Electronic Supplementary Material

Post-treatment of Ti-MWW zeolite with potassium fluoride for propylene epoxidation

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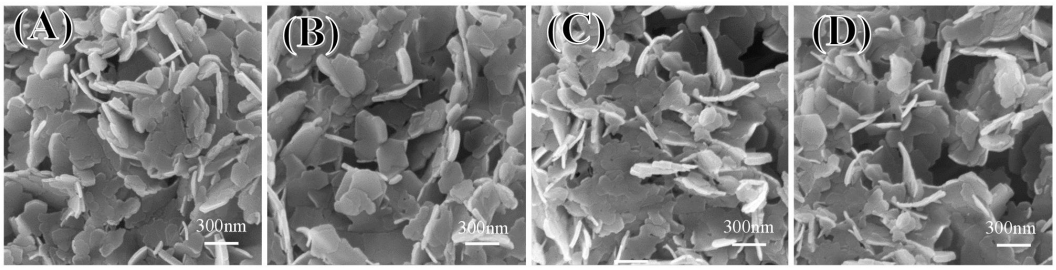


Fig. S1 SEM images of Bf-Ti-MWW (A), Bf-Ti-MWW-KF (B), Bf-Ti-MWW-$KHCO_3$ (C) and Bf-Ti-MWW-NH_4F (D).

No amorphous silica phase was observed in recrystallized Ti-MWW extrudates, indicating the binder has been converted into crystalline MWW zeolite. The post treatment with different potassium salts did not change the crystal morphology of Ti-MWW catalysts.

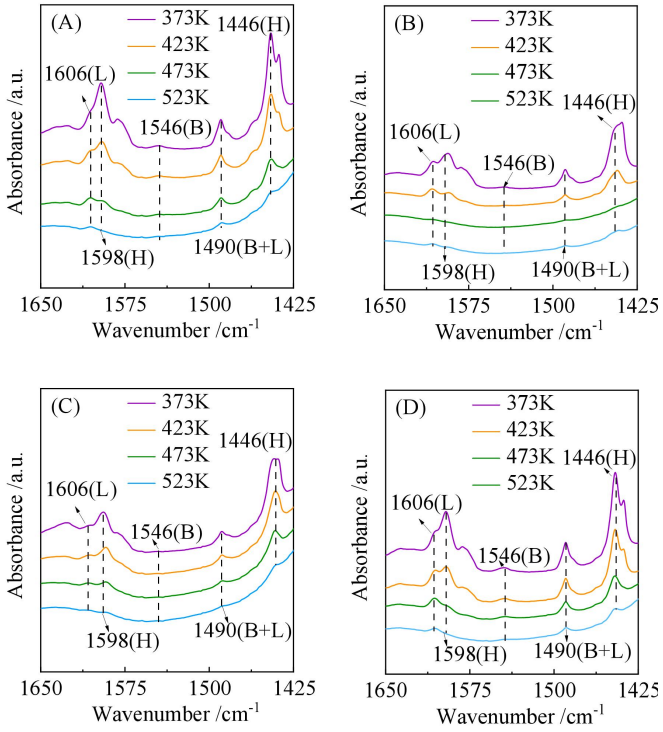


Fig. S2 Pyridine-adsorbed FT-IR spectra of Bf-Ti-MWW (A), Bf-Ti-MWW-KF (B), Bf-Ti-MWW-$KHCO_3$ (C) and Bf-Ti-MWW-NH_4F (D) after evacuation at different temperatures. B: Brønsted acid sites (BAS); L: Lewis acid sites (LAS); H: hydrogen-bonded pyridine.

As shown in Fig. S2(B) and (C), the 1606 cm^{-1} band attributed to LAS and the 1490 cm^{-1} peak related to BAS and LAS gradually diminished with increasing desorption temperature, and disappeared completely at 523 K for the Bf-Ti-MWW-KF and Bf-Ti-MWW-$KHCO_3$. Meanwhile, in Fig. S2(A) and (D), the peaks at 1606 cm^{-1} and 1490 cm^{-1} also weakened, but there were still weak peaks at 523 K for the Bf-Ti-MWW and Bf-Ti-MWW-NH_4F. These results indicated that the acid sites can be effectively eliminated through the treatment of KF and $KHCO_3$.

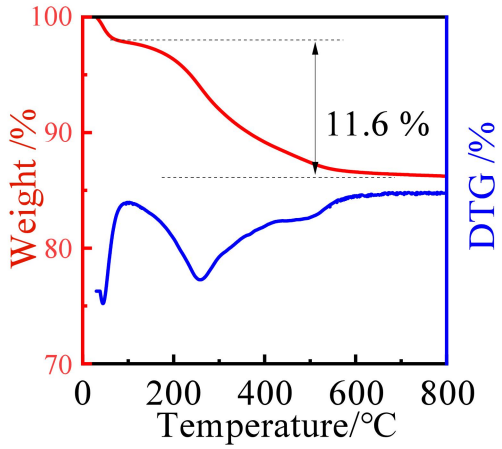


Fig. S3 TG and DTG curves after Bf-Ti-MWW-KF spent in continuous liquid-phase propylene epoxidation for 2700 h.

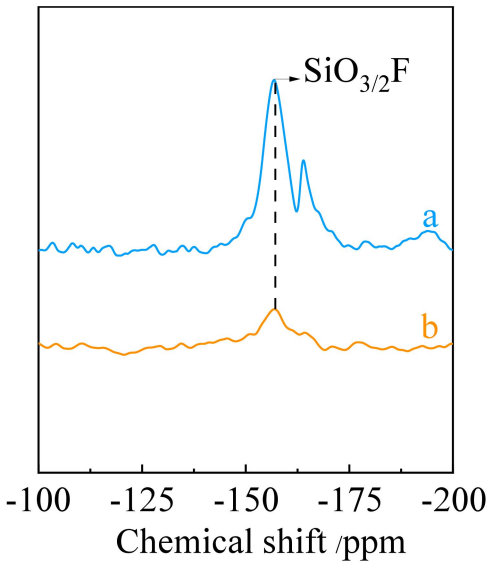


Fig. S4 ^{19}F MAS NMR spectra of fresh Bf-Ti-MWW-KF (a) and spent Bf-Ti-MWW-KF after continuous reaction (b).

Table S1 Propylene epoxidation over the Ti-MWW catalysts before and after the treatment with different amount of KF[a)]

Catalyst	Si/K[b)]	PO Yie. /%	H_2O_2 /%	
			conv.	eff.
Bf-Ti-MWW	-	48.8	52.5	85.7
Bf -Ti-MWW-KF-200[c)]	185	49.3	55.4	88.7
Bf -Ti-MWW-KF-100	103	54.4	60.2	90.3
Bf -Ti-MWW-KF-67	68	60.1	64.7	94.0
Bf -Ti-MWW-KF-50	54	53.3	59.3	90.5
Bf -Ti-MWW-KF-29	31	49.8	56.2	89.1

a) All the catalysts were grinded into powder for batchwise propylene epoxidation. Reaction conditions: catalyst, 0.03 g; H_2O_2 (30 wt.%), 30 mmol; solvent MeCN, 10 mL; propylene pressure, 0.4 MPa; temperature, 313 K; time, 1 h. b) Determined by ICP analysis. c) Bf-Ti-MWW-KF-*x*, *x* = Si/K ratio in treatment solution.

Table S2 Propylene epoxidation over the Ti-MWW catalysts before and after KF treatment for different time[a)]

Catalyst	Si/K[b)]	PO Yie. / %	H_2O_2 / %	
			conv.	eff.
Bf-Ti-MWW	-	48.8	52.5	85.7
Bf-Ti-MWW-KF-0.5h[c)]	74	48.5	55.6	86.4
Bf-Ti-MWW-KF-2h	65	58.0	62.1	93.0
Bf-Ti-MWW-KF-4h	68	60.1	64.7	94.0
Bf-Ti-MWW-KF-6h	68	59.2	63.3	93.5
Bf-Ti-MWW-KF-10h	67	60.1	63.1	95.2

a) All the catalysts were grinded into powder for batchwise propylene epoxidation. Reaction conditions: catalyst, 0.03 g; H_2O_2 (30 wt.%), 30 mmol; solvent MeCN, 10 mL; propylene pressure, 0.4 MPa; temperature, 313 K; time, 1 h. b) Determined by ICP analysis. c) Bf-Ti-MWW-*x*, *x* = treatment time in hour.

Table S3 Propylene epoxidation over the Ti-MWW catalysts before and after KF treatment at different temperature[a)]

Catalyst	Si/K[b)]	PO Yie. / %	H_2O_2 / %	
			conv.	eff.
Bf-Ti-MWW	-	48.8	52.5	85.7
Bf-Ti-MWW-KF-313K[c)]	65	50.1	55.1	84.6
Bf-Ti-MWW-KF-353K	68	60.1	64.7	94.0
Bf-Ti-MWW-KF-373K	68	55.3	62.7	90.0
Bf-Ti-MWW-KF-393K	91	51.5	56.4	89.8
Bf-Ti-MWW-KF-413K	96	52.0	59.7	88.1

a) All the catalysts were grinded into powder for batchwise propylene epoxidation. Reaction conditions: catalyst, 0.03 g; H_2O_2 (30 wt.%), 30 mmol; solvent MeCN, 10 mL; propylene pressure, 0.4 MPa; temperature, 313 K; time, 1 h. b) Determined by ICP analysis. c) Bf-Ti-MWW-*x*, *x* = treatment temperature.

Table S4 Propylene epoxidation over the Ti-MWW catalysts before and after KF treatment at different solid-to-liquid ratio[a)]

Catalyst	Si/K[b)]	PO Yie. / %	H_2O_2 / %	
			conv.	eff.
Bf-Ti-MWW	-	48.8	52.5	85.7
Bf-Ti-MWW-KF-1:3[c)]	65	59.2	63.4	93.6
Bf-Ti-MWW-KF-1:5	65	60.1	64.7	94.0
Bf-Ti-MWW-KF-1:10	73	57.5	62.5	92.0
Bf-Ti-MWW-KF-1:20	89	53.4	60.1	88.0
Bf-Ti-MWW-KF-1:40	111	54.0	59.7	90.1

a) All the catalysts were grinded into powder for batchwise propylene epoxidation. Reaction conditions: catalyst, 0.03 g; H_2O_2 (30 wt.%), 30 mmol; solvent MeCN, 10 mL; propylene pressure, 0.4 MPa; temperature, 313 K; time, 1 h. b) Determined by ICP analysis. c) Bf-Ti-MWW-*x*, *x* = solid-to-liquid weight ratio.

Table S5 Recycling experiment of Bf-Ti-MWW-KF in batchwise reactor.[a)]

Catalyst	Si/Ti[b)]	Si/K[b)]	PO Yie.	H_2O_2 /%

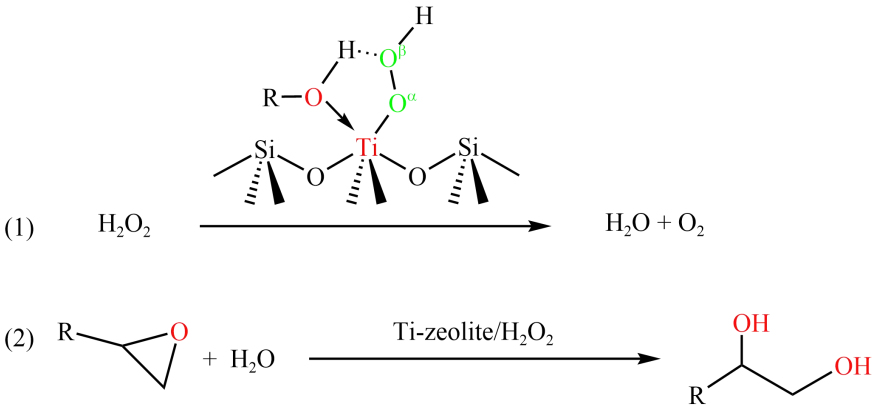
			/ %	conv.	eff.
Fresh Bf-Ti-MWW-KF	53	68	60.1	64.7	94.0
Bf-Ti-MWW-KF after the first run	52	69	59.7	63.2	95.0
Bf-Ti-MWW-KF after 2 runs and further calcination	53	69	59.3	63.5	93.4

a) All the catalysts were grounded into powder for batchwise propylene epoxidation. Reaction conditions: catalyst, 0.03 g; H_2O_2 (30 wt.%), 30 mmol; solvent MeCN, 10 mL; propylene pressure, 0.4 MPa; temperature, 313 K; time, 1 h. b) Determined by ICP analysis.

Table S6 Catalytic properties of propylene epoxidation over the fresh, spent and regenerated Bf-Ti-MWW-KF catalysts.[a)]

Catalyst	Si/Ti[b)]	Si/K[b)]	PO Yie. / %	H_2O_2 /%	
				conv.	eff.
Fresh Bf-Ti-MWW-KF	53	68	60.1	64.7	94.0
Spent Bf-Ti-MWW-KF	52	350	2.3	5.7	23.3
Regenerated Bf-Ti-MWW-KF	53	69	60.5	65.7	92.1

a) All the catalysts were grounded into powder for batchwise propylene epoxidation. Reaction conditions: catalyst, 0.03 g; H_2O_2 (30 wt.%), 30 mmol; solvent MeCN, 10 mL; propylene pressure, 0.4 MPa; temperature, 313 K; time, 1 h. b) Determined by ICP analysis.



Scheme S1. Pathways of side reactions in protic molecules-involved HPPO reaction, including non-productive decomposition of H_2O_2 (1) and hydrolysis of PO (2).