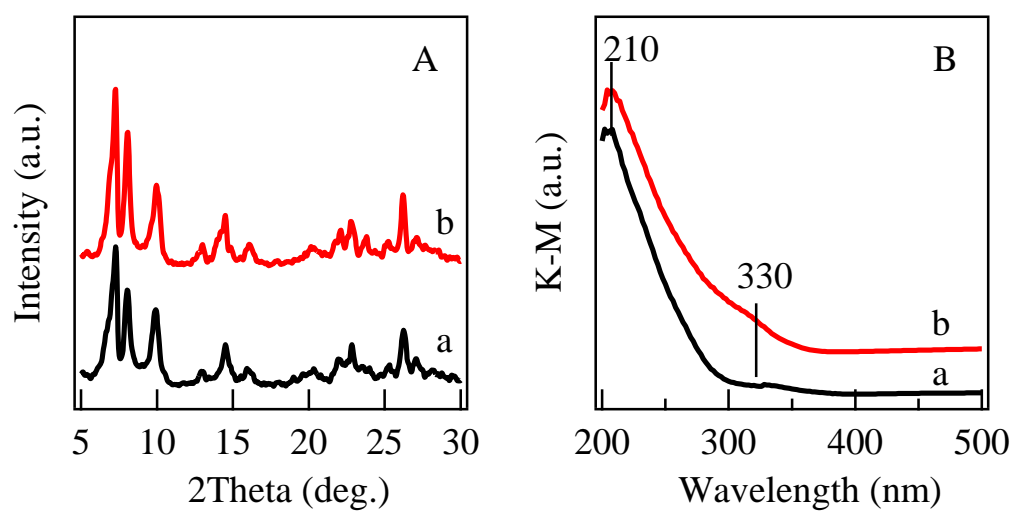


Fig. S1 X-ray diffraction patterns (A) and UV-Vis spectra (B) of Ti-MWW (a) and F-Ti-MWW (b) prepared the same precursor (Si/Ti = 25).

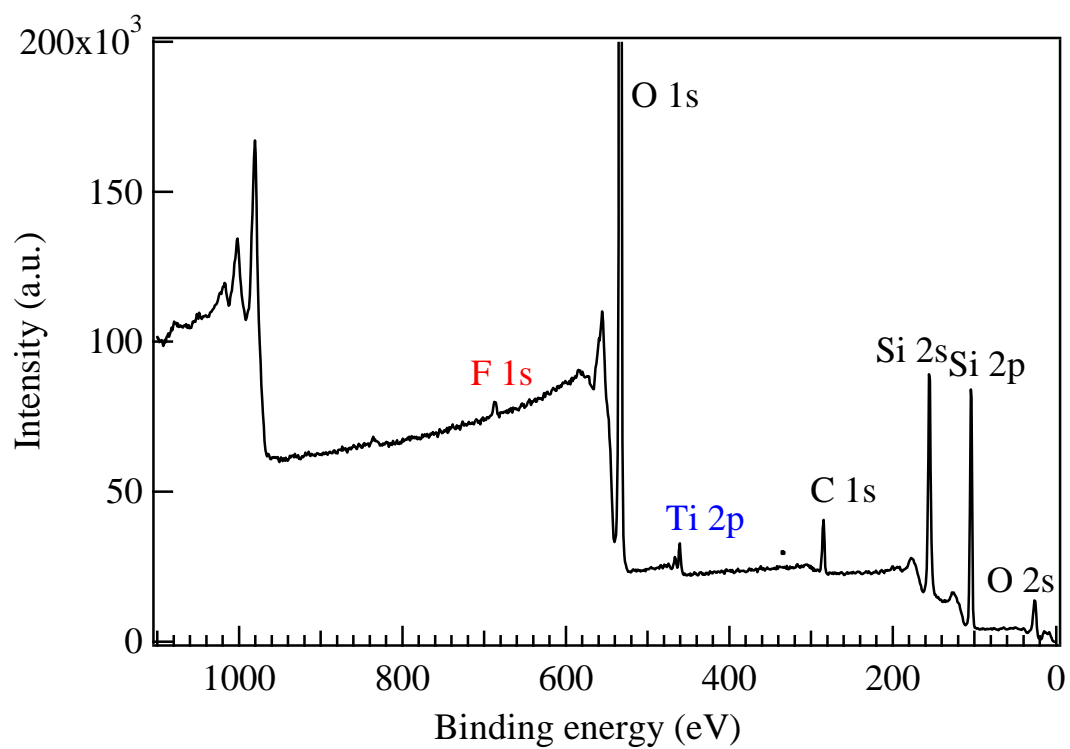


Fig. S2 XPS spectrum of calcined F-Ti-MWW.

Table S1 XPS characterization results of F-Ti-MWW

Peak	BE (eV)	FWHM (eV)	Atomic cont. (%)	Mass cont. (%)
Si 2p	104.0	1.787	23.70	35.18
C 1s	284.8	1.709	5.63	3.57
Ti 2p	460.7	1.863	0.81	2.05
O 1s	533.3	1.694	69.15	58.48
F 1s	688.0	2.618	0.71	0.71

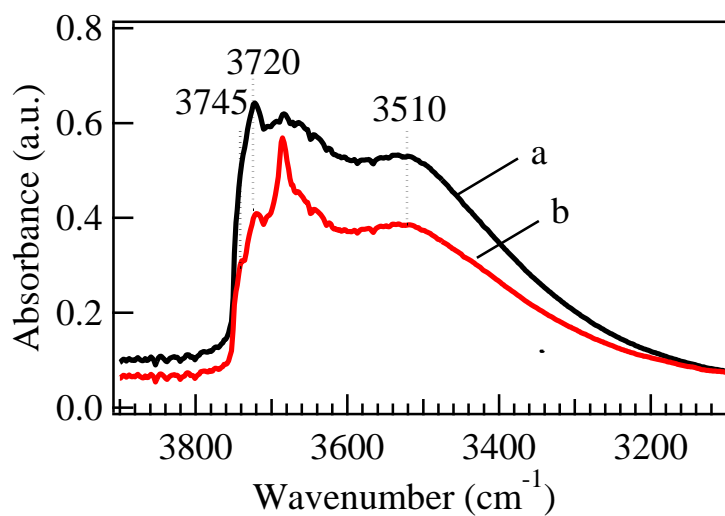


Fig. S3 FT-IR spectra in the region of hydroxyl stretching (a) Ti-MWW and (b) F-Ti-MWW.

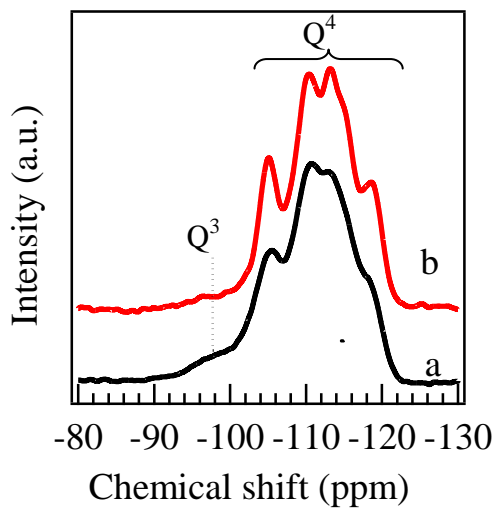


Fig. S4 Solid-state ²⁹Si MAS NMR spectra of Ti-MWW (a) and F-Ti-MWW (b).

Both IR and ²⁹Si MAS NMR investigations verified that the F modification removed partially the hydroxyl groups of Ti-MWW, which then would enhance its hydrophobicity.

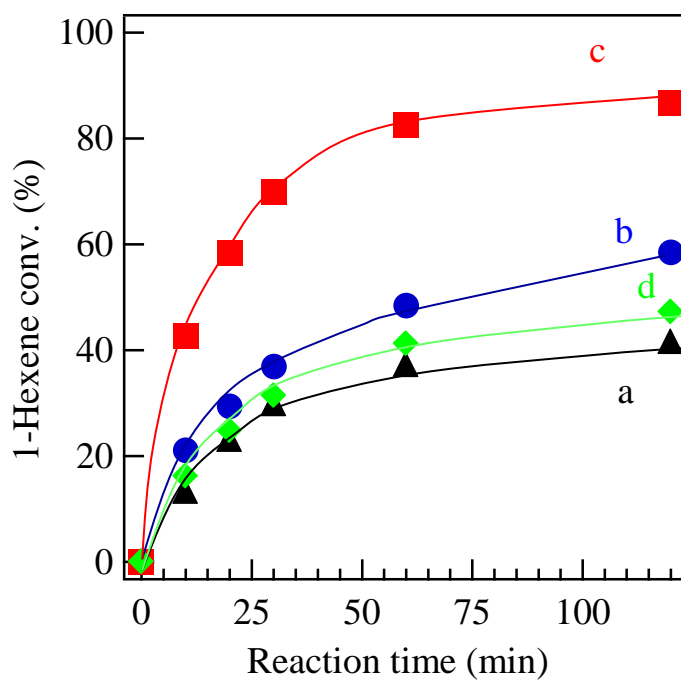


Fig. S5 Typical time courses for the epoxidation of 1-hexene over (a) Ti-MWW, (b) F-Ti-MWW, (c) F-Ti-MWW-K and (d) Re-Ti-MWW. The catalysts were prepared from the same lamellar precursor (Si/Ti = 25).

Reaction conditions: cat. 0.05 g, CH₃CN 10 mL, 1-hexene 10 mmol, H₂O₂ 10 mmol, 333 K, 2h.

Table S1 Epoxidation of various alkenes

No.	Alkene	Ti-MWW		F-Ti-MWW		F-Ti-MWW-K	
		Conv. /%	Oxide sel. /%	Conv. /%	Oxide sel. /%	Conv. /%	Oxide sel. /%
1	Heptene	26.0	98.1	34.0	97.2	39.4	98.4
2	Cyclopentene	15.9	95.2	17.4	93.7	37.4	95.7
3	Octene	20.2	92.4	18.1	91.2	24.8	97.8

Reaction conditions: cat. 0.05 g, CH₃CN 10 mL, 1-hexene 10 mmol, H₂O₂ 10 mmol, 333 K, 2 h.