Supporting information

Functional-mother-liquor reversed titanium species to green construct anatase-free hollow TS-1 with tunable titanium micro-environment via kinetics-thermodynamics co-regulatory pathway

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Notes:

The authors declare no competing financial interest.

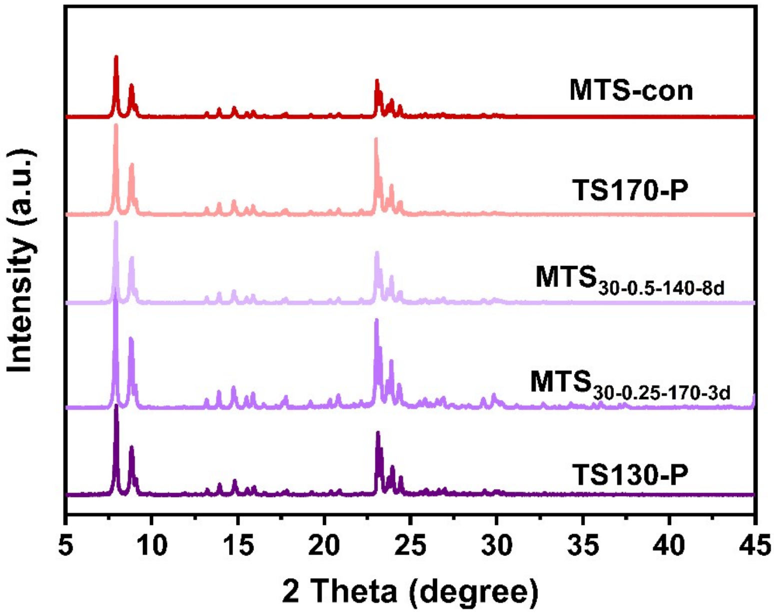


Figure S1. XRD patterns of recrystallized samples and parent samples

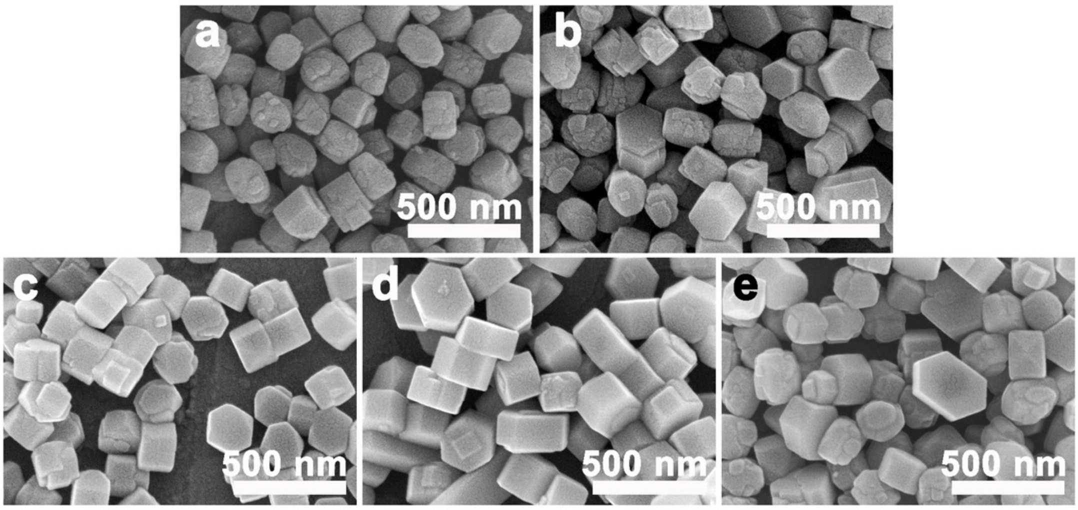


Figure S2. SEM images of recrystallized samples and parent samples: (a) TS130-P; (b) TS170-P; (c) MTS30-0.5-140-8d; (d) MTS30-0.25-170-3d and (e) MTS-con

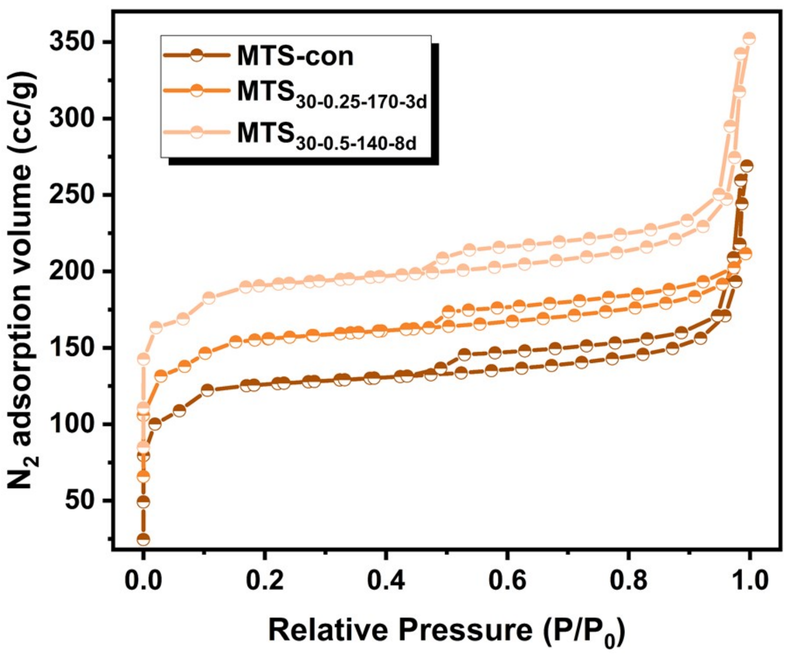


Figure S3. N_2 adsorption-desorption isotherms of recrystallized samples

Table S1. Textual parameters of synthesized zeolites at various synthetic conditions

sample	S_{BET}[a] (m^2/g)	S_{ext}[b] (m^2/g)	V_{micro}[b] (cm^3/g)	V_{meso}[c] (cm^3/g)	V_{total}[d] (cm^3/g)
$MTS_{30\text{-}0.125\text{-}170\text{-}3d}$	382.16	29.66	0.182	0.120	0.292
$MTS_{30\text{-}0.25\text{-}170\text{-}3d}$	398.72	41.26	0.182	0.172	0.351
$MTS_{30\text{-}0.5\text{-}170\text{-}3d}$	419.74	47.54	0.183	0.186	0.359
$MTS_{30\text{-}0.75\text{-}170\text{-}3d}$	419.60	44.82	0.180	0.230	0.393
$MTS_{30\text{-}1\text{-}170\text{-}3d}$	400.15	46.05	0.184	0.182	0.346
$MTS_{30\text{-}0.5\text{-}140\text{-}3d}$	427.54	49.46	0.185	0.285	0.452
$MTS_{30\text{-}0.5\text{-}150\text{-}3d}$	399.41	45.76	0.182	0.176	0.349
$MTS_{30\text{-}0.5\text{-}180\text{-}3d}$	376.31	50.35	0.162	0.219	0.371
$MTS_{30\text{-}0.5\text{-}140\text{-}8d}$	420.74	61.49	0.174	0.278	0.452
MTS-con	401.30	43.47	0.178	0.242	0.415

[a]Measured from multipoint BET method; [b]Measured from t-plot method; [c]V_{meso} calculated by using BJH method, [d]Determined from adsorbed volume at P/P_0=0.99.

Table S2. Various titanium content of different TS-1 samples

Sample	Ti content[a] (wt%)	Framework Ti content[b] (wt%)	Extra-framework Ti content[b] (wt%)	Anatase content[b] (wt%)
$MTS_{30\text{-}0.125\text{-}170\text{-}3d}$	1.67	1.11	0.56	0.00
$MTS_{30\text{-}0.25\text{-}170\text{-}3d}$	1.42	0.79	0.63	0.00
$MTS_{30\text{-}0.5\text{-}170\text{-}3d}$	1.50	0.62	0.65	0.23
$MTS_{30\text{-}0.75\text{-}170\text{-}3d}$	1.74	0.83	0.52	0.39
$MTS_{30\text{-}1\text{-}170\text{-}3d}$	1.25	0.74	0.33	0.18
$MTS_{30\text{-}0.5\text{-}140\text{-}3d}$	1.11	0.40	0.71	0.00
$MTS_{30\text{-}0.5\text{-}150\text{-}3d}$	1.14	0.44	0.53	0.17
$MTS_{30\text{-}0.5\text{-}180\text{-}3d}$	1.79	0.96	0.00	0.83
$MTS_{30\text{-}0.5\text{-}140\text{-}8d}$	1.24	0.57	0.67	0.00
TS130-P	1.19	0.86	0.33	0.00
TS170-P	1.70	1.35	0.35	0.00
MTS-con	2.06	1.37	0.45	0.24

[a]Measured by ICP; [b]determined by ICP and UV-vis spectra.

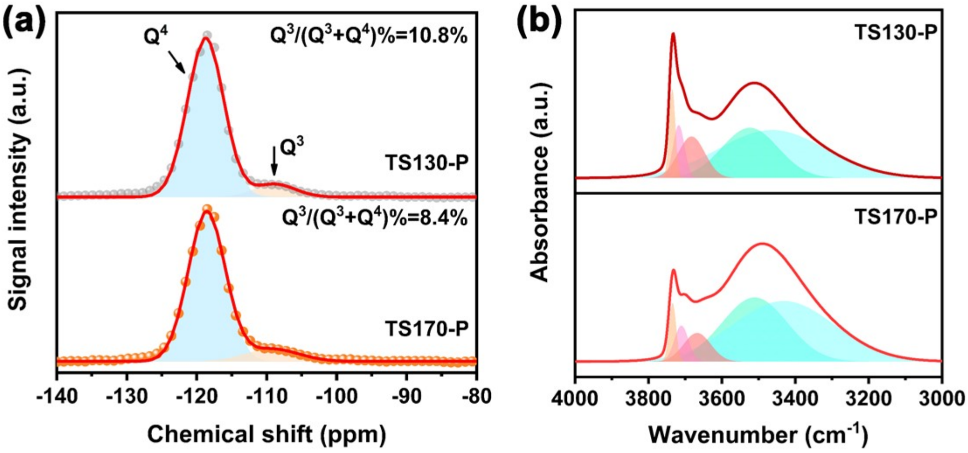


Figure S4. (a) Si MAS NMR spectra of parent zeolites and (b) FT-IR spectra in hydroxyl vibration region of parent zeolites

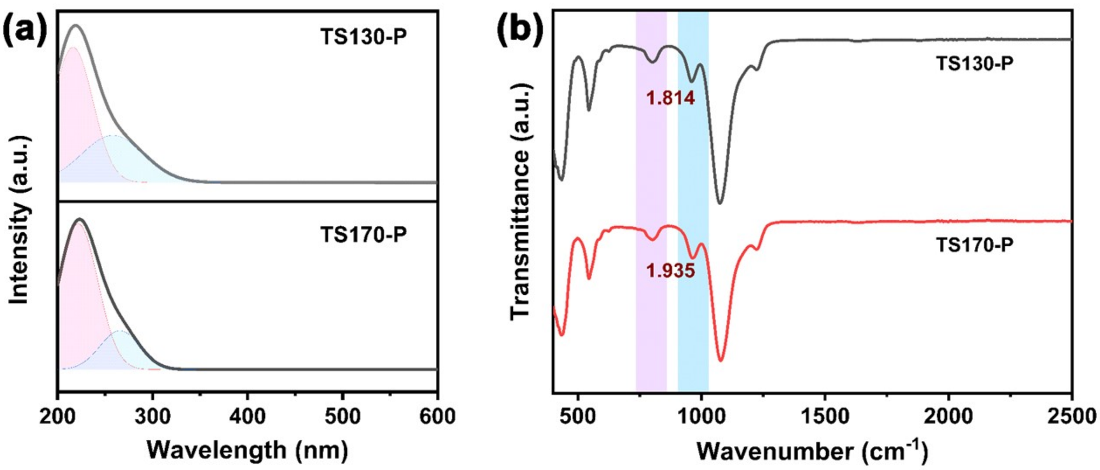


Figure S5. UV-vis spectra and FT-IR spectra of parent samples (TS130-P and TS170-P)

Table S3. Utilization results of different TS-1 zeolites

Sample	Parent zeolite weight (g)	Recrystallized sample weight (g)	Species Utilization (%)
$MTS_{30\text{-}0.125\text{-}170\text{-}3d}$	0.125	0.382	83.3
$MTS_{30\text{-}0.25\text{-}170\text{-}3d}$	0.25	0.565	86.8
$MTS_{30\text{-}0.5\text{-}170\text{-}3d}$	0.50	0.801	86.0
$MTS_{30\text{-}0.75\text{-}170\text{-}3d}$	0.75	0.993	82.4
$MTS_{30\text{-}1\text{-}170\text{-}3d}$	1.00	1.210	80.3
$MTS_{30\text{-}0.5\text{-}140\text{-}3d}$	0.50	0.582	72.4
$MTS_{30\text{-}0.5\text{-}150\text{-}3d}$	0.50	0.620	74.8
$MTS_{30\text{-}0.5\text{-}180\text{-}3d}$	0.50	0.756	83.2
$MTS_{30\text{-}0.5\text{-}140\text{-}8d}$	0.50	0.679	78.4
MTS-con	0.25	0.225	83.4
TS130-P	--	--	67.3
TS170-P	--	--	85.0

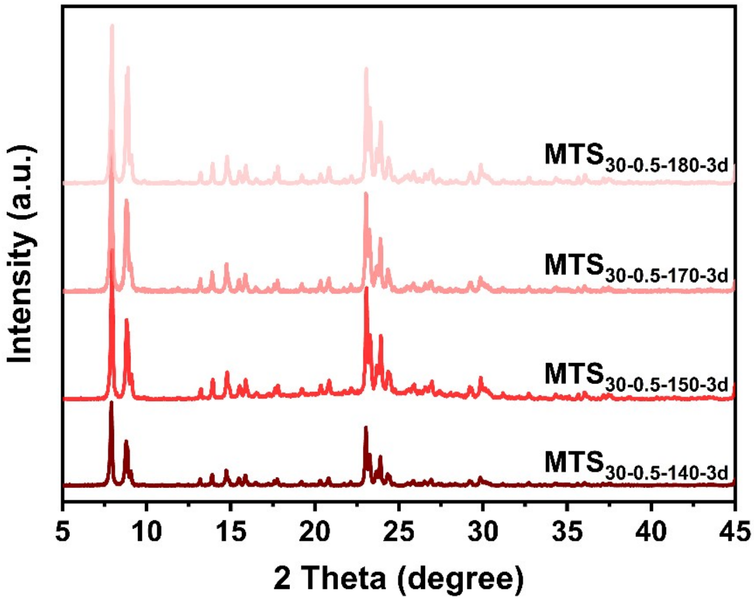


Figure S6. XRD patterns of post-treated samples at different recrystallization temperatures

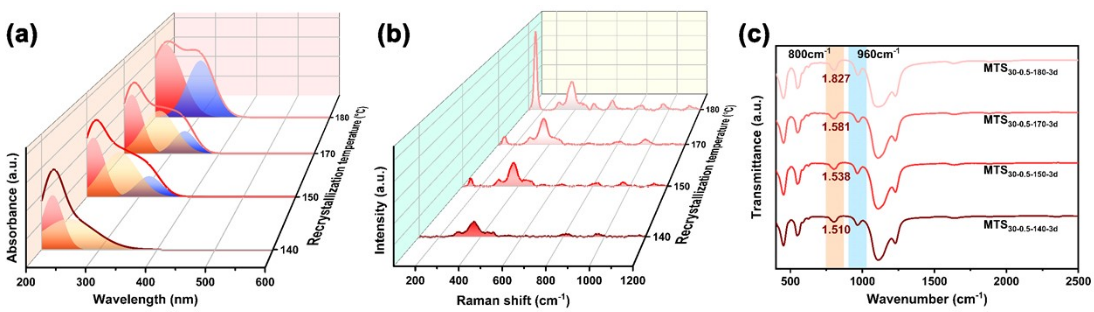


Figure S7. (a) UV-vis spectra, (b) Raman spectra and (c) FT-IR spectra of post-treated samples at different recrystallization temperatures.

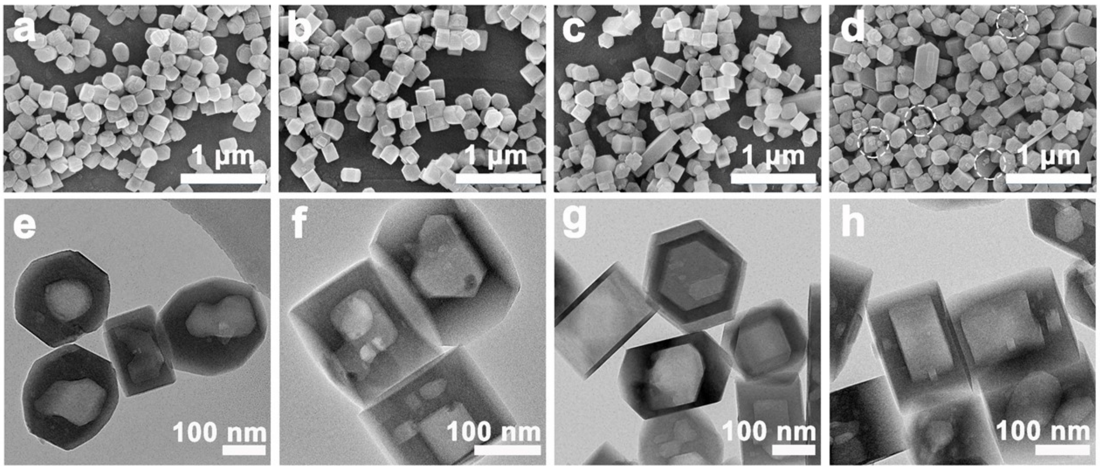


Figure S8. SEM and TEM images of post-treated samples at different recrystallization temperatures: (a, e) 413 K; (b, f) 423 K; (c, g) 443 K and (d, h) 453 K

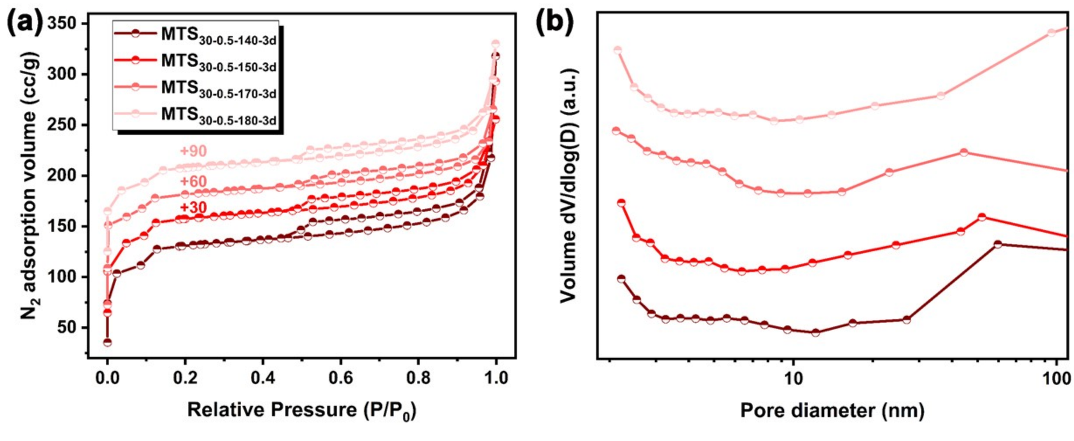


Figure S9. N_2 adsorption-desorption isotherms and pore size distributions of post-treated samples at different recrystallization temperatures

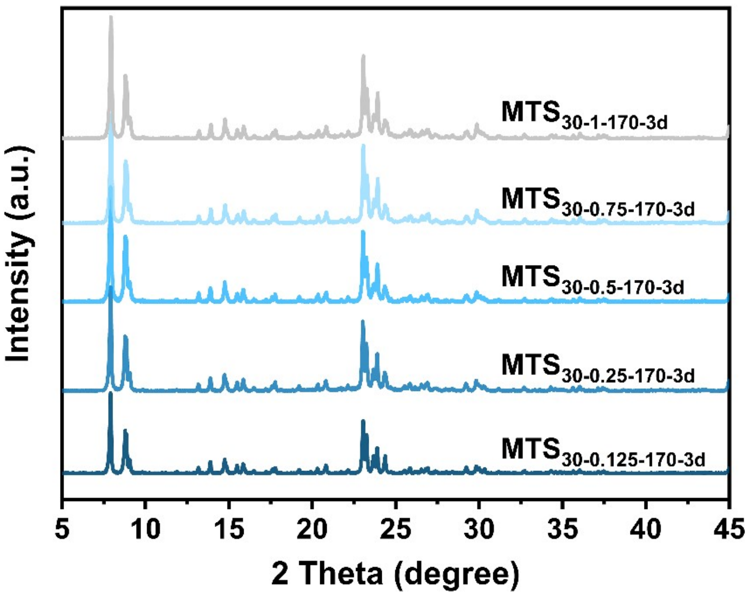


Figure S10. XRD patterns of post-treated samples at different liquid-to-solid ratios

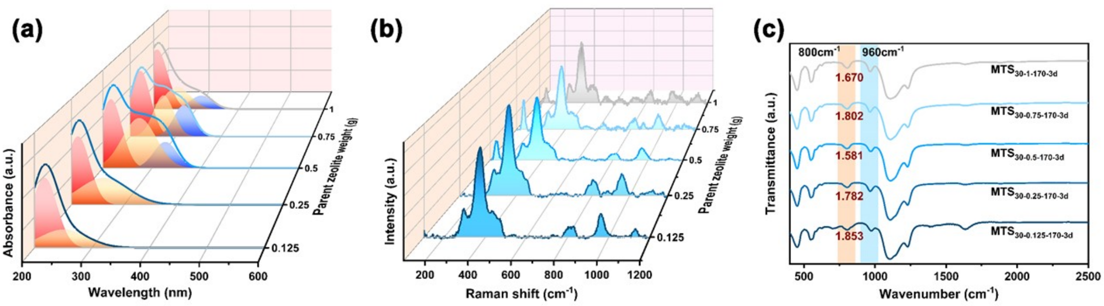


Figure S11. (a) UV-vis spectra, (b) Raman spectra and (c) FT-IR spectra of post-treated samples at different liquid-to-solid ratios.

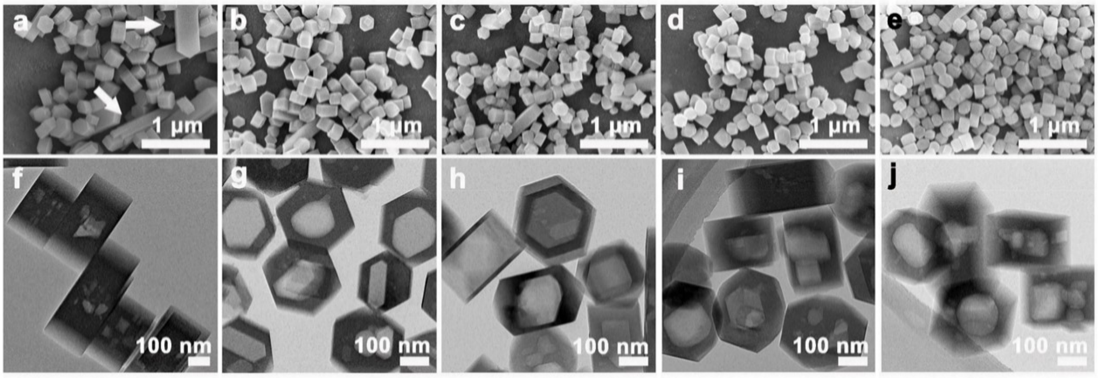


Figure S12. SEM and TEM images of post-treated samples at different liquid-to-solid ratios: (a, f) 160 ($MTS_{30\text{-}0.125\text{-}170\text{-}3d}$); (b, g) 80 ($MTS_{30\text{-}0.25\text{-}170\text{-}3d}$); (c, h) 40 ($MTS_{30\text{-}0.5\text{-}170\text{-}3d}$); (d, i) 27 ($MTS_{30\text{-}0.75\text{-}170\text{-}3d}$) and (e, j) 20 ($MTS_{30\text{-}1\text{-}170\text{-}3d}$)

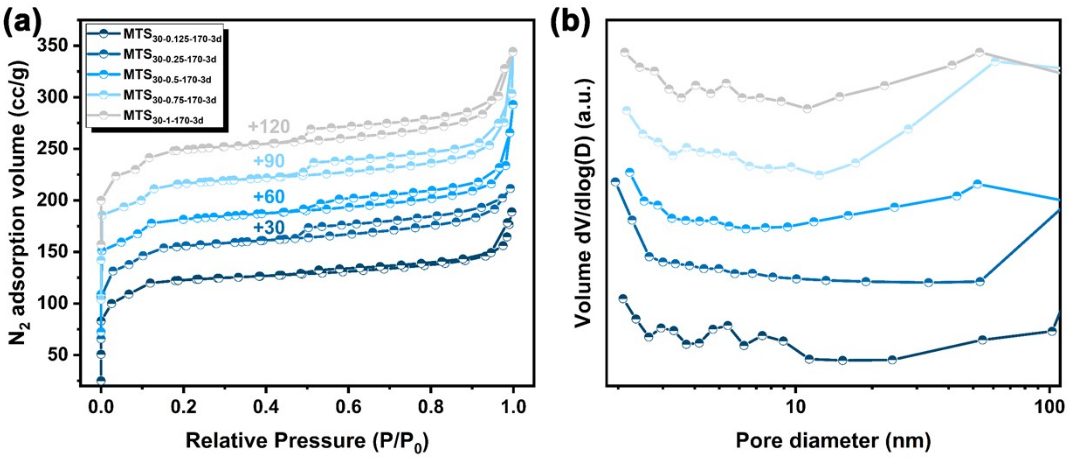


Figure S13. N_2 adsorption-desorption isotherms and pore size distributions of post-treated samples at different liquid-to-solid ratios

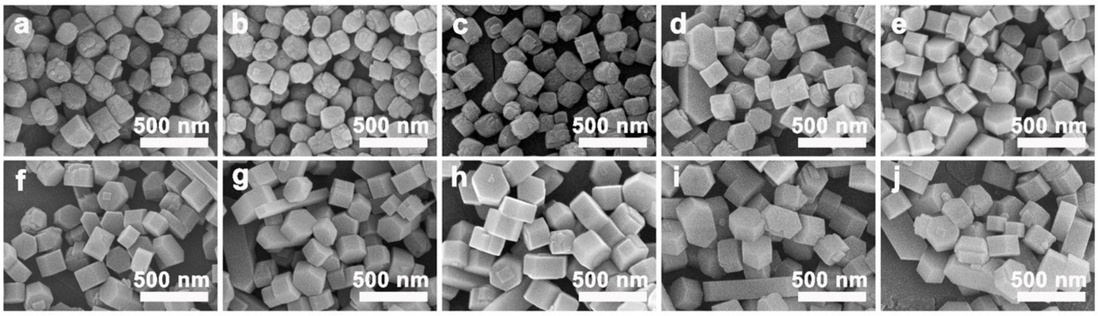


Figure S14. SEM images of $MTS_{30\text{-}0.25\text{-}170\text{-}xh}$ samples: x=(a) 0; (b) 2; (c) 6; (d) 12; (e) 24; (f) 48; (g) 60; (h) 72; (i) 84; (j) 96

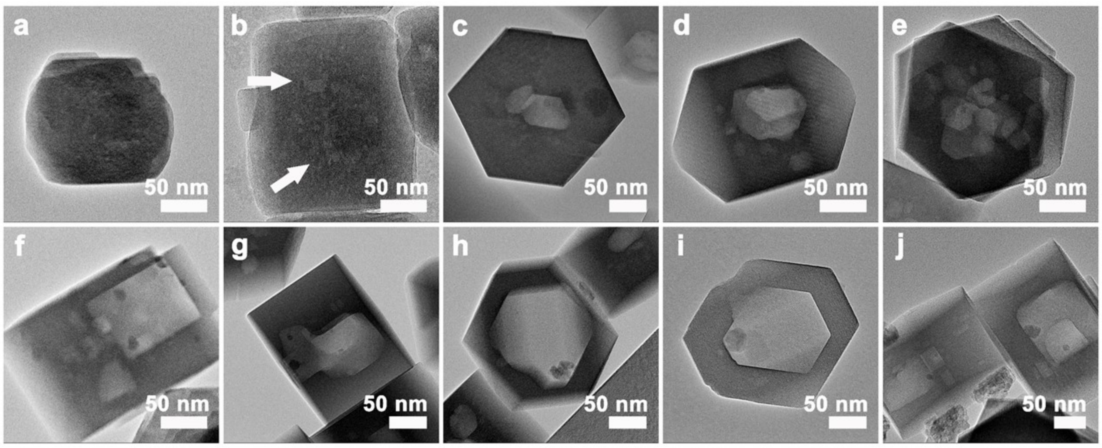


Figure S15. TEM images of $MTS_{30\text{-}0.25\text{-}170\text{-}xh}$ samples: x= (a) 0; (b) 2; (c) 6; (d) 12; (e) 24; (f) 48; (g) 60; (h) 72; (i) 84; (j) 96

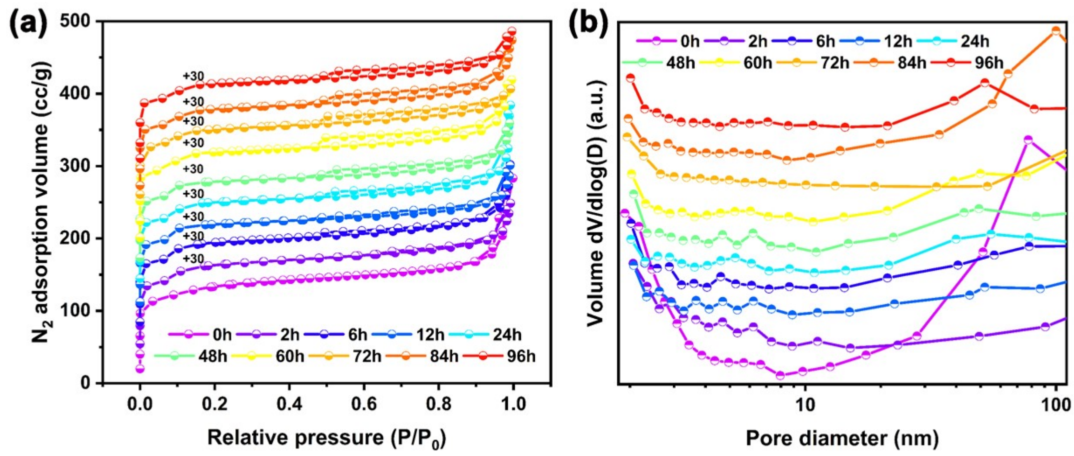


Figure S16. N_2 adsorption-desorption isotherms and pore size distributions of $MTS_{30-0.25-170-xh}$ samples at different time points

Table S4. Textual parameters of $MTS_{30-0.25-170-xh}$ at different time points

sample	S_{BET}[a] (m^2/g)	S_{ext}[b] (m^2/g)	V_{micro}[b] (cm^3/g)	V_{meso}[c] (cm^3/g)	V_{total}[d] (cm^3/g)
TS130-P	435.67	35.44	0.198	0.110	0.268
$MTS_{30-0.25-170-2h}$	426.48	41.97	0.192	0.159	0.334
$MTS_{30-0.25-170-6h}$	434.66	46.90	0.189	0.196	0.375
$MTS_{30-0.25-170-12h}$	420.72	49.37	0.188	0.204	0.388
$MTS_{30-0.25-170-24h}$	419.25	50.47	0.187	0.253	0.435
$MTS_{30-0.25-170-48h}$	409.44	42.35	0.186	0.206	0.372
$MTS_{30-0.25-170-60h}$	406.96	38.12	0.184	0.181	0.370
$MTS_{30-0.25-170-72h}$	398.72	41.26	0.182	0.172	0.351
$MTS_{30-0.25-170-84h}$	404.71	43.21	0.185	0.173	0.346
$MTS_{30-0.25-170-96h}$	399.66	38.65	0.179	0.183	0.350

[a]Measured from multipoint BET method; [b]Measured from t-plot method; [c]V_{meso} calculated by using BJH method, [d]Determined from adsorbed volume at P/P_0=0.99.

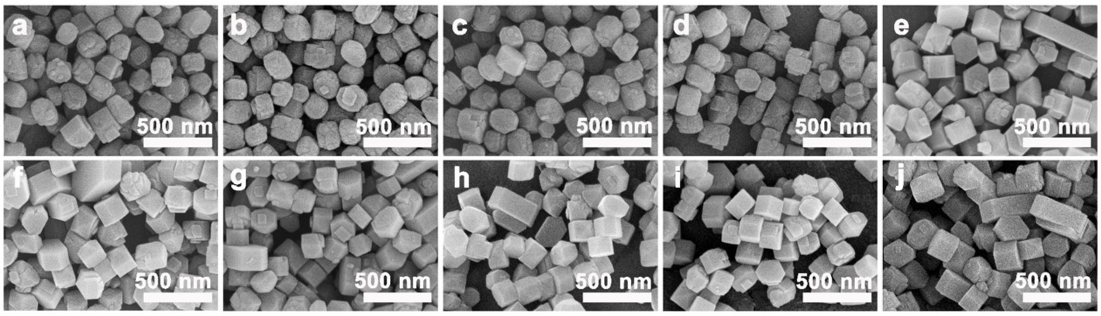


Figure S17. SEM images of $MTS_{30\text{-}0.5\text{-}170\text{-}xh}$ samples: x= (a) 0; (b) 2; (c) 6; (d) 12; (e) 24; (f) 48; (g) 60; (h) 72; (i) 84; (j) 96

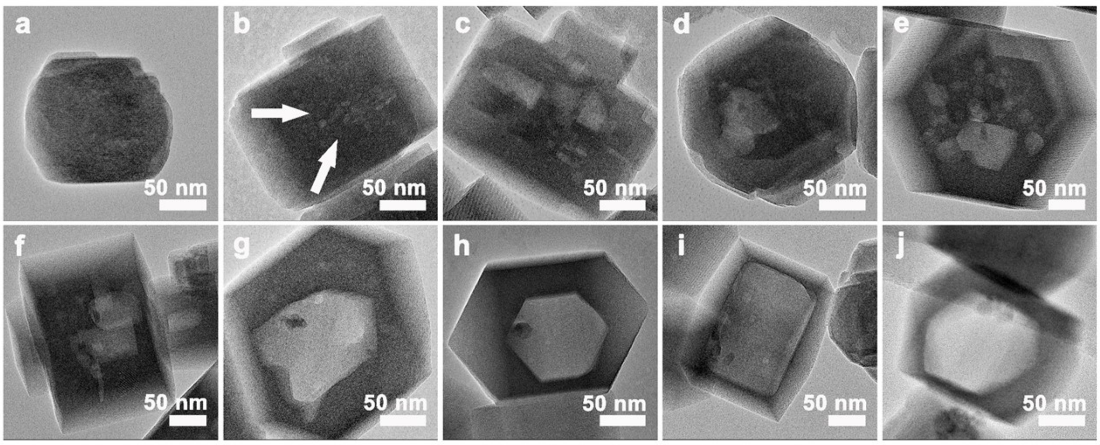


Figure S18. TEM images of $MTS_{30\text{-}0.5\text{-}170\text{-}xh}$ samples: x= (a) 0; (b) 2; (c) 6; (d) 12; (e) 24; (f) 48; (g) 60; (h) 72; (i) 84; (j) 96

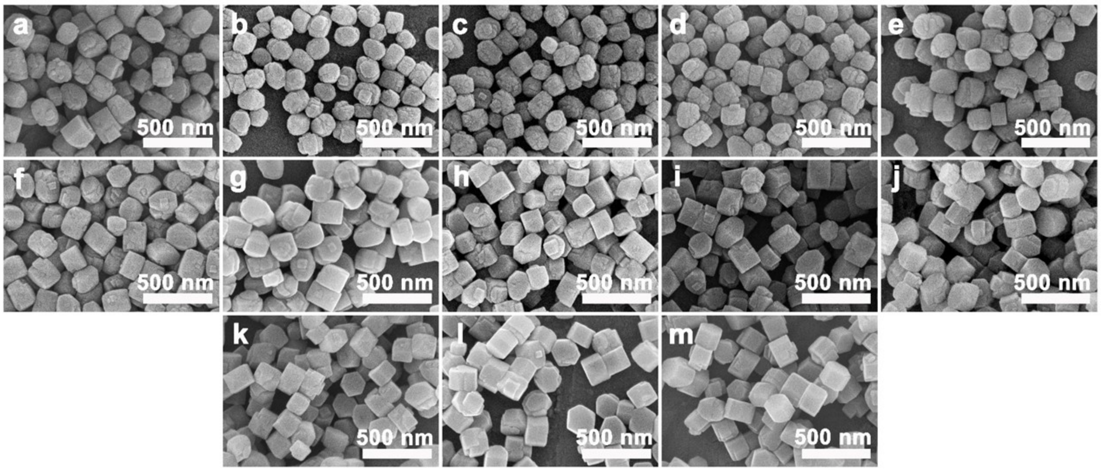


Figure S19. SEM images of $MTS_{30\text{-}0.5\text{-}140\text{-}xh}$ samples: (a) 0; (b) 2; (c) 6; (d) 12; (e) 24; (f) 48; (g) 72; (h) 96; (i)120; (j) 144; (k) 168; (l) 192 and (m) 216

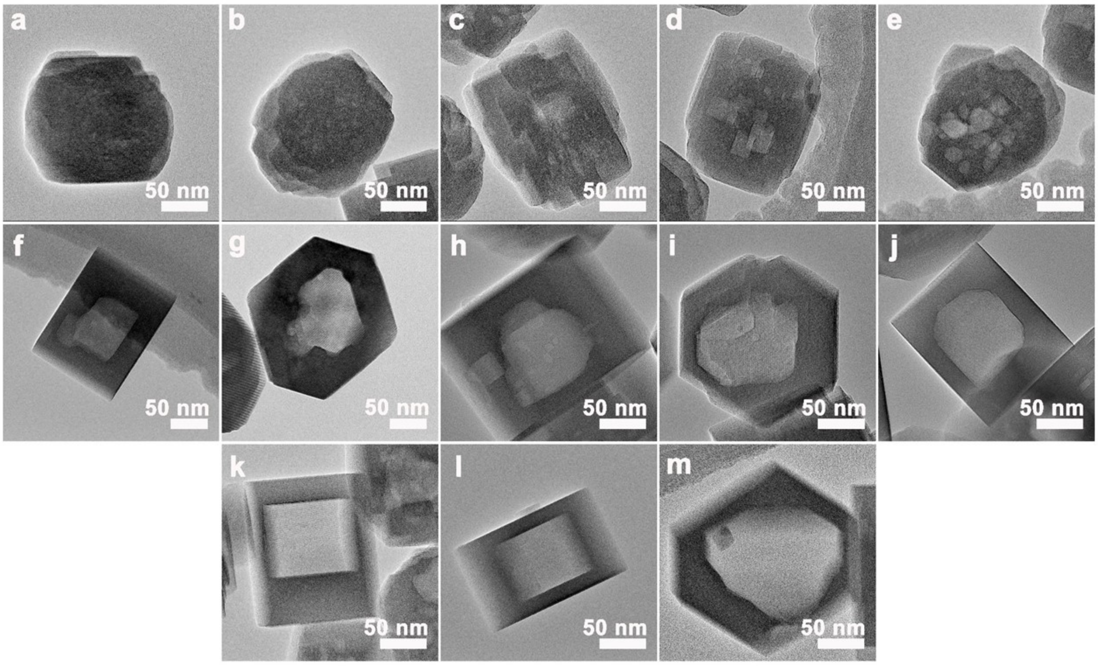


Figure S20. TEM images of $MTS_{30\text{-}0.5\text{-}140\text{-}xh}$ samples: (a) 0; (b) 2; (c) 6; (d) 12; (e) 24; (f) 48; (g) 72; (h) 96; (i)120; (j) 144; (k) 168; (l) 192 and (m) 216

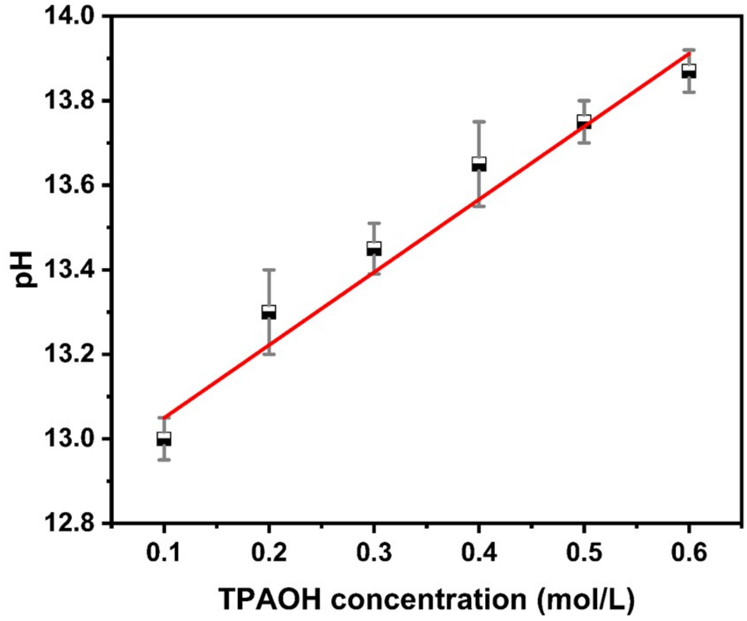


Figure S21. Fitting curve of pH and TPAOH solution concentration

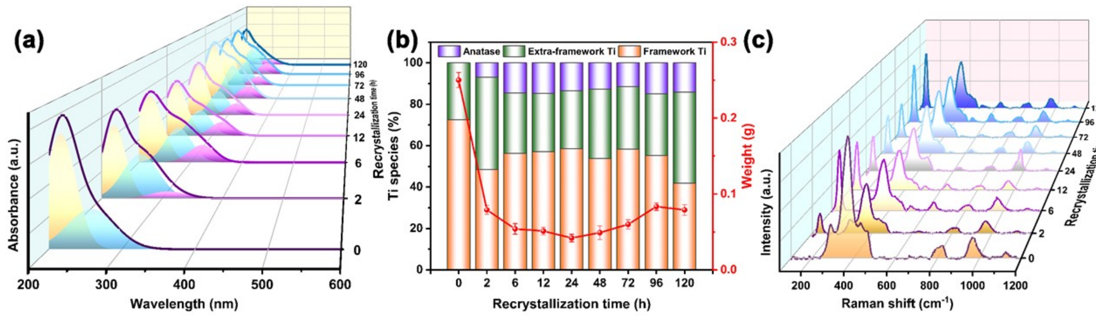


Figure S22. (a) UV-vis spectra, (b) distributions of titanium species and weight varying (c) Raman spectra of recrystallized TS130-P samples by 0.2 M TPAOH at different time points

Table S5. Catalysis test results of different TS-1 zeolites

catalyst	Ti content[a] (wt%)	Ti content[b] (wt%)	1-Hexene[c]			Phenol[d]		
			Conv. (%)	Selectivity (%)		Conv. (%)	Selectivity (%)	
				Epoxide	Others		DHB (HQ/CAT)	BQ
$MTS_{30-0.125-170-3d}$	1.11	1.33	46.1	97.4	2.6	22.2	94.1(46.4/47.7)	5.9
$MTS_{30-0.25-170-3d}$	0.79	1.40	48.8	97.9	2.1	27.8	98.0(48.0/50.0)	2.0
$MTS_{30-0.5-170-3d}$	0.62	1.17	42.5	98.7	1.3	22.5	98.5(48.1/50.4)	1.5
$MTS_{30-0.75-170-3d}$	0.83	0.92	39.6	99.5	0.5	19.9	97.6(49.8/47.8)	2.4
$MTS_{30-1-170-3d}$	0.74	0.90	40.3	95.5	4.5	23.7	98.8(50.8/48.0)	1.2
$MTS_{30-0.5-140-3d}$	0.40	0.85	37.9	99.4	0.6	16.3	98.7(45.0/53.7)	1.3
$MTS_{30-0.5-150-3d}$	0.44	1.00	41.7	98.9	1.1	19.4	98.6(48.1/50.5)	1.4
$MTS_{30-0.5-180-3d}$	0.96	1.24	44.8	99.8	0.2	24.3	94.7(47.8/46.9)	5.3
TS130-P	0.86	0.95	40.5	99.1	0.9	19.7	99.1(45.8/53.3)	0.9

[a]Framework Ti contents were determined by ICP and UV-vis; [b]Surface non-anatase content were determined by EDS and UV-vis; [c]Reaction conditions: catalyst 50 mg, 1-hexene 10 mmol, H_2O_2 10 mmol (molar ratio of hexene: H_2O_2=1:1), methanol 10 mL, temp 333 K, time 4 h; [d]Reaction conditions: catalyst 100 mg, phenol 10 mmol, H_2O_2 3.3 mmol (molar ratio of phenol: H_2O_2=3:1), water 10 mL, temp 333 K, time 6 h.

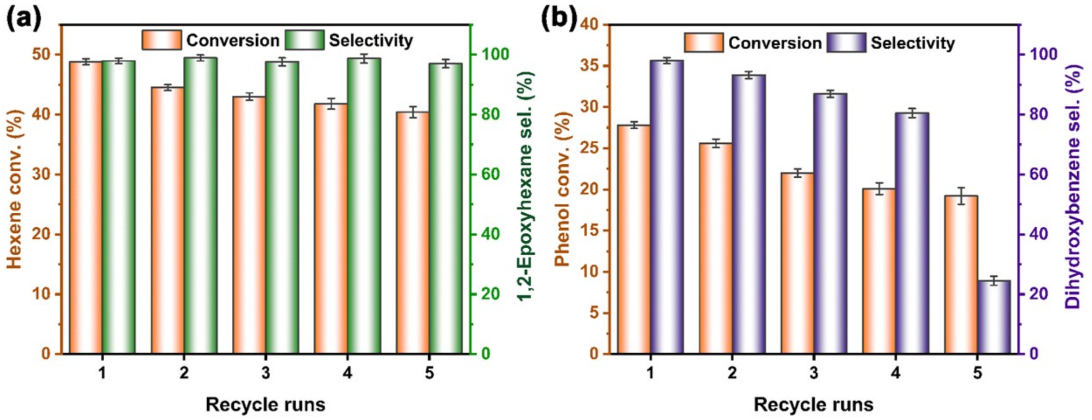
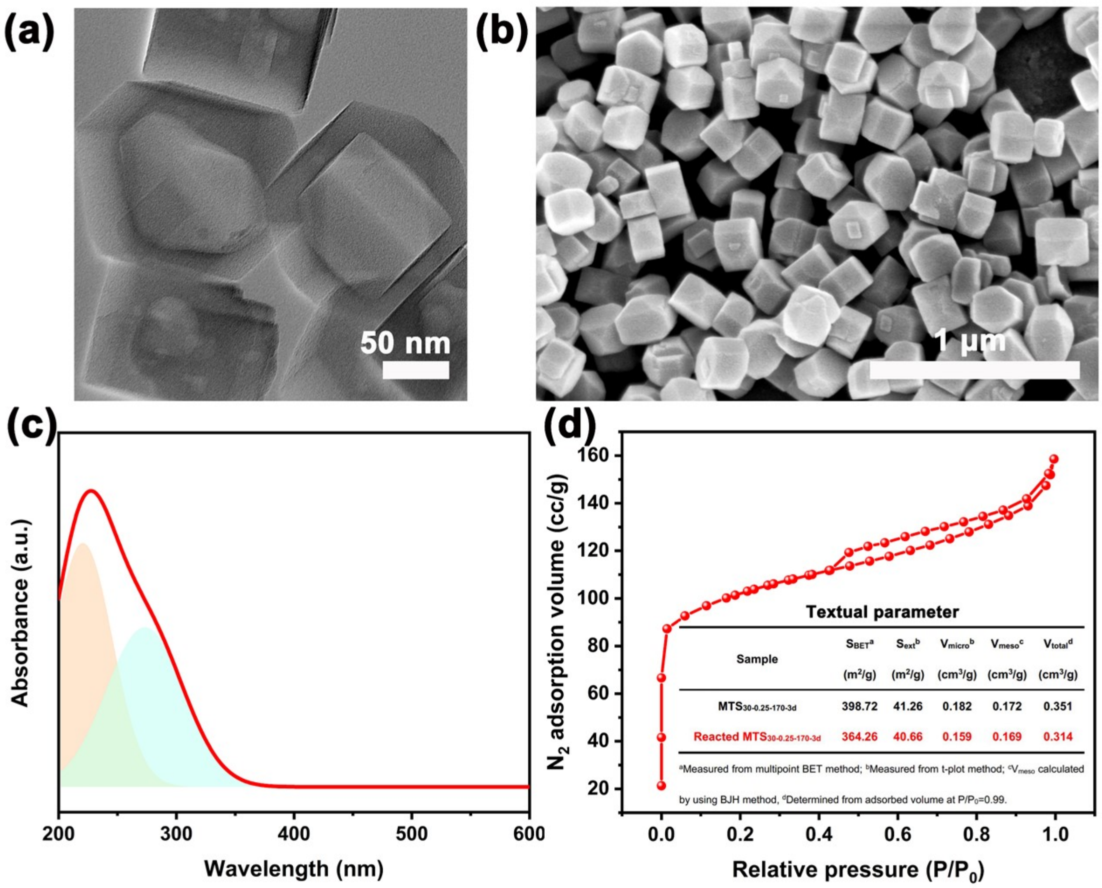


Figure S23. Recycle tests of $MTS_{30\text{-}0.25\text{-}170\text{-}3d}$: (a) 1-hexene epoxidation and (b) phenol hydroxylation



Sample	S_{BET}[a] (m^2/g)	S_{ext}[b] (m^2/g)	V_{micro}[b] (cm^3/g)	V_{meso}[c] (cm^3/g)	V_{total}[d] (cm^3/g)
$MTS_{30\text{-}0.25\text{-}170\text{-}3d}$	398.72	41.26	0.182	0.172	0.351
Reacted $MTS_{30\text{-}0.25\text{-}170\text{-}3d}$	364.26	40.66	0.159	0.169	0.314

[a]Measured from multipoint BET method; [b]Measured from t-plot method; [c]V_{meso} calculated by using BJH method, [d]Determined from adsorbed volume at P/P_0=0.99.

Figure S24. TEM images(a), SEM images (b), UV-vis spectra (c) and N_2 physisorption results (d) of recycled $MTS_{30\text{-}0.25\text{-}170\text{-}3d}$ after phenol hydroxylation.