Electronic Supplementary Information (ESI)

Hollow core-shell structured TS-1@S-1 as an efficient catalyst for alkene epoxidation

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Supplementary information captions:

Fig. S1 TEM images of HCS-TS with different synthetic contents of H-TS-1.

(a) TEOS: H-TS-1-80=0.25:9.75; (b) TEOS: H-TS-1-80=0.5:9.5;

(c) TEOS: H-TS-1-80=0.75:9.25; (d) TEOS: H-TS-1-80=1:9.

Fig. S2 N_2 adsorption-desorption isotherms of (a) TS-1; (b) H-TS-1; (c) HCS-TS and (d) HCS-TS^P.

Fig. S3 The FT-IR spectra (A and B) of the prepared samples. (a) TS-1; (b) H-TS-1; (c) HCS-TS; (d) HCS-TS^P and Liquid-infrared spectra of TPOAH.

Fig. S4 ^{29}Si MAS NMR spectra of prepared samples. (a) TS-1; (b) H-TS-1; (c) HCS-TS; (d) HCS-TS^P.

Fig. S5 TG profile (A) and ^{13}C MAS NMR spectra (B) of HCS-TS^P sample.

Fig. S6 The curve of the conversion of 1-hexene (A) and the curve of $\mathbf{I_{960/550}}$ (B) with different parent Ti/ (Si+Ti) ratio.

Fig. S7 The reuse of HCS-TS and HCS-TS^P in 1-hexene epoxidation.

Fig. S8 The UV/Vis spectra of the prepared catalysts. (a) TS-1; (b) H-TS-1; (c) CS-TS.

Fig. S9 TEM images of CS-TS.

Fig. S10 TEM images of samples with different synthetic conditions: (a) H-TS-1-TEOS; (b) H-TS-1-TPAOH; (c) S-1.

Table S1. Physicochemical properties of different samples.

Table S2. Elemental composition of different samples.

Table S3. Q_3/Q_4 ratio of different samples.

Table S4. Epoxidation of different alkenes with H_2O_2 over various catalysts.

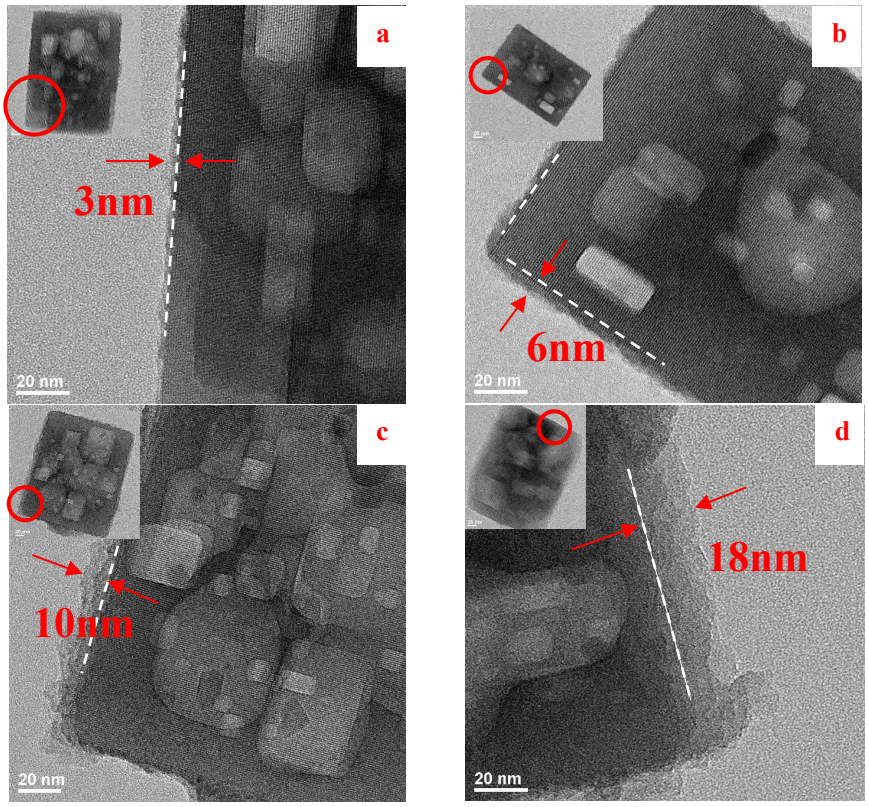


Fig. S1 TEM images of HCS-TS with different synthetic contents of H-TS-1.

(a) TEOS: H-TS-1-80=0.25: 9.75; (b) TEOS: H-TS-1-80=0.5: 9.5; (c) TEOS: H-TS-1-80=0.75: 9.25; (d) TEOS: H-TS-1-80=1: 9.

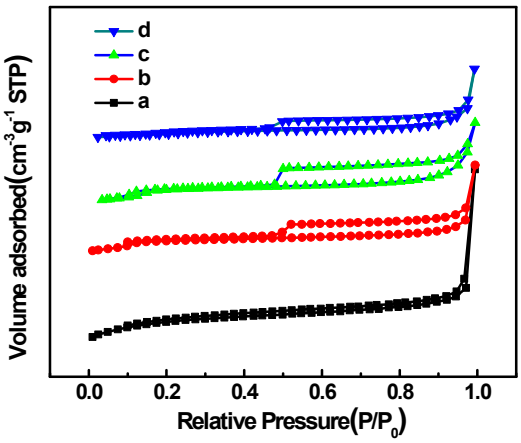


Fig. S2 N_2 adsorption-desorption isotherms of (a) TS-1; (b) H-TS-1; (c) HCS-TS and (d) HCS-TS^P.

Table S1. Physicochemical properties of different samples.

No.	Samples	$S_{micro.}$ (m^2g^{-1})[a]	$S_{exter.}$ (m^2g^{-1})[a]	$V_{tol.}$ (cm^3g^{-1})[a]	$V_{micro.}$ (cm^3g^{-1})[a]	$V_{meso.}$ (cm^3g^{-1})[a]
1	TS-1	322	54	0.22	0.138	0.079
2	H-TS-1	314	51	0.43	0.136	0.292
3	HCS-TS	358	57	0.42	0.150	0.271
4	HCS-TS^P	101	68	0.31	0.047	0.260

[a] Obtained by BET method. Calculated by BET method. S_{micro}(m^2g^{-1}), V_{micro}(cm^3g^{-1}) and V_{meso}(cm^3g^{-1}) stand for microporous surface area, microporous volume and mesoporous volume, respectively.

Table S2. Elemental composition of different samples.

No.	Samples	Si/Ti (Bulk)[a]	Si/Ti (Surface)[b]	Ti2p3/2 BE (eV)[b]
1	TS-1	90	159	460.5
2	H-TS-1	90	184	460.5
3	HTS-CS	98	229	460.5
4	HTS-CS^{P}	98	216	460.5 , 459.1

[a] Detected by ICP.

[b] Detected by XPS.

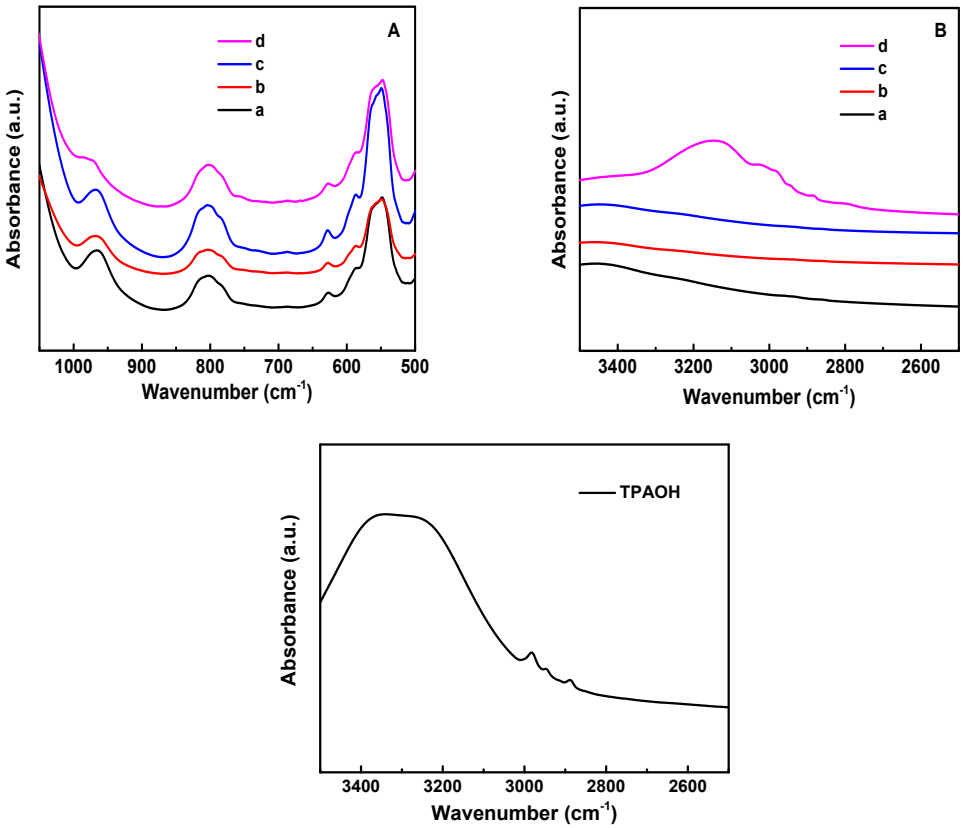


Fig. S3 The FT-IR spectra (A and B) of the prepared samples. (a) TS-1; (b) H-TS-1; (c) HCS-TS; (d) HCS-TS^{P} and Liquid-infrared spectra of TPOAH.

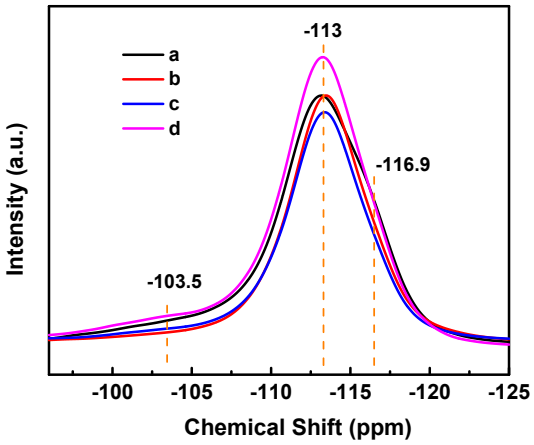


Fig. S4 ^{29}Si MAS NMR spectra of prepared samples: (a) TS-1; (b) H-TS-1; (c) HCS-TS; (d) HCS-TS^{P}.

Table S3. Q_3/Q_4 ratio of different samples.

	TS-1	H-TS-1	HCS-TS	HCS-TS^{P}
Q_3/Q_4	11.7%	8.1%	10.5%	10.0%

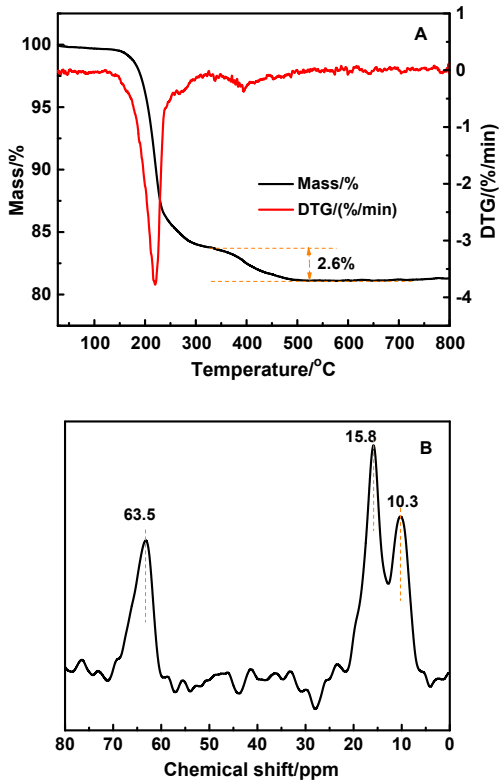


Fig. S5 TGA profile (A) and ^{13}C MAS NMR spectra (B) of HCS-TS^{P} sample.

Table S4. Epoxidation of different alkenes with H_2O_2 over various catalysts.

			1-Hexene				
No.	**Catalyst**	**Si/Ti[a]**	**Conv.(1-Hex.)/%**	**Conv.(H_2O_2)/%**	**Eff.(H_2O_2)/%**	**Sel.(Epo.)/%**	**TON**
1	TS-1	90	16.5	19.3	85.2	98.9	180
2	H-TS-1	90	16.4	19.5	83.7	97.4	179
3	HTS-CS	98	21.5	25.3	84.9	97.8	256
4	HTS-CS[P]	98	25.1	27.7	86.1	95.0	299

			Cyclopentene					Cyclohexene	
No.	**Catalyst**	**Si/Ti[a]**	**Conv./%**	**Conv.(H_2O_2)/%**	**Eff.(H_2O_2)/%**	**Sel.(Epo.)/%**	**TON**	**Conv./%**	**TON**
1	TS-1	90	23.8	34.6	67.8	98.7	260	0.5	-
2	H-TS-1	90	20.3	27.2	74.6	99.3	222	0.5	-
3	HTS-CS	98	23.8	28.3	82.9	98.6	283	0.4	-
4	HTS-CS[P]	98	48.1	52.7	87.7	96.1	572	0.9	-

Reaction conditions: cat. 50mg, alkene 10mmol, H_2O_2 10mmol, CH_3OH 10ml, Temp. 333K, time 2h.

a Detected by ICP.

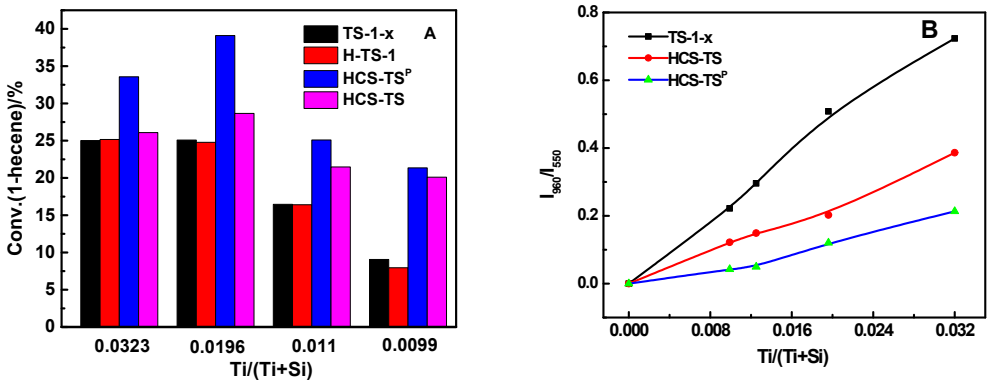


Fig. S6 The curve of the conversion of 1-hexene (A) and the curve of $\mathbf{I_{960/550}}$ (B) with different parent Ti/(Si+Ti) ratio.

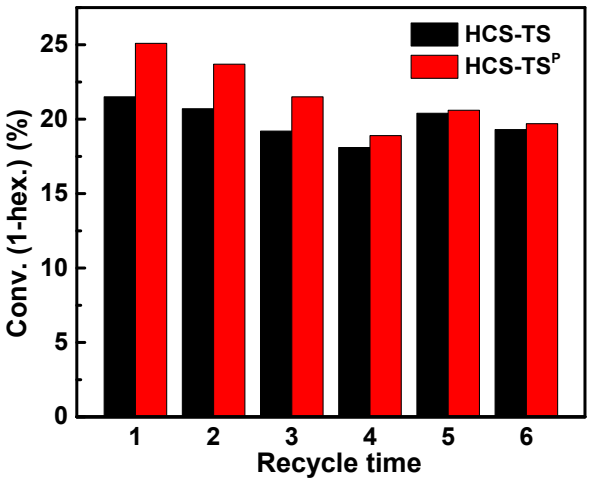
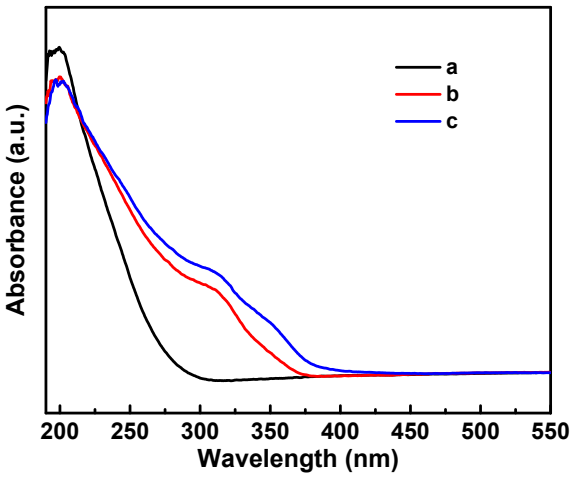


Fig. S7 The reuse of HCS-TS and HCS-TS^P in 1-hexene epoxidation.

Reaction conditions for the first run: catalyst: 0.1g, 1-hexene: 10mmol, H_2O_2: 10mmol, CH_3OH: 10ml, Temp.: 333K, time: 2h. The next catalytic runs proceed at a constant ratio of catalyst-oxidant-solvent. (1-4: the samples were recycled after separation by centrifugation then washed with acetone and reused in the conversion of 1-hexene; 5, 6: the samples were recycled after being calcined at 823 K for 6 h and reused in the conversion of 1-hexene).



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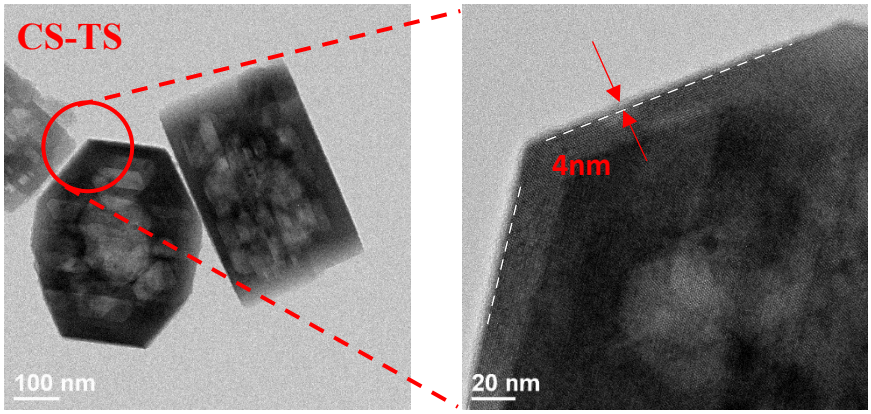

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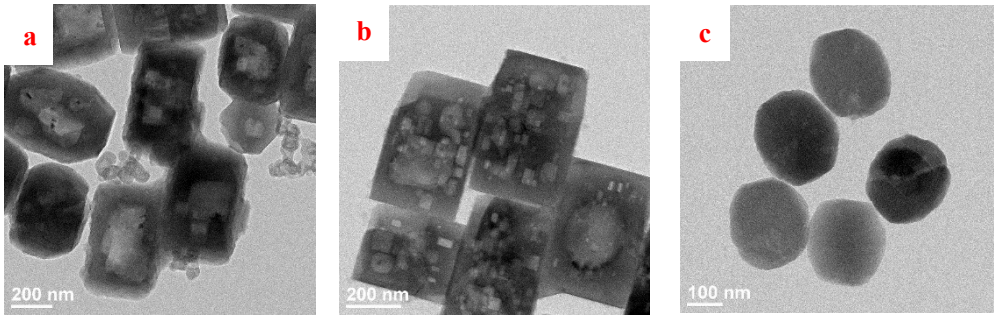

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