

Supplementary Material

Controllable Construction of Highly Active Ti Species in TS-1 Zeolite by Organic Base-Treatment

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Characterization methods

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer with a Ni-filtered CuK α X-ray source ($\lambda = 1.541 \text{ \AA}$). Scanning electron microscopy (SEM) was carried out on a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) was taken on a JSM-2010F microscope. UV resonance Raman spectra were collected on a triple spectrograph Raman system UV-Raman-100 with 244 nm laser. The chemical compositions of sample were analyzed via inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. The CHN elementary analysis was carried out on an Elementar Vario III instrument. N₂ and H₂O physisorption measurements were performed on a BELSORP instrument at 77 K. The adsorption and diffusion properties of organic molecules were also measured by thermogravimetric analysis. The as-made samples (~5 mg) with organics were pretreated at 423 K for 2 h in a N₂ flow to remove adsorbed water until no mass loss was observed, while the pretreatment of calcined samples was performed at a higher temperature of 823 K to remove not only adsorbed water but also organic impurities. Then the sample was cooled to 333 K and the adsorption data were obtained according to the increased weight when the N₂ flow (30 mL min⁻¹) together with organic vapor passing through the sample until the weight increase leveled off. The spectra in the framework vibration region and in the hydroxyl-stretching region were collected after evacuation at 473 K for 3 h. In order to eliminate the physically absorbed water, the self-supported sample wafers were placed in a quartz IR cell sealed with CaF₂ or KBr windows and evacuated through a vacuum system at 473 K for 3 h before measurements. X-ray photoelectron spectroscopy (XPS) was measured on the Kratos AXIS Supra equipment. UV-vis spectra were obtained on a PerkinElmer UV-vis Lambda 35 spectrophotometer using pure BaSO₄ as a reference. The ¹³C and ²⁹Si solid MAS NMR spectra were performed on a VARIAN VNMRS-400WB spectrometer.

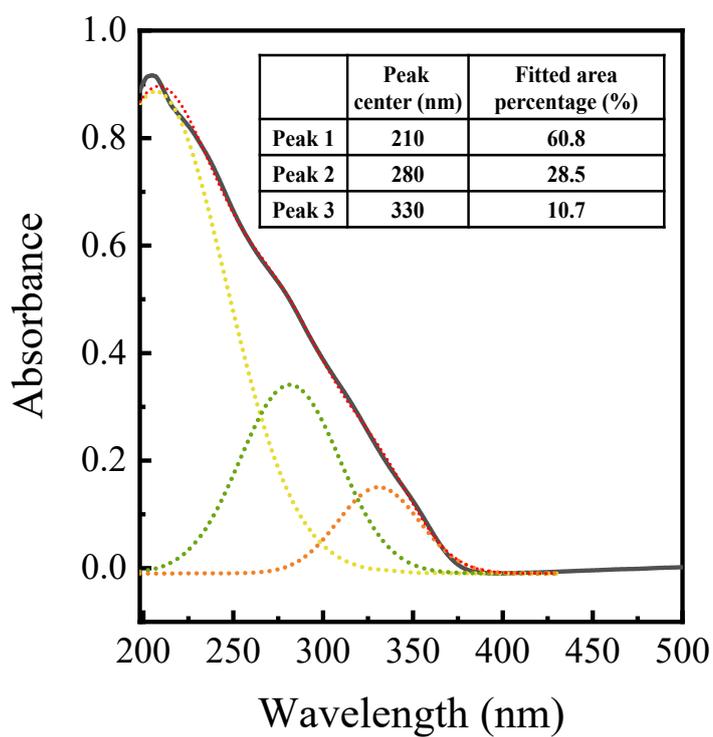


Fig. S1 The deconvoluted UV-vis spectrum of TS-PN-am.

Table S1 A comparison of 1-hexene epoxidation over various TS-1 samples in different solvents ^a

Catalyst	Si/T i	Solvent	1-hexene		TON ^b	H ₂ O ₂ (%)	
			conv. (%)	epoxide sel. (%)		conv.	eff.
- ^c	-	MeOH	0.2	50.0	-	9.3	2.1
		MeOH	18.0	92.1	89	26.8	67.2
		MeCN	13.9	99.0	69	19.1	72.8
TS	40	<i>t</i> -BuOH	7.8	97.7	39	12.0	65.2
		MeOH	23.7	97.0	123	31.3	75.8
		MeCN	15.4	99.1	80	20.2	76.4
TS-P	42	<i>t</i> -BuOH	9.9	98.2	51	14.1	70.3
		MeOH	28.7	98.1	146	35.5	81.3
		MeCN	16.7	99.0	85	20.2	82.6
TS-PN	41	<i>t</i> -BuOH	11.2	98.0	57	15.0	74.7
		MeOH	35.5	98.6	180	41.7	85.1
		MeCN	23.6	99.2	120	28.3	83.4
TS-PN-am	41	<i>t</i> -BuOH	15.0	98.5	76	18.7	80.3

^a Reaction conditions: cat., 50 mg; 1-hexene, 10 mmol; solvent, 10 mL; H₂O₂ (30 wt.%), 10 mmol; temp., 333 K; time 2 h.

^b TON = the mole of product/the mole of Ti sites

^c Reaction conditions: 1-hexene, 10 mmol; MeOH, 10 mL; H₂O₂ (30 wt.%), 10 mmol; temp., 333 K; time 2 h.

Table S2 A comparison of 1-hexene epoxidation over various TS-1 samples ^a

Catalyst	Si/Ti ^b	1-hexene		H ₂ O ₂ (%)	
		conv. (%)	epoxide sel. (%)	conv.	eff.
TS	40	18.0	92.1	26.8	67.2
TS-P	42	23.7	97.0	31.3	75.8
TS-P-am	42	26.8	97.4	33.0	81.2
TS-PN	41	28.7	98.1	35.5	81.3
TS-PN-am	41	35.5	98.2	41.7	85.1
TS-NH ₄ Cl ^c	40	18.5	95.8	29.3	63.2
TS-TPAOH ^d	40	18.5	94.6	28.1	65.8
TS-TPA ^e	40	23.2	95.9	31.0	74.8

^a Reaction conditions: cat., 50 mg; 1-hexene, 10 mmol; MeOH, 10 mL; H₂O₂ (30 wt.%), 10 mmol; temp., 333 K; time, 2 h.

^b Determined by ICP.

^c Treatment conditions: NH₄Cl/Si = 0.06; H₂O/Si = 18; temp., 443 K; time, 2 d.

^d Treatment conditions: TPAOH/Si = 0.03; H₂O/Si = 18; temp., 353 K; time, 1 d.

^e Treatment conditions: TPA/Si = 0.03; *n*-hexane/Si = 18; temp., 373 K; time, 1 d.

Table S3 Effect of amines on 1-hexene epoxidation over various TS-1 samples ^a

Catalyst	1-hexene		H ₂ O ₂ (%)	
	conv. (%)	epoxide sel. (%)	conv.	eff.
TS-PN-am	35.5	98.2	41.7	85.1
TS-PN	28.7	98.1	35.5	81.3
TS-PN-TPA ^b	33.4	98.5	40.5	82.4
TS-PN-DPA ^c	31.5	97.9	38.9	80.9
TS-PN-TPA' ^d	24.3	98.6	32.2	75.4
TS-PN-DPA' ^e	20.9	98.3	27.2	76.9

^a Reaction conditions: cat., 50 mg; 1-hexene, 10 mmol; MeOH, 10 mL; H₂O₂ (30 wt.%), 10 mmol; temp., 333 K; time, 2 h.

^b Treatment conditions: TPA/Si = 0.03; *n*-hexane/Si = 18; temp., 373 K; time, 1 d.

^c Treatment conditions: DPA/Si = 0.03; *n*-hexane/Si = 18; temp., 373 K; time, 1 d.

^d 0.005 mmol tripropylamine (TPA) was added into the reaction system.

^e 0.005 mmol dipropylamine (DPA) was added into the reaction system.

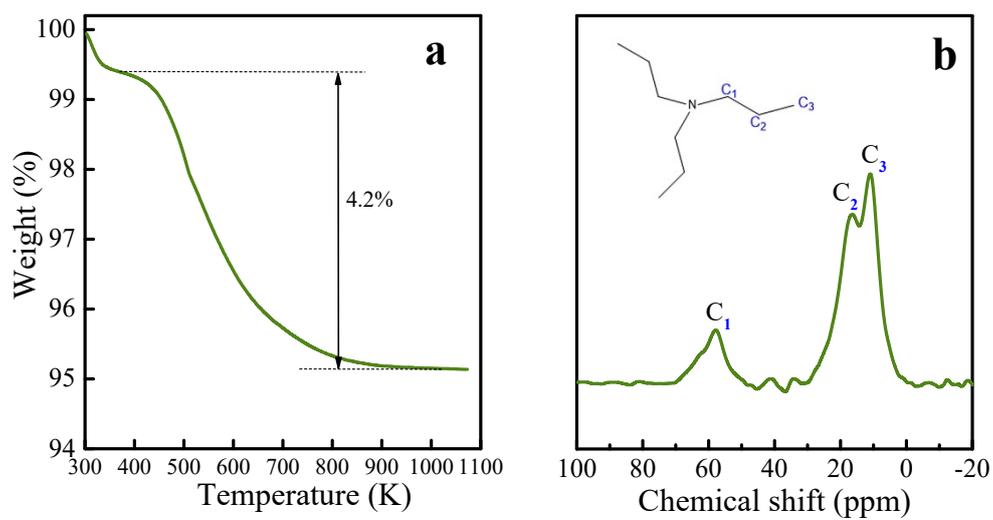


Fig. S2 TG-DTG curve (a) and ¹³C NMR spectrum (b) of TS-PN-TPA.

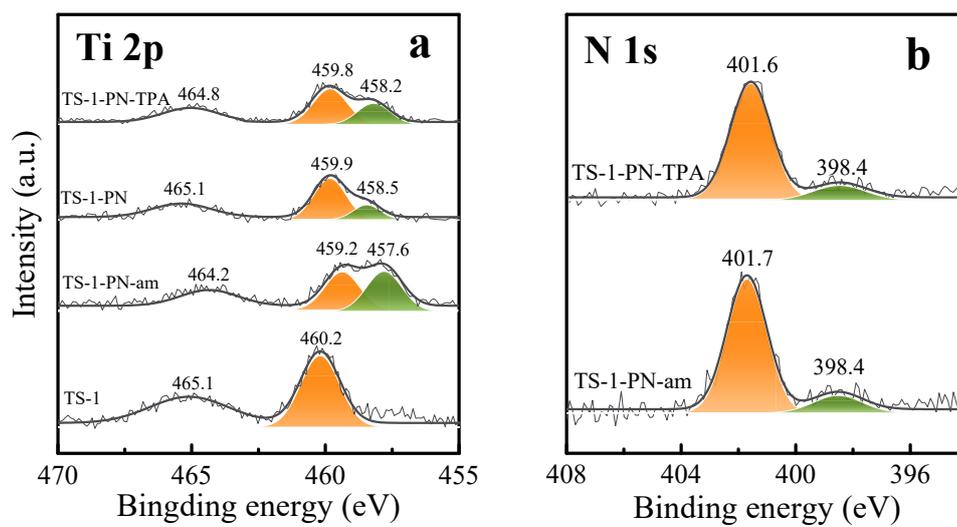


Fig. S3 Ti 2p (a) and N 1s (b) XPS spectra of various titanosilicates.

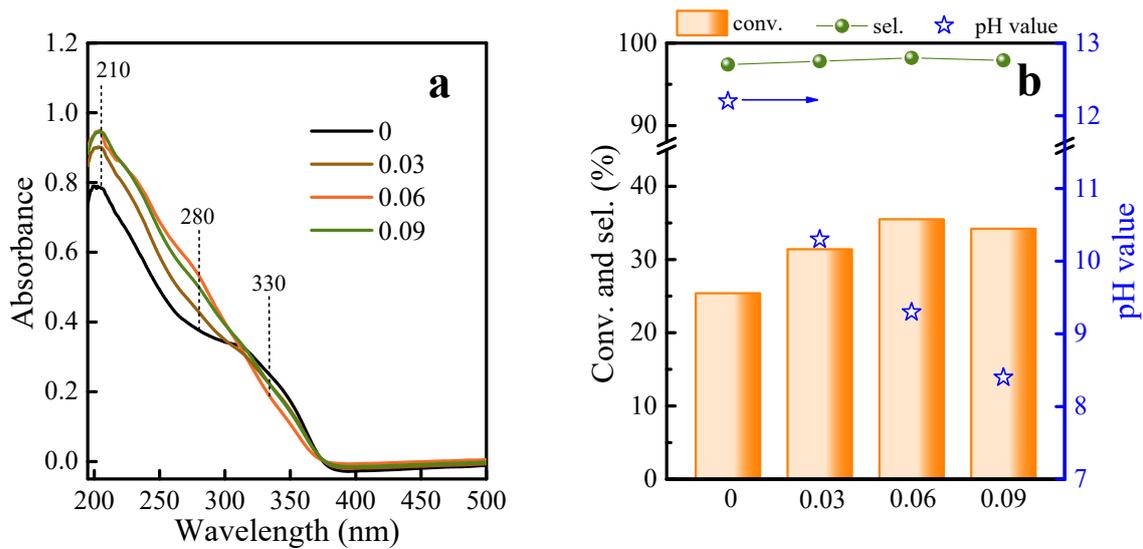


Fig. S4 UV-vis spectra (a) of TS-1 modified with various molar ratio of NH₄Cl/Si and the corresponding catalytic performance in 1-hexene epoxidation (b). Reaction conditions see **Table S2**.

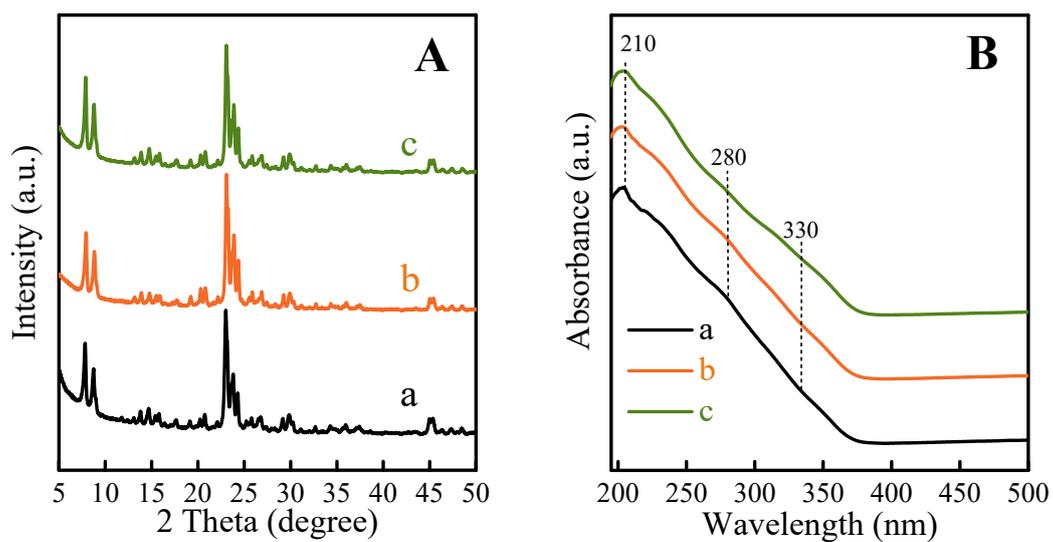


Fig. S5 XRD patterns (A) and UV-vis spectra (B) of fresh (a), used (b) and regenerated (c) TS-PN-am in the recycle experiments.