Supporting Information

for

Selective synthesis of epichlorohydrin *via* liquid-phase allyl chloride epoxidation over modified Ti-MWW zeolite in a continuous slurry bed reactor

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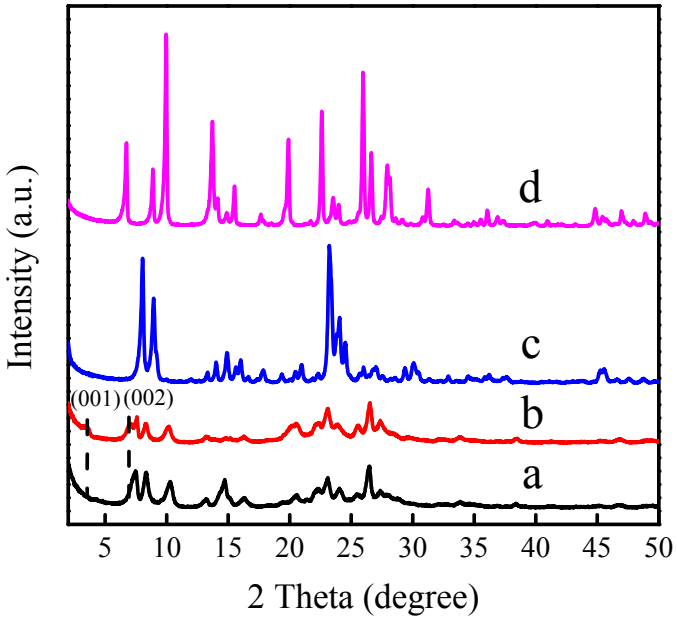


Fig. S1 XRD patterns of Ti-MWW (a), Ti-MWW-PI (b), TS-1 (c), Ti-MOR (d).

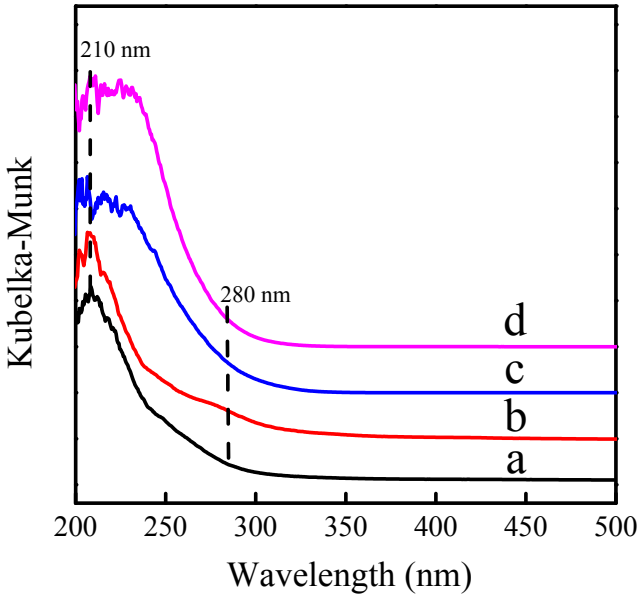


Fig. S2 UV-Vis spectra of Ti-MWW (a), Ti-MWW-PI (b), TS-1 (c), Ti-MOR (d).

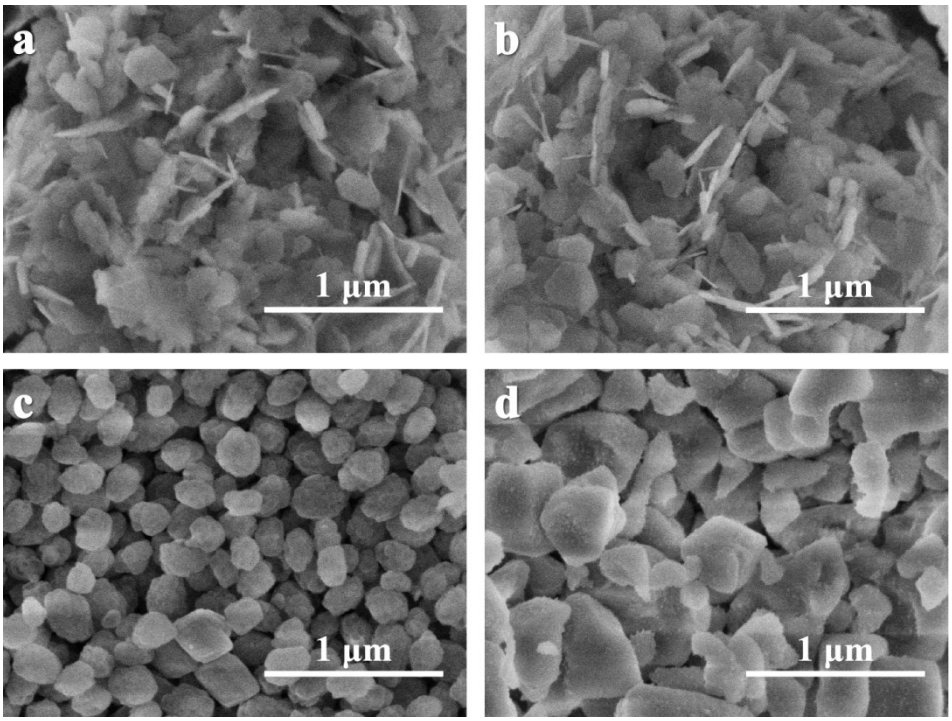


Fig. S3 Scanning electron micrograph images of Ti-MWW (a), Ti-MWW-PI (b), TS-1 (c), Ti-MOR (d).

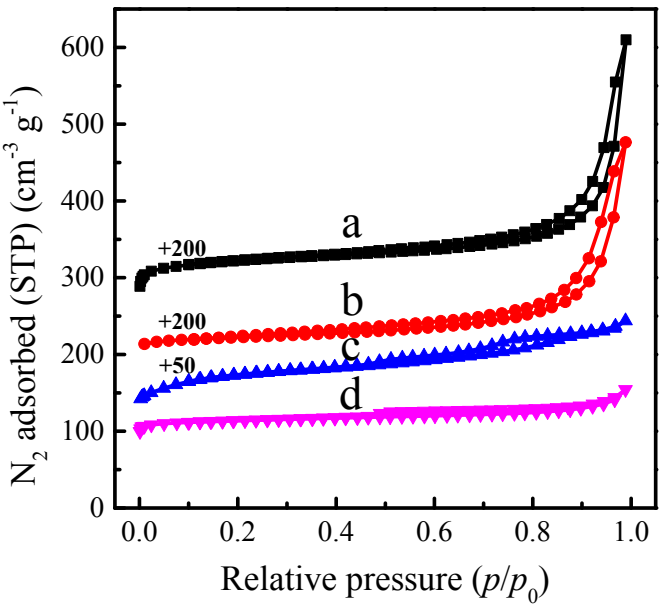


Fig. S4 N_2 adsorption-desorption isotherms of Ti-MWW (a), Ti-MWW-PI (b), TS-1 (c) and Ti-MOR (d).

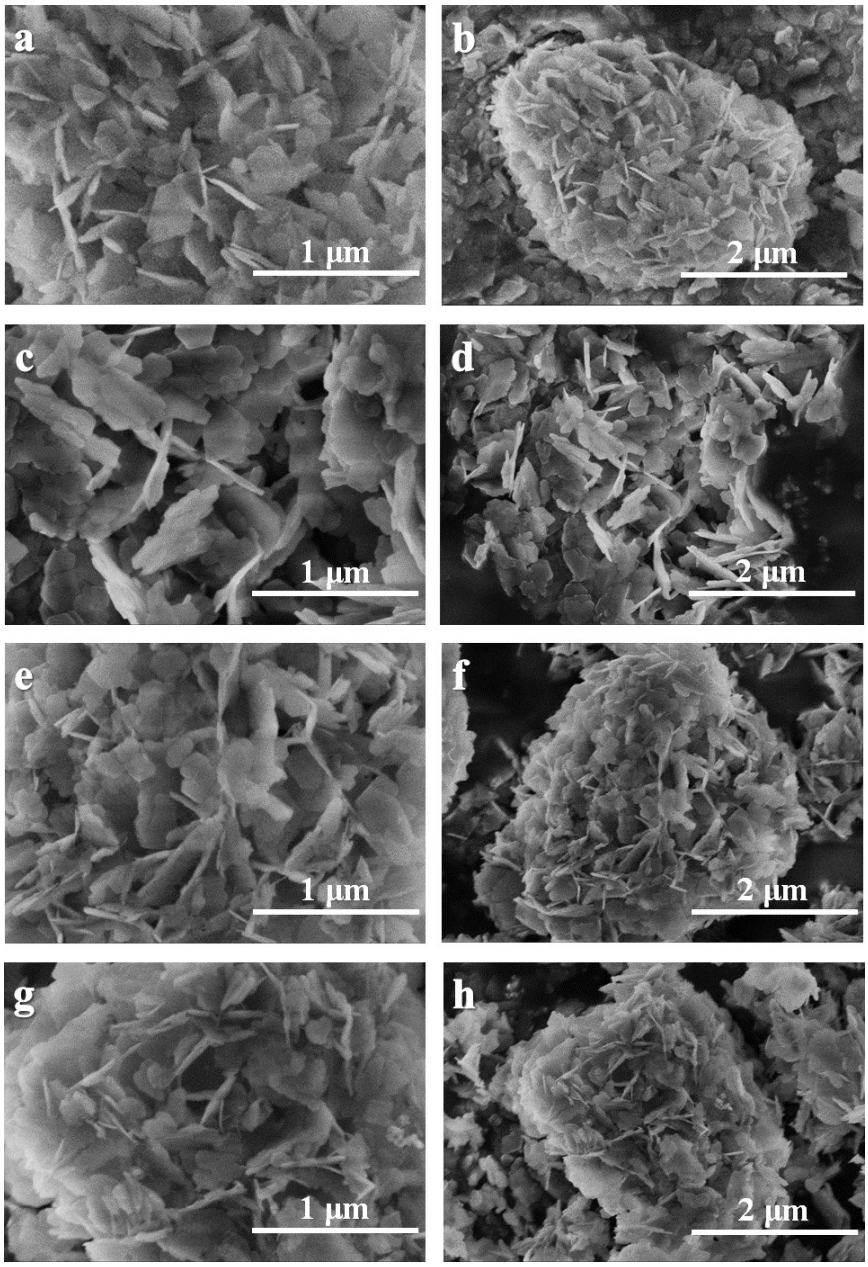


Fig. S5 Scanning electron micrograph images of Ti-MWW (a, b), fresh Ti-MWW-PI (c, d), deactivated Ti-MWW-PI (e, f) and regenerated Ti-MWW-PI (g, h).

Table S1 The physicochemical properties of various titanosilicates

Catalyst	Structure code	Crystal size[a] (μm)	Si/Ti[b]	SSA[c] (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	
					total[d]	micro.[e]
Ti-MWW	MWW	0.6 × 0.6 × 0.1	39	461	0.636	0.152
Ti-MWW-PI	MWW	0.6 × 0.6 × 0.1	39	79	0.427	0.010
TS-1	MFI	0.2 - 0.4	45	450	0.300	0.146
Ti-MOR	MOR	0.2 - 0.5	54	440	0.239	0.159

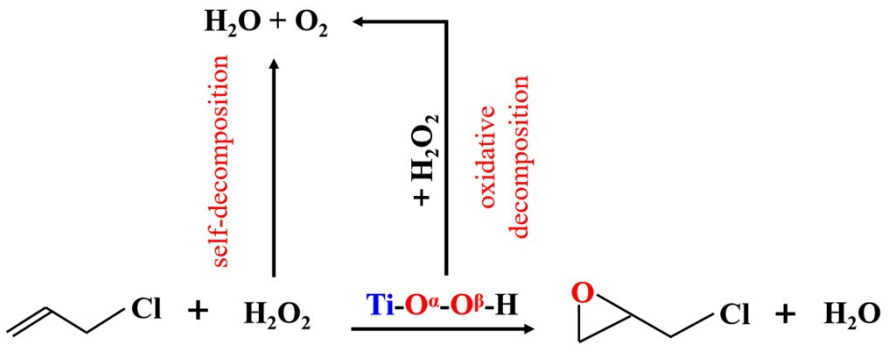
[a] Obtained by SEM

[b] Determined by ICP analysis

[c] SSA: specific surface area, determined by N_2 adsorption isotherms

[d] Total Pore volume, given by N_2 adsorption at $p/p_0 = 0.99$

[e] Micropore volume given by *t*-plot method



Scheme S1 The proposed reaction pathways of the hydrogen peroxide in the epoxidation of ALC.

The non-productive decomposition reactions of H_2O_2 included the H_2O_2 self-decomposition and the oxidative decomposition of H_2O_2 with the Ti-O^{α}-O^{β}-H intermediate species. The invalid decomposition of H_2O_2 and the consuming of H_2O_2 in ALC epoxidation were competitive.

Table S2 The catalytic performance of selective poisoned Ti-MWW-PI in ALC epoxidation[a]

Catalyst	Poisoning reagent	ALC conv. (%)	ECH sel. (%)	H_2O_2 (%)	
				conv.	eff.
Ti-MWW-PI	None	90.0	99.8	92.0	97.8
	TPA	1.6	73.8	29.8	5.4
	TPhA	88.8	99.7	93.1	95.4

[a] Reaction conditions: catalyst, 0.05 g; allyl chloride, 10 mmol; H_2O_2 (30 wt. %), 10 mmol; TBA, 5 mL; TPA (tripropylamine), 2 mmol; TPhA (triphenylamine), 2 mmol; temp., 333 K; time, 1 h

The selective poisoning experiment was conducted over Ti-MWW-PI, so as to determine where the allyl chloride (ALC) epoxidation occurred. The poisoning reagent tripropylamine (TPA) with small molecule size was able to reach all the Ti sites, while the bulky triphenylamine (TPhA) hardly entered into the 10- membered ring (MR) channels and thus selectively poisoned the Ti sites within the 12-MR side cups on the external surface. The amount of amine (2 mmol) was sufficient to poison the accessible Ti sites according to the Ti amount (0.02 mmol) in the added catalyst. As shown in Table S2, the ALC and H_2O_2 conversion were decreased from 90.0% and 92.0% to 1.6% and 29.8% when TPA was added, while the bulky TPhA had little impact on the catalytic performance. This indicated that most of Ti species located at the external 12-MR side cups did not involve in the catalytic reaction, and the ALC epoxidation mainly occurred in the intralayer 10-MR channels.

Table S3 The reaction results of ALC epoxidation over Ti-MWW with piperidine addition[a]

Catalyst	piperidine	ALC conv. (%)	ECH sel. (%)	H_2O_2 (%)	
				conv.	eff.
Ti-MWW	No	71.8	99.0	79.6	90.2
	Yes	11.7	98.8	30.2	38.7

[a] Reaction conditions: catalyst, 0.05 g; allyl chloride, 10 mmol; H_2O_2 (30 wt. %), 10 mmol; TBA, 5 mL; piperidine, 0.1 mmol; temp., 333 K; time, 1 h