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Bolaform surfactant-directed synthesis of TS-1 zeolite nanosheets for catalytic epoxidation of bulky cyclic olefins

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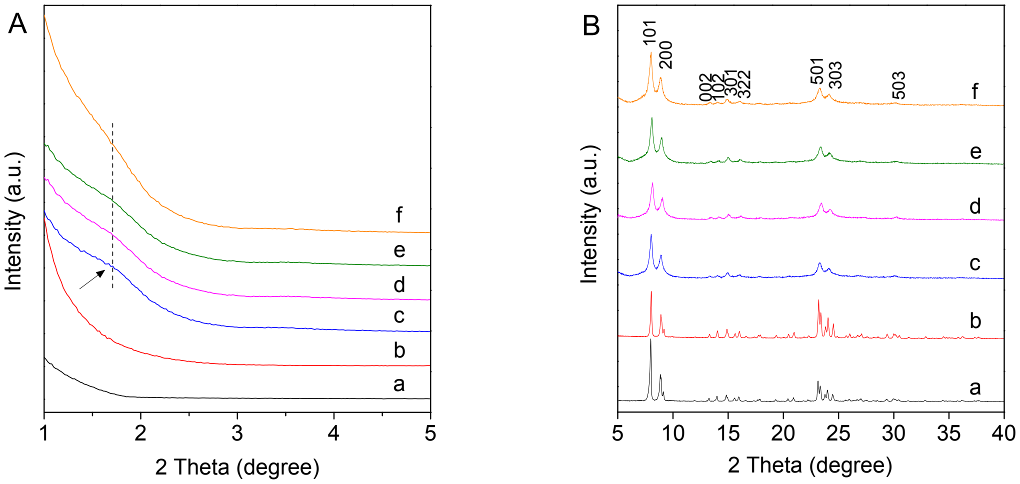

Figure S1. (A) Low-angle and (B) wide-angle X-ray diffraction patterns of (a) CTS-1, (b) MTS-1, (c) HTS-1_25, (d) HTS-1_50, (e) HTS-1_75 and (f) HTS-1_100 after the removal of organic structure-directing agents by calcination.

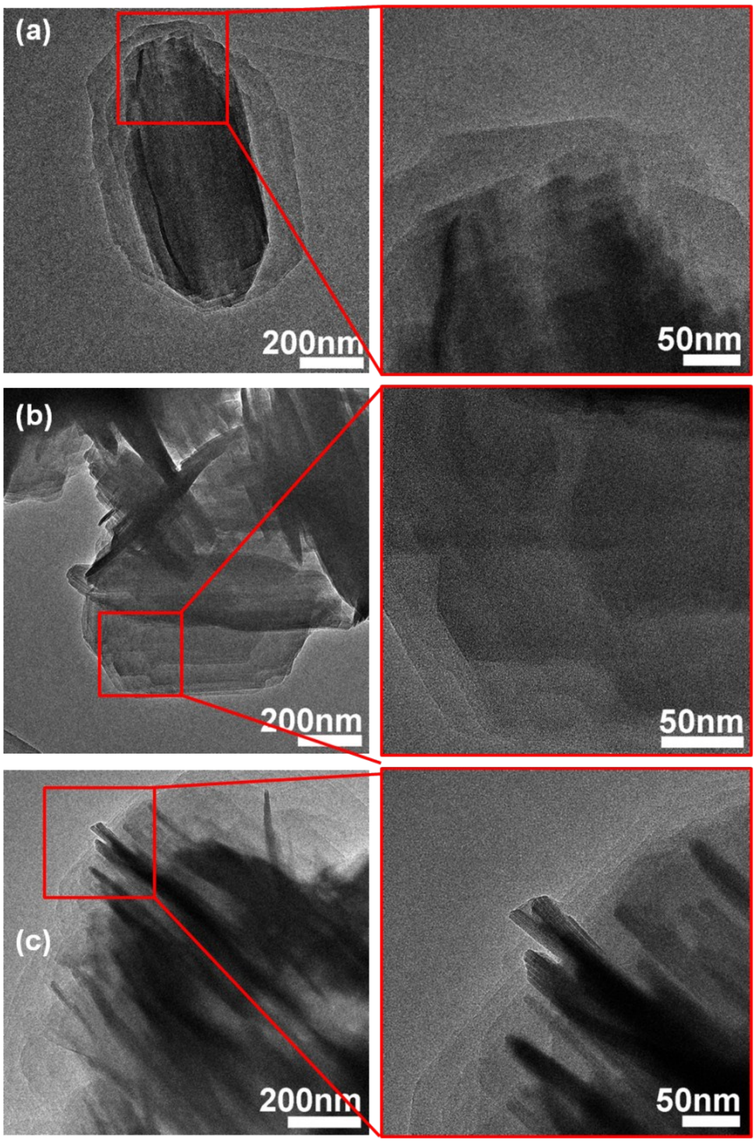

Figure S2. TEM images of (a) HTS-1_25, (b) HTS-1_75 and (c) HTS-1_100..

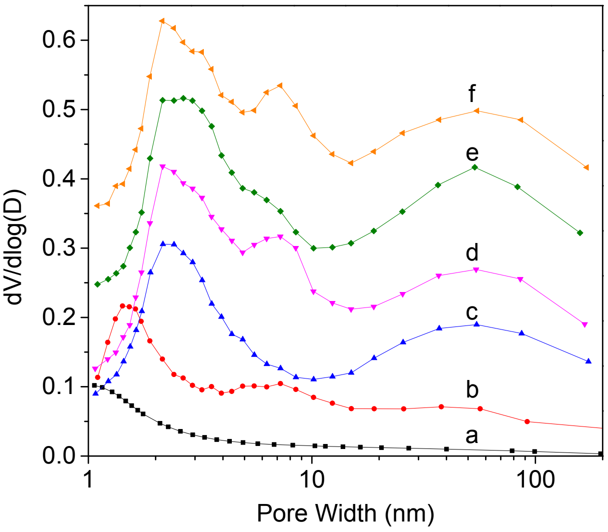

Figure S3. BJH pore size distributions calculated from the adsorption branches of the isotherms of (a) CTS-1, (b) MTS-1, (c) HTS-1_25, (d) HTS-1_50, (e) HTS-1_75 and (f) HTS-1_100.

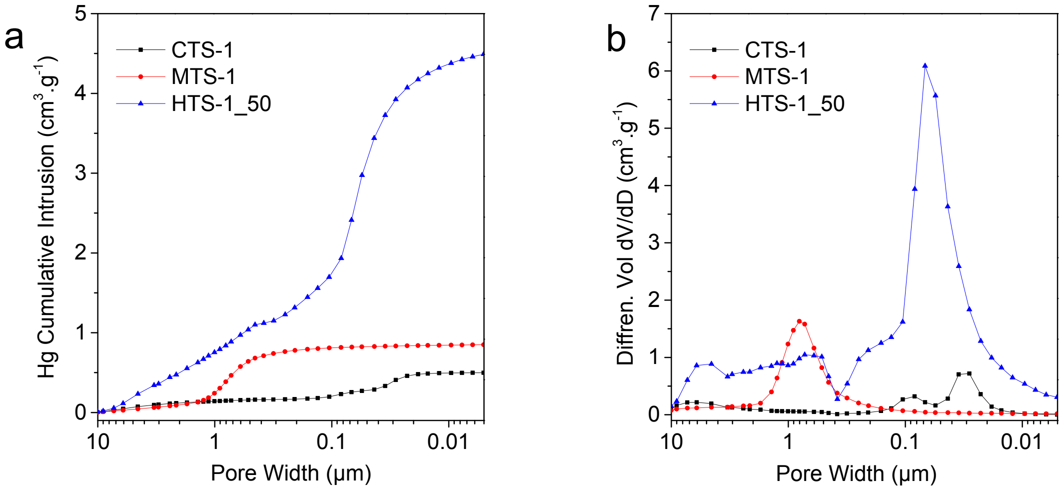

Figure S4. (a) Hg intrusion curves and (b) pore size distributions of CTS-1, MTS-1 and HTS-1_50 derived from Hg intrusion measurements.

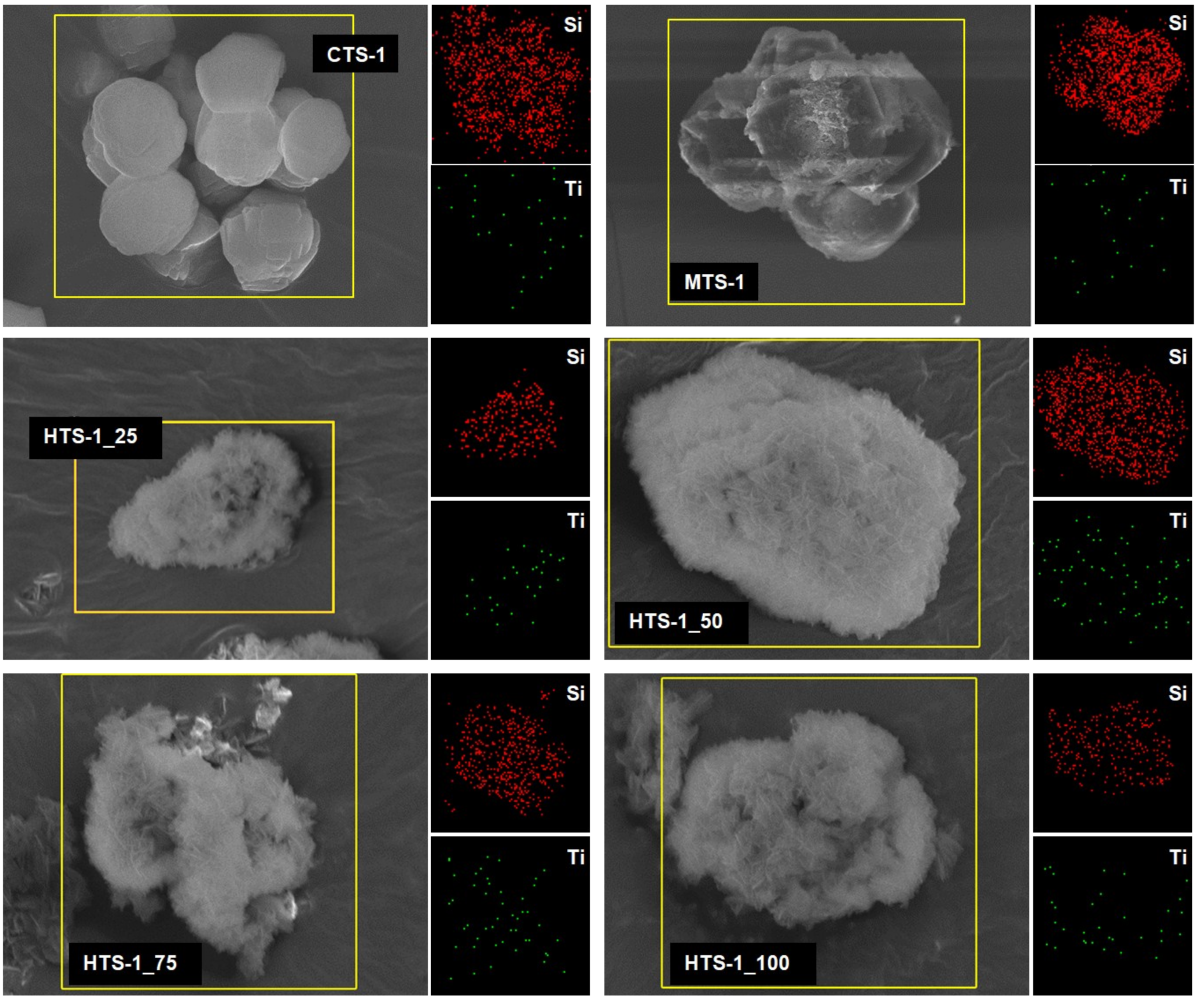

Figure S5. SEM images and EDS elemental distributions of various TS-1 samples.

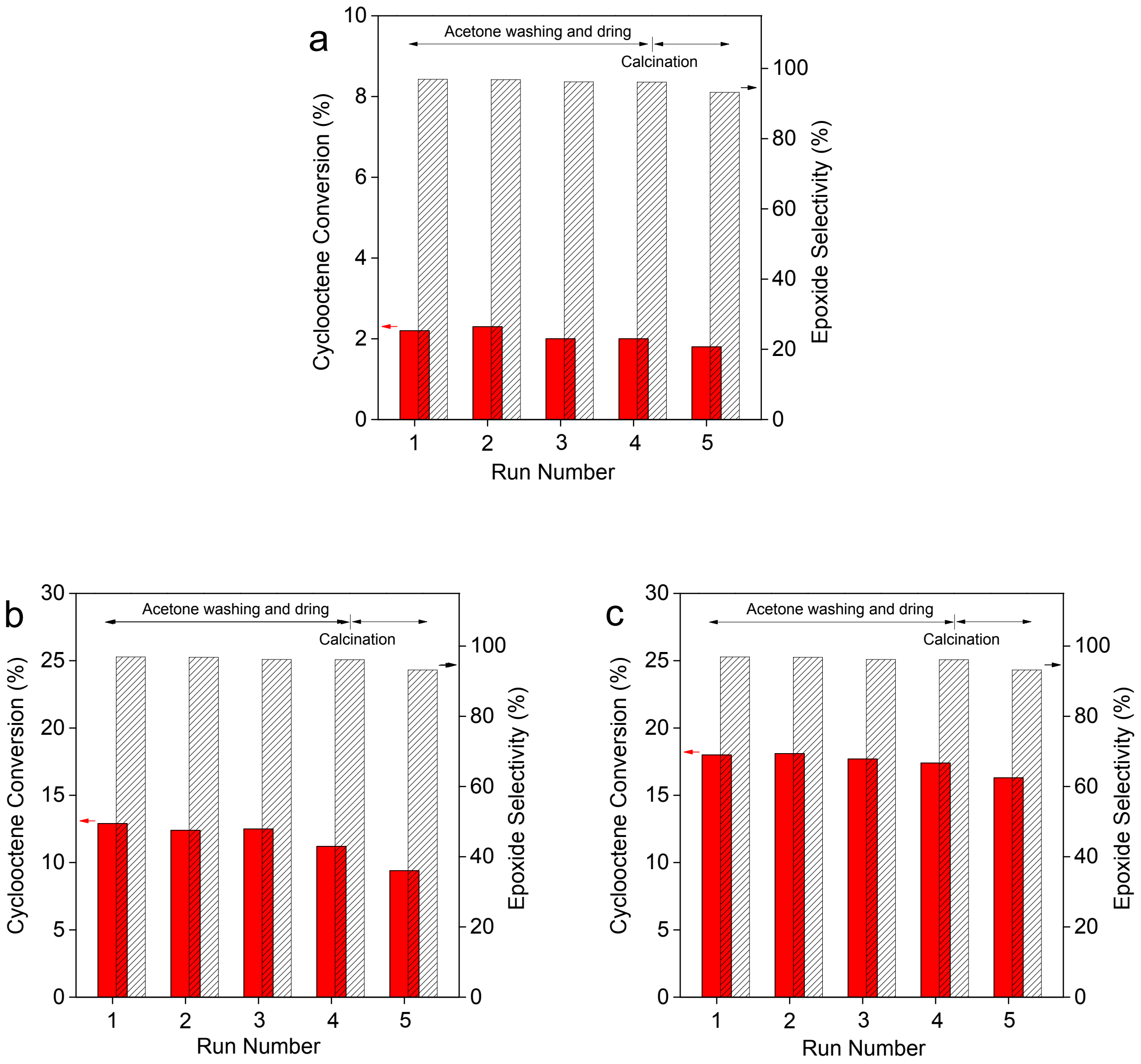

Figure S6. Changes of cyclooctene conversion and epoxide selectivity with the reaction run numbers over (a) CTS-1, (b) MTS-1 and (c) HTS-1. Reaction conditions: 10 mmol cyclic olefins, 0.05 g catalyst, 10 ml CH_3CN, 10 mmol H_2O_2 (30 wt%), 60^oC, 2 h. Because 5-10 wt% weight loss of catalysts happened in every catalytic run during collection, the next catalytic run proceeded in a reduced system with a constant ratio of catalyst-reactant-oxidant-solvent.

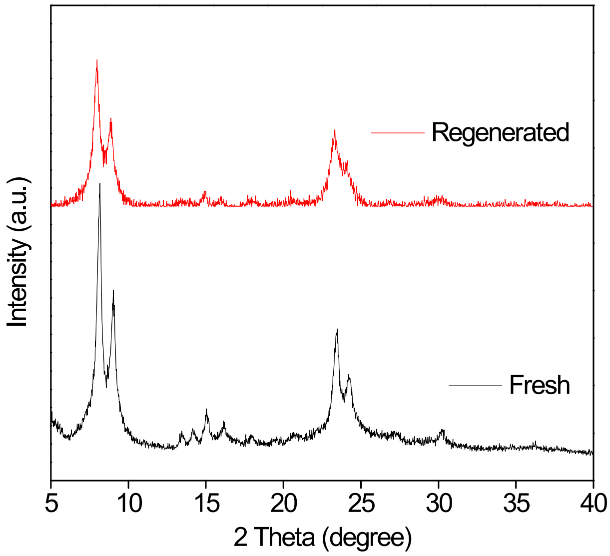

Figure S7. X-ray diffraction patterns of the fresh and regenerated HTS-1_50 catalyst.

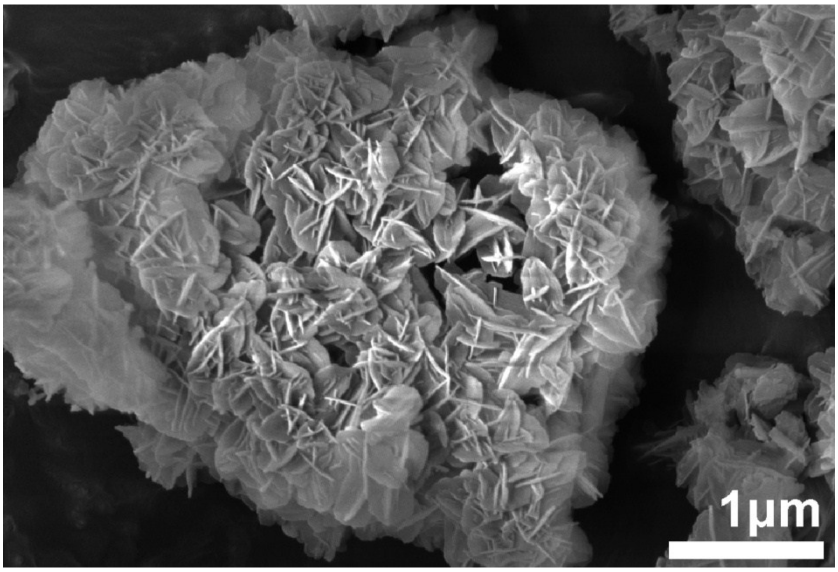

Figure S8. The SEM image of the regenerated HTS-1_50 catalyst by calcination.

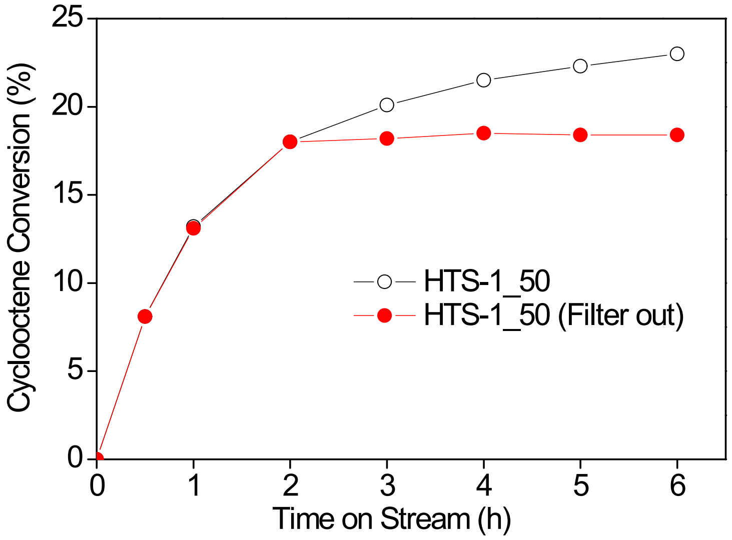

Figure S9. The leaching test of HTS-1_50. It was found that the conversion of cyclooctene almost stopped after the catalyst was filtered out at 2 hours, and the Ti content of the sample after leaching was 238 μmol.g^{-1} determined by ICP-OES, closed to the value (238 μmol.g^{-1}) of the fresh sample, indicating that the leaching of Ti active sites in HTS-1_50 was effectively suppressed.

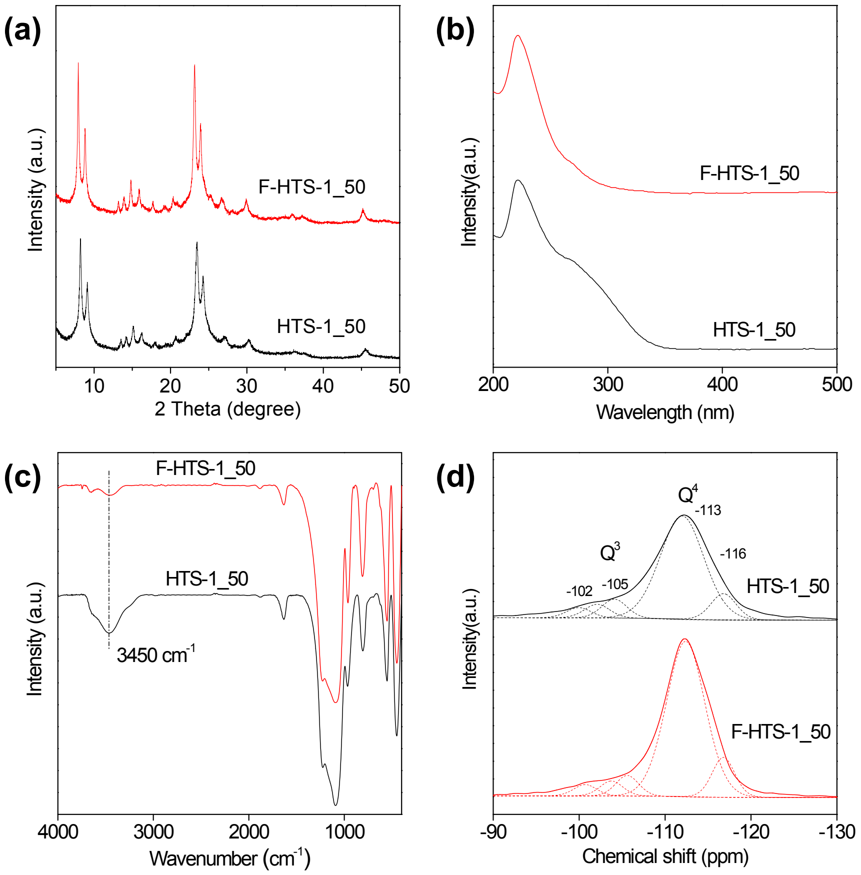

Figure S10. (a) X-ray diffraction patterns, (b) FTIR spectra, (c) UV-visible spectra and (d) ^{29}Si MAS NMR spectra of HTS-1_50 before and after the fluoride treatment

Table S1. Textural properties of the CTS-1, MTS-1 and HTS-1_50 zeolites from Hg intrusion measurements.

Samples	V_{total} [$cm^3.g^{-1}$]	S_{total} [$m^2.g^{-1}$]	D_{Bulk} [$g.cm^{-3}$]	$D_{Skeletal}$ [$g.cm^{-3}$]	Porosity [%]
CTS-1	0.51	11.45	0.90	1.65	45.69
MTS-1	0.89	22.52	0.70	1.83	61.87
HTS-1_50	4.68	123.41	0.17	0.91	81.00

V_{total}:total intrusion volume, S_{total}:total pore area, D_{Bulk}: bulk density, $D_{Skeletal}$: skeletal density.

Table S2. Recyclability of the CTS-1, MTS-1 and HTS-1_50 catalysts in the epoxidation of cyclooctene [a]

Samples	Run Number [b]	Conversion [%]	Recyclability [c] [%]	Product selectivity [%] [d]	
				Epoxide	Diol
CTS-1	1st run	2.2	100.0	98.2	1.8
	2nd run	2.2	100.0	98.4	1.6
	3rd run	2.0	90.9	98.3	1.7
	4th run	2.0	90.9	98.1	1.9
	5th run	1.8	81.8	98.1	1.9
MTS-1	1st run	12.9	100.0	92.3	7.7
	2nd run	12.4	96.1	92.6	7.4
	3rd run	12.5	96.9	92.1	7.9
	4th run	11.2	86.8	91.5	8.5
	5th run	9.4	72.9	91.1	8.9
HTS-1_50	1st run	18.0	100.0	96.9	3.1
	2nd run	18.1	100.0	96.8	3.2
	3rd run	17.7	98.3	95.2	4.8
	4th run	17.4	96.7	96.1	3.9
	5th run	16.9	93.9	96.6	3.4

[a] Reaction conditions: 10 mmol cyclic olefins, 0.05 g catalyst, 10 ml CH_3CN, 10 mmol H_2O_2 (30 wt%), 60°C, 2 h. Because 5-10 wt% weight loss of catalysts happened in every catalytic run during collection, the next catalytic run proceeded in a reduced system with a constant ratio of catalyst-reactant-oxidant-solvent.

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

[c] Recyclability is defined as the percentage retention of conversion ($\frac{\text{Conv.}_{\text{current run}}}{\text{Conv.}_{\text{1st run}}} \times 100\%$).

[d] Epoxide: cyclooctene oxide; Diol: 1, 2-cyclooctenediol.