Carbon-encapsulated hierarchical TS-1 zeolites with enhanced hydrophobicity and catalytic epoxidation performance

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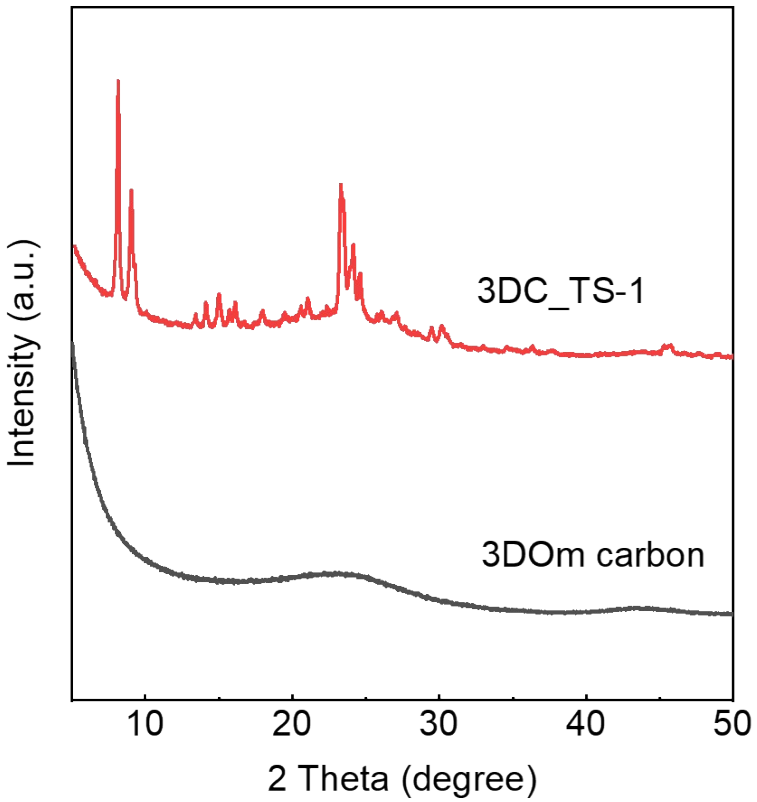

Fig. S1 XRD patterns of the 3DC_TS-1 and 3DOm carbon.

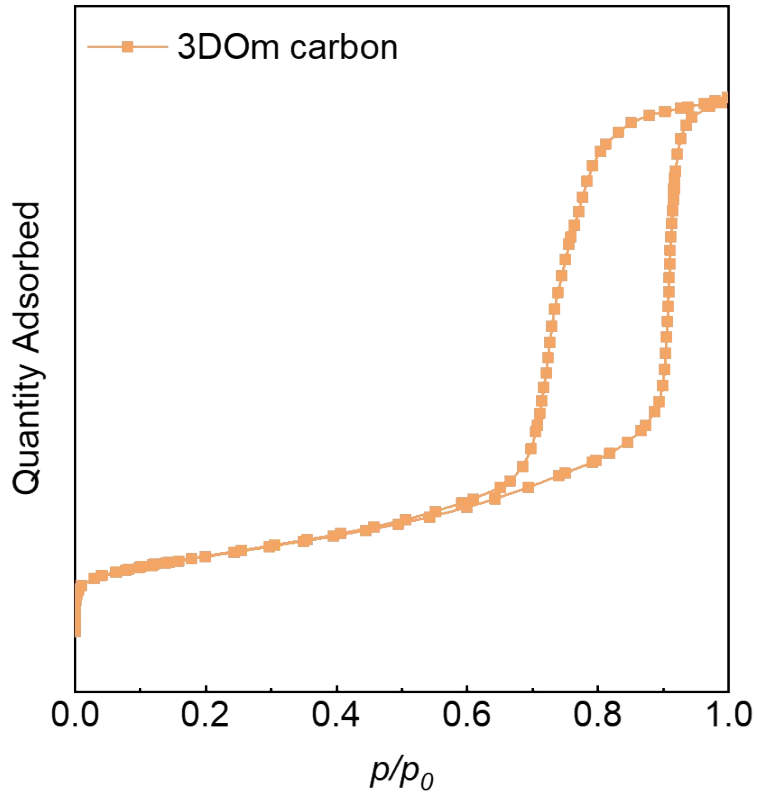

Fig. S2 N_2 adsorption-desorption isotherm of 3DOm carbon.

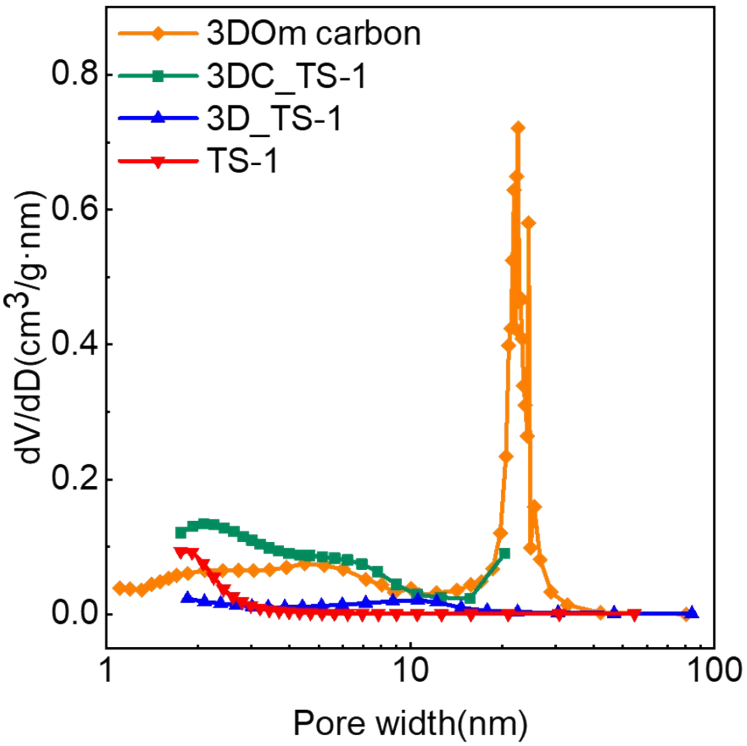

Fig. S3 BJH pore size distributions of 3DOm carbon and various titanosilicate zeolites.

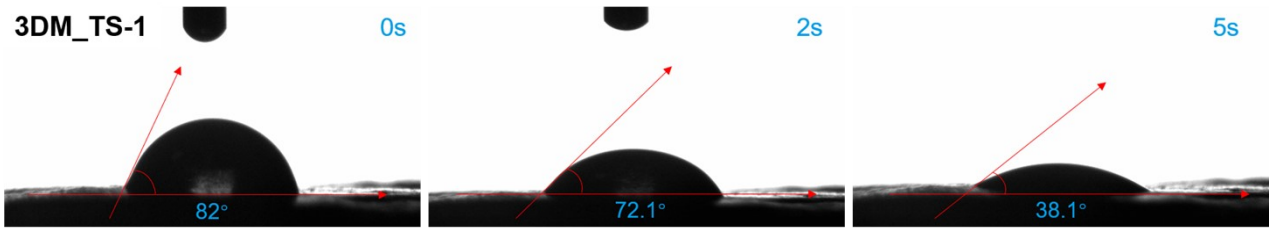

Fig. S4 Water contact angles of 3DM_TS-1.

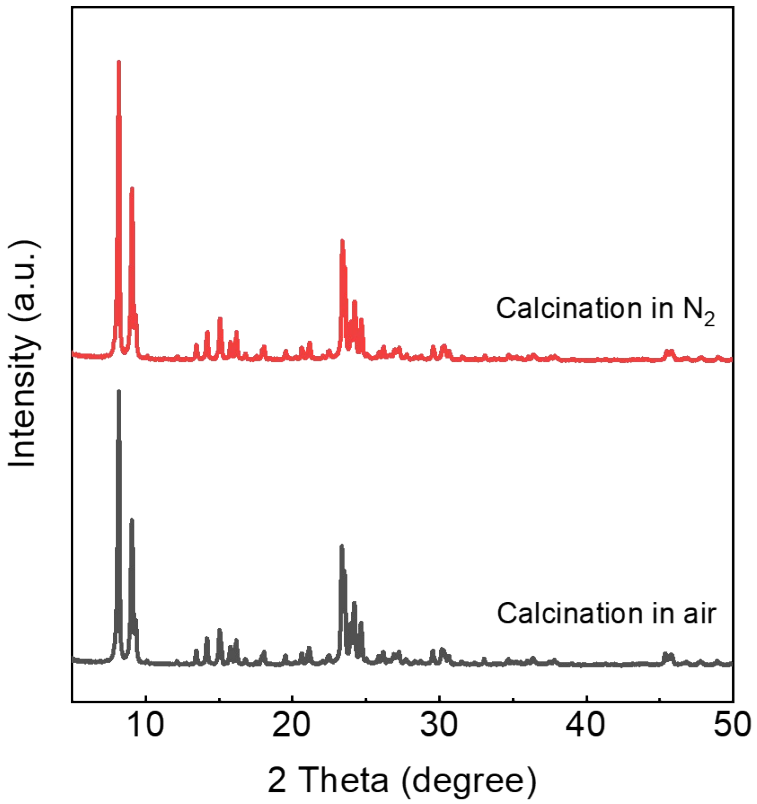

Fig. S5 XRD patterns of the conventional TS-1 calcined in air and N_2, respectively.

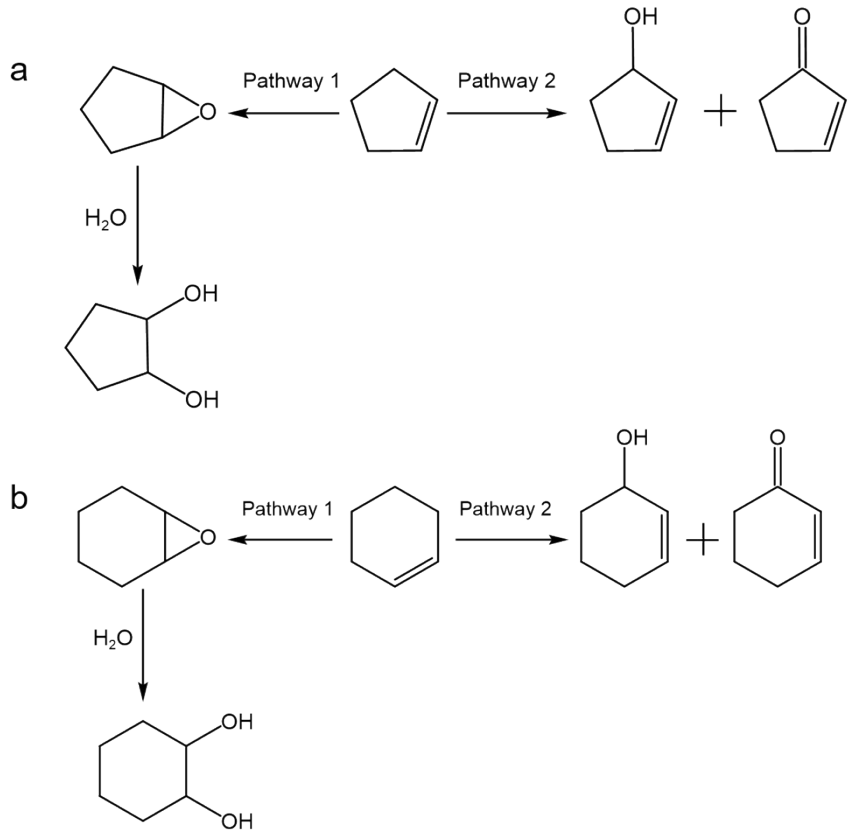

Fig. S6 Cyclopentene and cyclohexene conversion through (1) epoxidation pathway and (2) allylic oxidation pathway.

Table S1 Catalytic performance of TS-1, 3D_TS-1, 3DC_TS-1 in cyclopentene epoxidation with H_2O_2 [a]

Catalysts	Ti content [b] ($\mu mol \cdot g^{-1}$)	Con. (%)	Sel. [c](%)			TOF (h^{-1})	Yield (%)
			Epoxide	Diol	Others		
TS-1 [d]	194.9	14.4	86.2	9.2	4.6	74	12.4
TS-1 [e]	-	12.3	90.0	1.5	8.5	-	12.0
3D_TS-1	376.4	14.0	84.1	1.6	14.3	37	11.8
3DC_TS-1	106.7	10.3	97.3	0.7	2.0	97	10.0

[a] Reaction condition: 10 mmol cyclopentene, 50 mg catalyst, 10 mmol H_2O_2 (30 wt%) as oxidant, 10 ml CH_3CN as solvent, 60 °C, 2 h.

[b] Detected by ICP-OES.

[c] Epoxide: 1,2-epoxycyclopentane. Diol: 1,2-cyclopentandiol. Others: cyclopentene-1-one and 2-cyclopenten-1-ol.

[d] Calcined in air.

[e] Calcined in N_2.

Table S2 Catalytic performance of TS-1, 3D_TS-1, 3DC_TS-1 in cyclohexene epoxidation with H_2O_2 [a]

Catalysts	Ti content [b] ($\mu mol \cdot g^{-1}$)	Con. (%)	Sel. [c](%)			TOF (h^{-1})	Yield (%)
			Epoxide	Diol	Others		
TS-1	194.9	1.6	38.9	45.3	15.8	8	0.6
3D_TS-1	376.4	1.7	28.8	56.7	14.5	5	0.5
3DC_TS-1	106.7	0.8	77.3	20.1	2.6	8	0.7

[a] Reaction condition: 10 mmol cyclohexene, 50 mg catalyst, 10 mmol H_2O_2 (30 wt%) as oxidant, 10 ml CH_3CN as solvent, 60 °C, 2 h.

[b] Detected by ICP-OES.

[c] Epoxide: 1,2-epoxycyclohextane. Diol: 1,2-cyclohexanediol. Others: cyclohexen-1-one and 2-cyclohexe-1-ol.

Table S3 Catalytic performance of 3DC_TS-1 and 3DM_TS-1 in cyclopentene and cyclohexene epoxidation with H_2O_2 [a]

Catalysts	Cyclopentene					Cyclohexene				
	Con. (%)	Sel. [b](%)			Yield (%)	Con. (%)	Sel. [c](%)			Yield (%)
		Epoxide	Diol	Others			Epoxide	Diol	Others	
3DC_TS-1	10.3	97.3	0.7	2	10.0	0.8	77.3	20.1	2.6	0.7
3DM_TS-1	10.9	86.0	9.3	4.7	9.4	0.9	38.4	46.7	14.9	0.4

[a] Reaction condition: 10 mmol cyclohexene, 50 mg catalyst, 10 mmol H_2O_2 (30 wt%) as oxidant, 10 ml CH_3CN as solvent, 60 °C, 2 h.

[b] Epoxide: 1,2-epoxycyclopentane. Diol: 1,2-cyclopentandiol. Others: cyclopentene-1-one and 2-cyclopenten-1-ol.

[c] Epoxide: 1,2-epoxycyclohextane. Diol: 1,2-cyclohexanediol. Others: cyclohexen-1-one and 2-cyclohexe-1-ol.

Table S4 Cyclopentene epoxidation performance of 3D_TS-1 before and after toxification [a]

Catalysts	Sel. [b](%)			Yield (%)
	Epoxide	Diol	Others	
3D_TS-1	84.1	1.6	14.3	11.8
3D_TS-1(PPA)	83.1	1.4	15.5	5.2

[a] The poisoning of the sample was conducted by adding 10 mmol of phenylphosphonic acid (PPA) into the reaction mixture.

[b] Epoxide: 1,2-Epoxycyclopentane. Diol: 1,2-Cyclopentandiol. Others: cyclopentene-1-one and 2-cyclopenten-1-ol.

Table S5 Recyclability of 3DC_TS-1 and 3D_TS-1 in cyclopentene epoxidation [a]

Run number [b]	3DC_TS-1		3D_TS-1	
	Yield (%)	Sel. [c](%)	Yield (%)	Sel. [c](%)
1	10.0	97.3	11.8	84.1
2	7.1	97.0	8.3	83.4
3	4.5	96.4	6.1	82.5
4	9.6	97.7	11.7	85.1

[a] Reaction conditions: 50 mg catalyst, 10 mmol cyclopentene, 10 ml CH_3CN, 10 mmol H_2O_2 (30 wt%), 60 ℃, 2 h.

[b] After the first three runs, the used catalysts were collected by filtration, simply washed by acetonitrile and then carried on the next run of reaction. After the three run, the used catalysts were calcined in nitrogen or air at 773 K for 6 h.

[c] Selectivity of epoxycyclopentane.