

Chlorohydration of Allyl Chloride with HCl and H₂O₂ to Produce Dichloropropanols Catalyzed by Hollow TS-1 Zeolite

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1. Experimental

1.1 Catalyst preparation

- a) Liquid TiCl_4 was commercially obtained from Sigma Aldrich company, with purity $\geq 99.0\%$.
- b) Amorphous TiO_2 was synthesized by hydrolysis of tetrabutyl titanate (TBOT). 8.5 g TBOT was dissolved into 78g 1M NaOH solution with vigorous stirring at room temperature for 3 hours. Then, the mixture was filtered and washed with distilled water until the pH of the filtrate below 9. Finally, the solid was dried at 110°C for 6 hours.
- c) Amorphous $\text{TiO}_2\text{-SiO}_2$ was prepared by hydrolysis of both tetraethyl orthosilicate (TEOS) and TBOT. 31.25g TEOS and 2.12g TBOT were mixed and stirred for 5 min. Then, the mixture was slowly added in 56.16g 1M NaOH aqueous solution with vigorous stirring at room temperature. After that, the product was filtered and washed by distilled water until pH of the filtrate below 9. The filter cake was then dried at 110°C for 6 hours.
- d) Crystalline TiO_2 powders, including anatase, rutile, brookite, were synthesized by hydrothermal treatment. 42.61g TBOT, 58.96g distilled water and 101.85g TPAOH(25wt%) were mixed and stirred vigorously for 3 hours, and then the temperature was raised to 60°C and stirred for 2 hours to remove alcohol. After that, the mixture was transferred into a Teflon-lined stainless-steel autoclave for hydrothermal treatment at 170°C for 24 hours. The product was then filtered, washed by distilled water and dried at 110°C for 6h. The material was then split into two part and calcined at 550°C for 4h and 800°C respectively to obtain anatase and rutile. Synthesis of brookite. 8.5g TBOT was added into 75g 0.1M NaOH aqueous with stirring for 1 hour. After that, the mixture was transferred into a Teflon-lined stainless-steel autoclave for hydrothermal treatment at 180°C for 24 hours. The product was filtered and washed by distilled water until pH of the filtrate below 9. The filter cake was then dried at 110°C for 6 hours.
- e) $\text{TiO}_2/\text{S-1}$ was prepared by impregnation of TiCl_4 on commercial S-1 zeolite. S-1 zeolite was supplied by Sinopec Hunan Jianchang Petrochemical Co., Ltd. To obtain $\text{TiO}_2/\text{S-1}$ sample, 0.71g TiCl_4 was dissolved in 15.26g HCl aqueous (10wt %) and stirred for 30 min. Then the liquid was slowly added into 15g S-1 to obtain a mixture. After S-1 was impregnated in the liquid at room temperature for 4 hours, the mixture was dried at 110°C for 6 hours and calcined at 550°C for 4 hours.

- f) TS-1 zeolite was synthesized according to the method reported by Thangaraj. 20.74g TPAOH was added into 35.42g TEOS with stirring for hydrolysis. After stirring for 3 hours, TBOT dissolved in anhydrous isopropyl alcohol was dropped into the hydrolyzed solution. Finally, 45.70 g distilled water was added and the mixture was stirred at 80 °C for 3 hours to remove alcohol. The chemical composition of the final gel was SiO₂: TiO₂: TPAOH: H₂O=1: 0.01: 0.3: 20 and it was transferred into a Teflon-lined stainless-steel autoclave. The crystallization was carried out under autogenous pressure at 170 °C for 3 days. The mixture obtained was filtered, washed with distilled water, dried at 110 °C for 6 h, and calcined at 550 °C for 5 h.
- g) HTS zeolite was supplied by Sinopec Hunan Jianchang Petrochemical Co., Ltd.

1.2 Catalyst characterization methods

X-ray diffraction (XRD) patterns were collected on a Philips Panalytical X'pert diffractometer with nickel-filtered Cu K α radiation (40 kV, 250 mA). The 2 θ scanning ranged from 5° to 35°, and the scanning rate was 0.4° min⁻¹. X-Ray Fluorescence (XRF) experiments were conducted on a Rigaku 3721E spectrometer with W radiation (40 kV). The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo-Fischer-VG ESCALAB250 with Al K α radiation, and the framework titanium content and extra-framework titanium content were integral results of the Ti 2p_{3/2} peaks at 460.3 eV and 458.7 eV.

N₂ adsorption–desorption isotherms were collected at 77 K on a Micromeritics ASAP 2405 apparatus. The samples were previously dried under vacuum (0.1 Pa) at 300 °C for 6 h. The surface properties were derived from the isotherms using BET and t-plot methods. The UV-visible (UV-Vis) spectra were recorded on a JASCO UV-visible 550 spectrometer. The samples were pressed into a self-supported wafer, and the spectra was recorded from 200 nm to 800 nm.

Scanning electron microscopy (SEM) images were taken from a Hitachi 4800 microscope (20 kV).

1.3 Catalytic evaluations

1.3.1 Chlorohydration of AC with H₂O₂ and HCl

Chlorohydration reaction was carried out in a three necked flask equipped with a condenser and a magnetic stirrer. In a typical reaction, 2.60g catalyst, 83.86g 10wt% HCl aqueous and 17.60g AC was added in the flask. Then 26.07g H₂O₂(30%) was added in by peristaltic pump with a speed of 5 mL/min. For the reaction catalyzed by TiCl₄, only 0.37g TiCl₄ was added to keep equivalent active center compared with HTS. The reaction temperature was controlled at 30°C, and the total reaction time was 120min. Then the product was filtrated and the liquid was collected for GC analysis.

1.3.2 Ring-opening of ECH with HCl

Ring-opening reaction was carried out in a three necked flask equipped with a condenser and a magnetic stirrer. Firstly, 2.60g HTS and 21.49g ECH was added in 83.86g HCl(10%) aqueous. Then the mixture was reacted at 30°C for 1.5 hour. After reaction was finished, the product was filtrated and the liquid was collected for GC analysis. A control group was carried out at the same condition except for no catalyst was added in.

1.3.3 Chlorohydration of AC with 1wt % Cl₂

Chlorohydration of AC with 1vol % Cl₂ diluted in N₂ was carried out in a three necked flask equipped with a condenser and a magnetic stirrer at atmospheric pressure. Cl₂ was fed in through a Teflon pipe from a Cl₂ cylinder. Before the experiment start, 100g distilled water and 17.60g AC were added. After that, Cl₂ was fed in for 120 min. The molar ratio of AC to Cl₂ is 5:1. The off-gas was absorbed by 1M NaOH aqueous.

2. Results and discussion

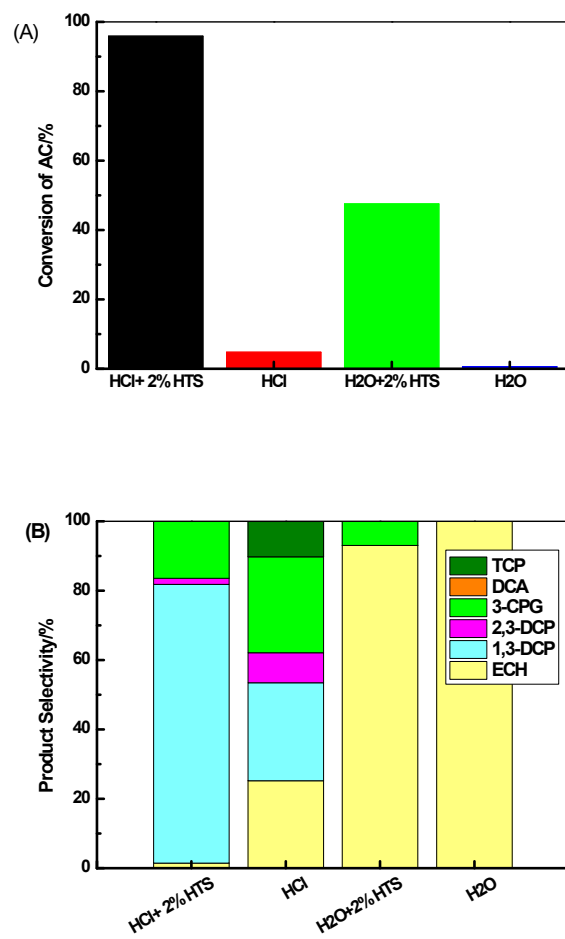


Fig. S1 AC conversion (A) and Product selectivity (B) of chlorohydrination and epoxidation reactions in the absence/presence of HTS zeolite catalyst.

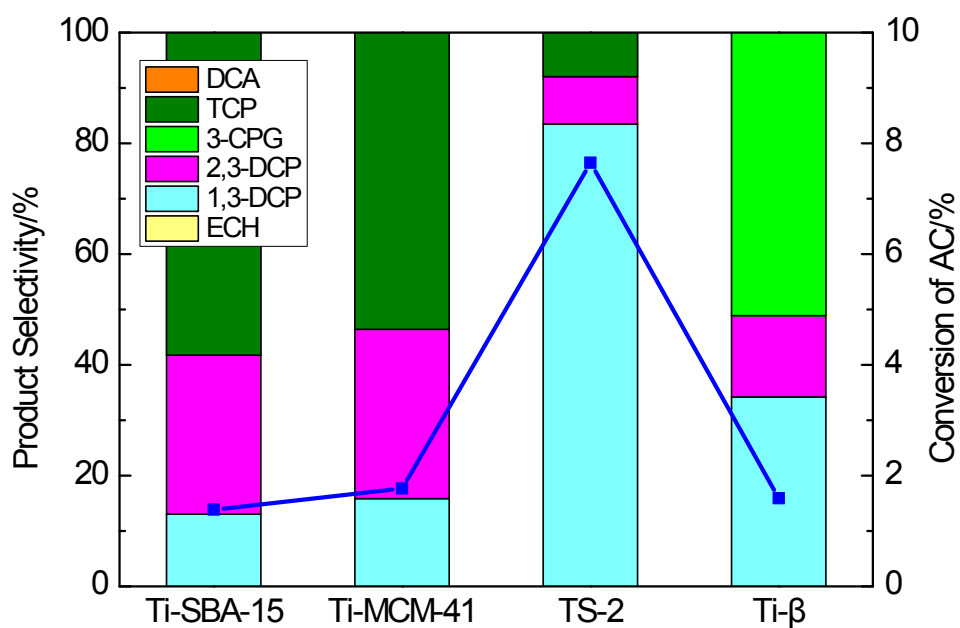


Fig.2 Chlorohydration of allyl chloride with H_2O_2 and HCl catalyzed by different Ti-containing catalysts (TS-2, Ti-β, Ti-MCM-41 and Ti-SBA-15) under the same conditions

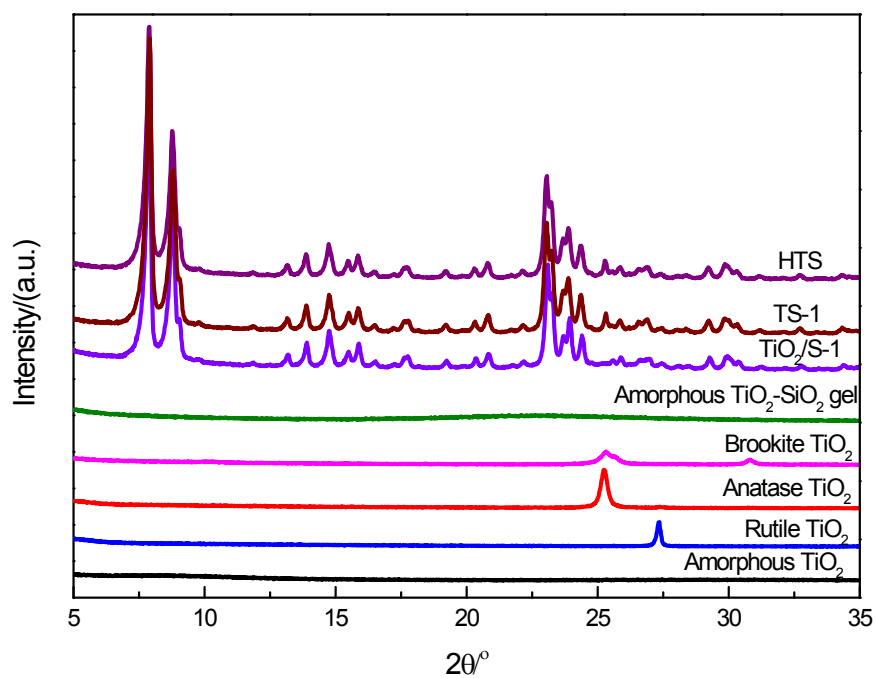


Fig.S3 XRD spectra of various Ti-containing catalysts for AC chlorohydration reaction with HCl and H₂O₂ under mild conditions

Table S1 Structural parameters of titanosilicates calculated from nitrogen sorption isotherms

Catalysts	Specific area (m ² /g)			Pore volume(cm ³ /g)	
	BET	Micro	ext	Micro	Total
Amorphous TiO ₂	6	-	-	-	0.029
Anatase TiO ₂	9	1	8	0.000	0.036
Amorphous TiO ₂ -SiO ₂	471	387	85	0.028	0.357
TiO ₂ /S-1	449	399	50	0.191	0.356
TS-1	448	406	42	0.191	0.280
HTS	447	384	53	0.178	0.352

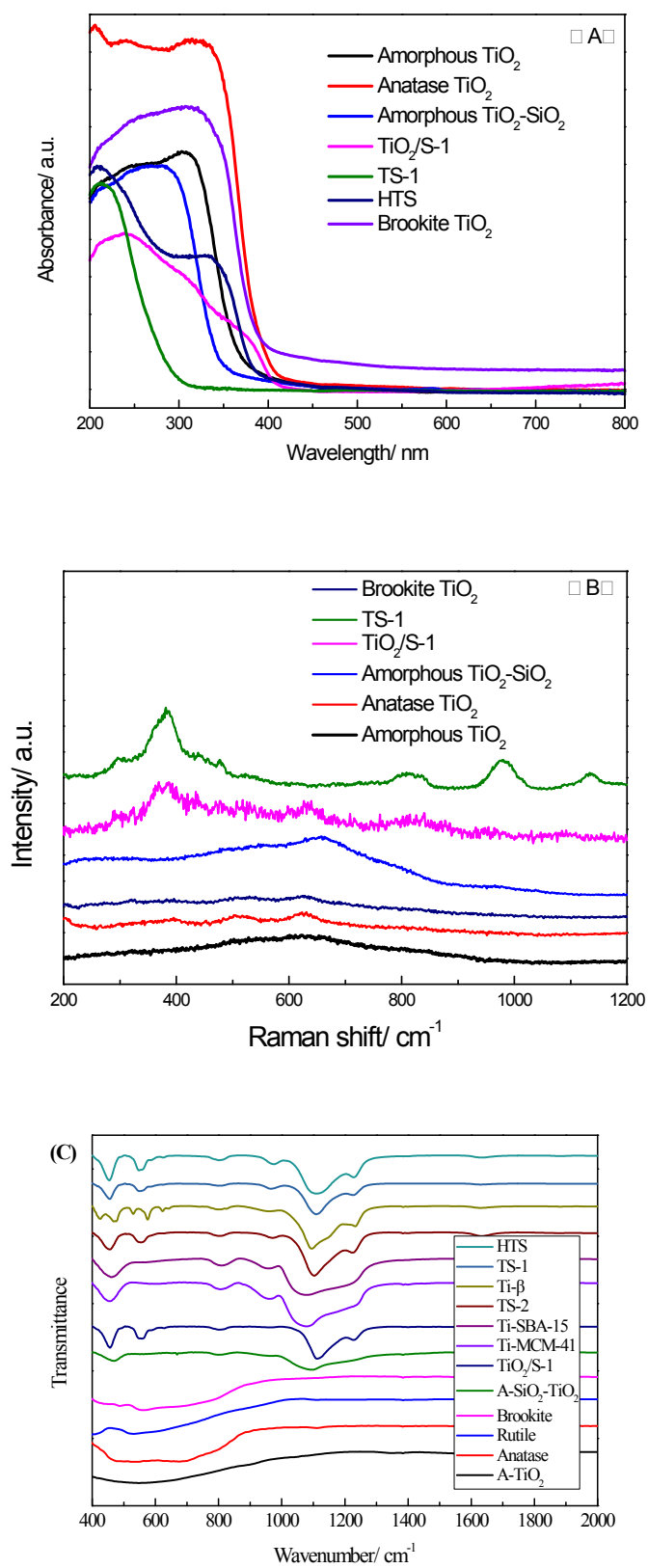


Fig. S4 UV-Vis (A) and Raman (B) and FT-IR (C) spectra of various Ti-containing catalysts for AC chlorohydration reaction with HCl and H₂O₂

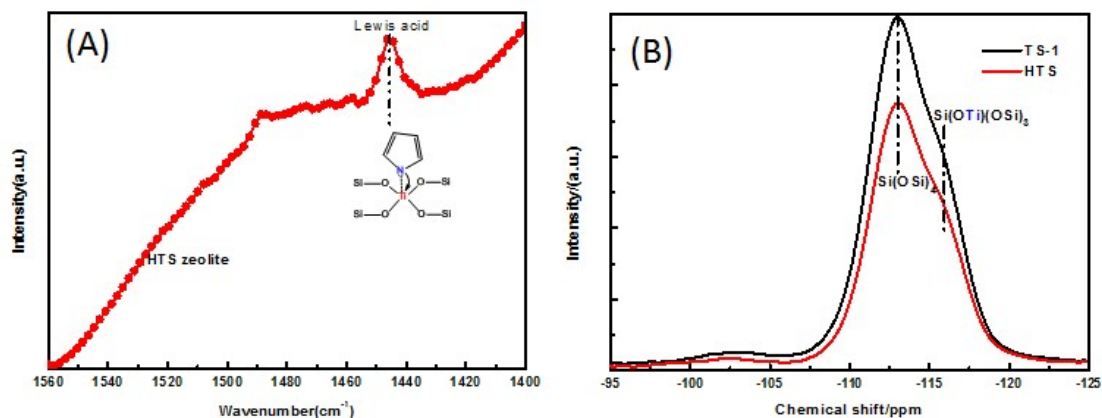


Fig.S5 Pyridine adsorbed IR spectrum and ^{29}Si MAS NMR spectra of HTS zeolite

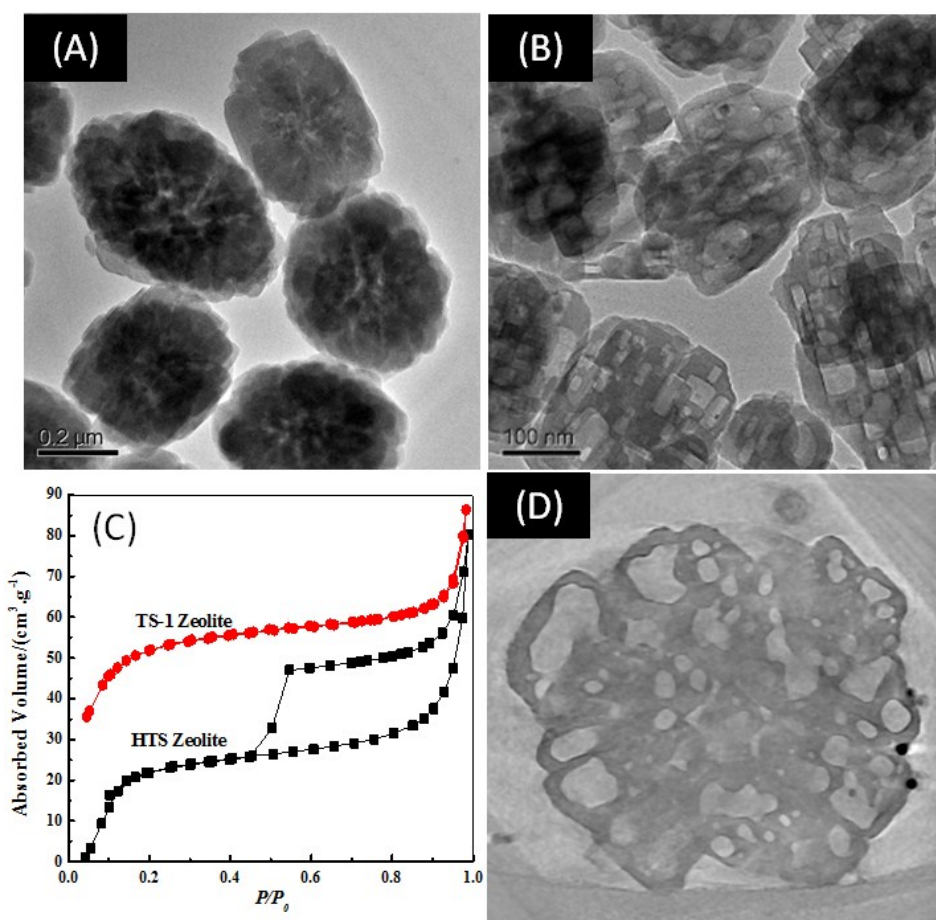


Fig.S6 Characterization of TS-1 and HTS zeolites, (A) TEM image of TS-1 zeolite; (B) TEM image of HTS zeolite; (C) BET analysis of TS-1 and HTS zeolites; (D) 3D-TEM image (electron tomography) of HTS zeolite : From a representative crystal, a tilt series of about 141 images was taken from about $\pm 70^\circ$ to $+70^\circ$ at 1° intervals of magnification 15 k or 20 k on one of two microscopes (Philips CM 200 FEG or a Tecnai 20) at 200 kV and with software for automated electron tomography.

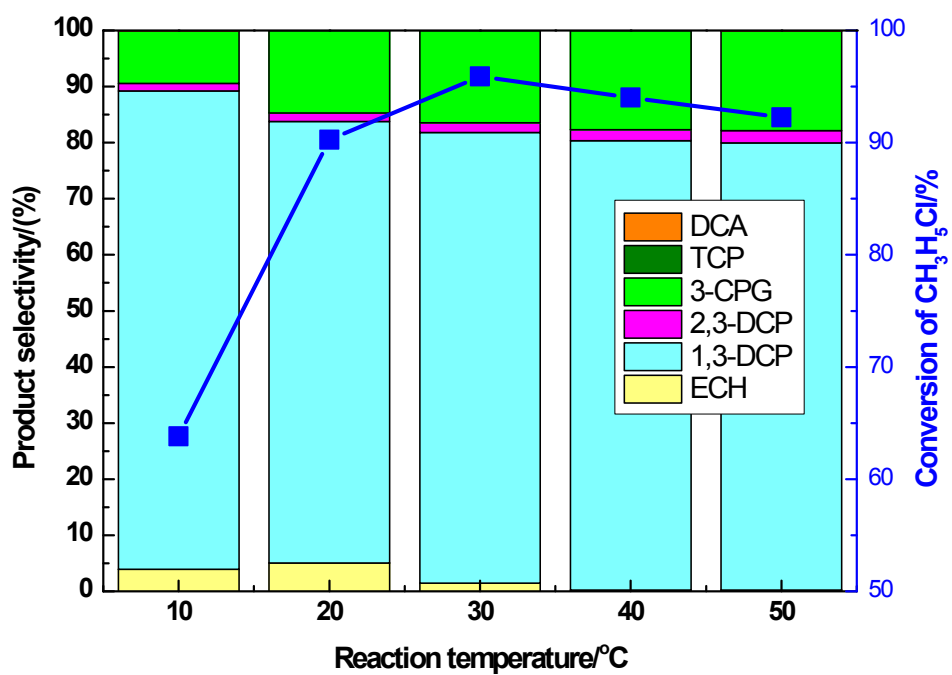


Fig. S7 Catalytic performance of HTS zeolite in AC chlorohydration with HCl and H₂O₂ at different reaction temperature

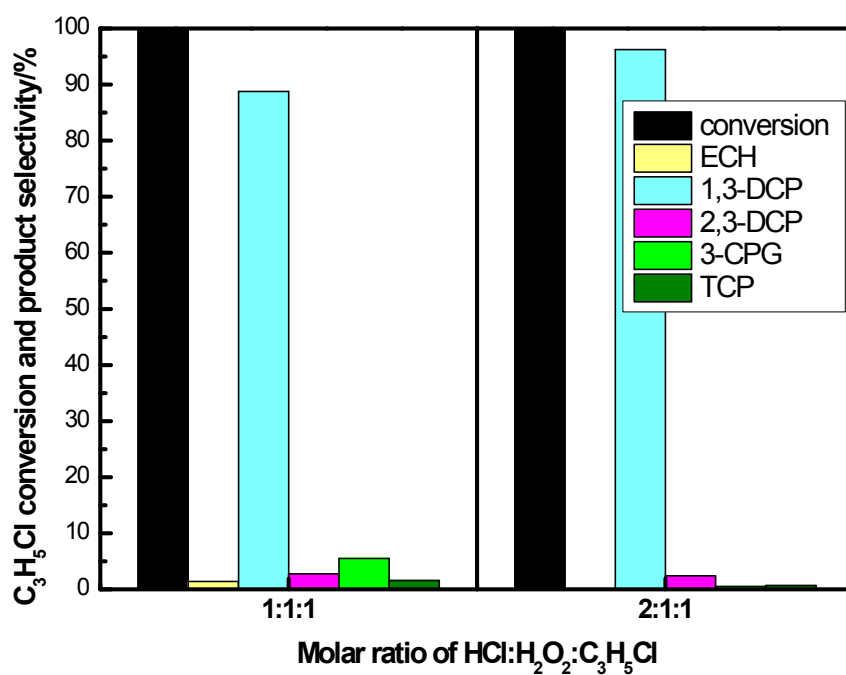


Fig. S8 catalytic performance of HTS zeolite in AC chlorohydration under different HCl/ H₂O₂ molar ratio

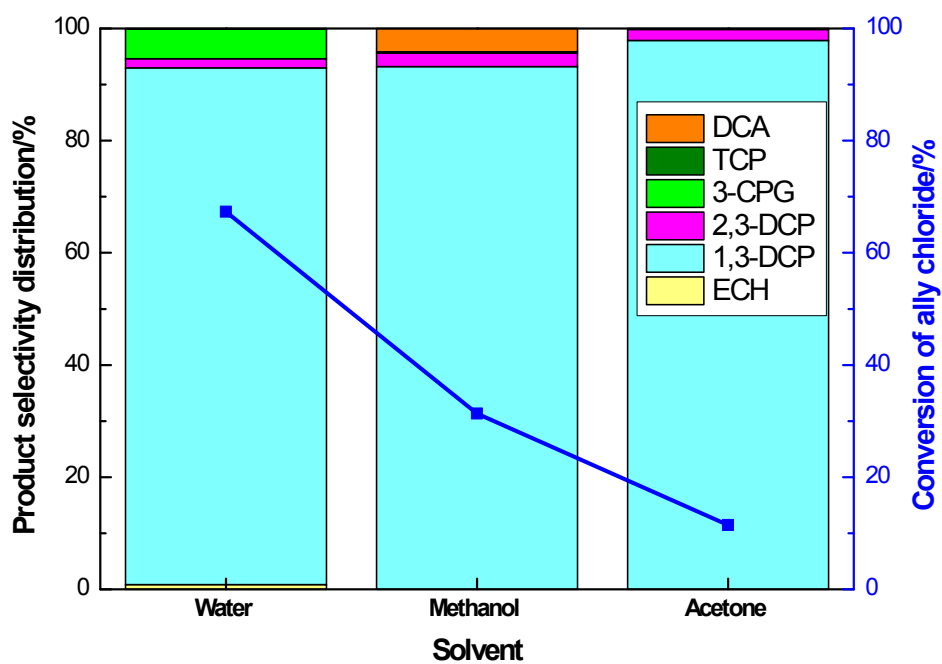


Fig. S9 Catalytic performance of HTS zeolite in AC chlorohydration with HCl and H₂O₂ in different solvent systems

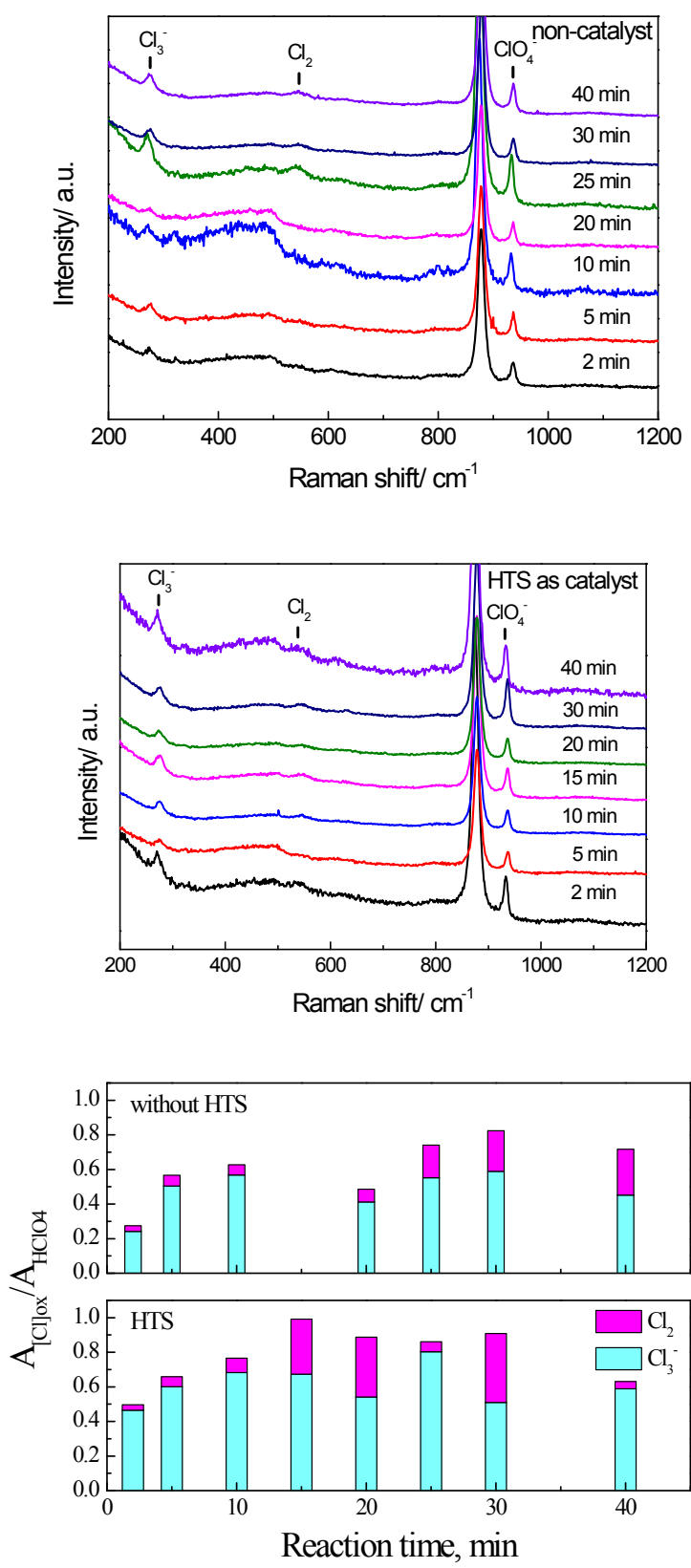
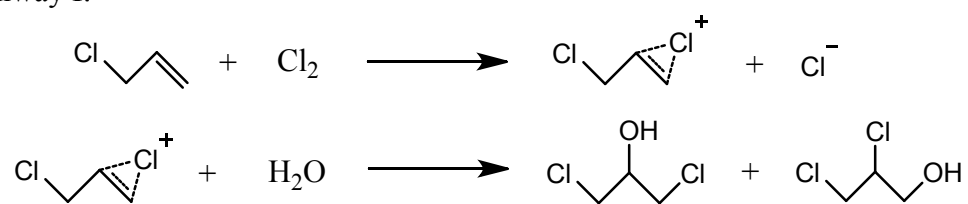


Fig. S10 Characterization of Chloride-containing species by UV-Raman spectroscopy (with 325nm irradiation light)

Pathway I:



Pathway II:

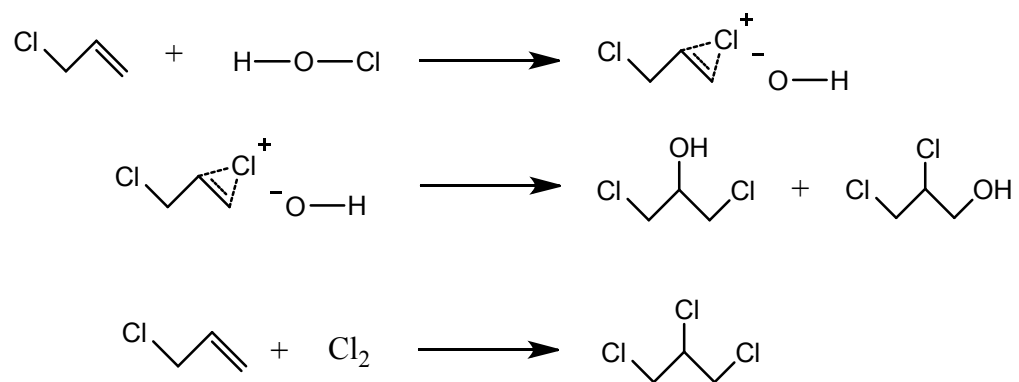


Fig. S11 Reaction mechanism of AC chlorohydration with Cl₂ in industry

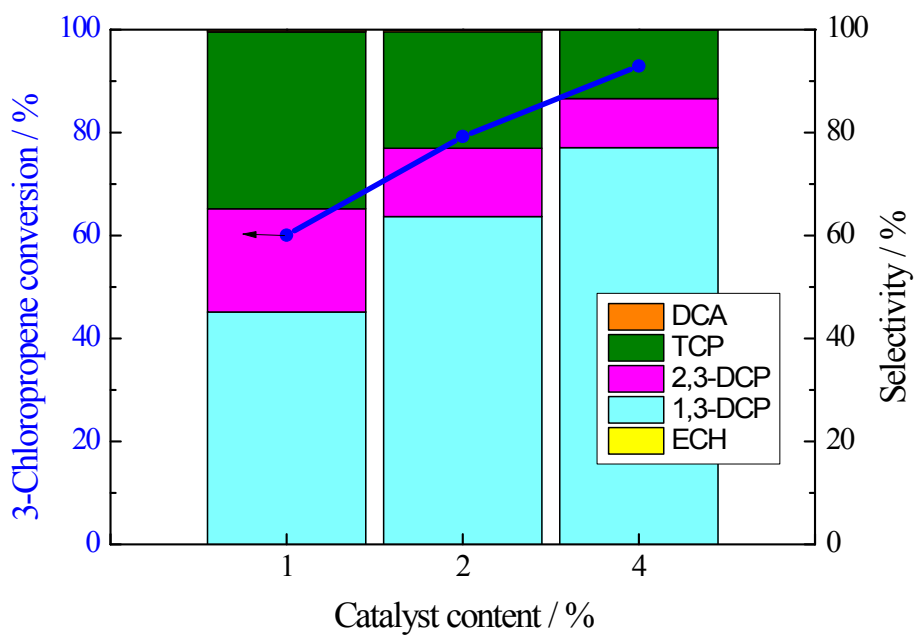


Fig. S12 Conversion and product selectivity in AC chlorohydration as a function of catalyst amount

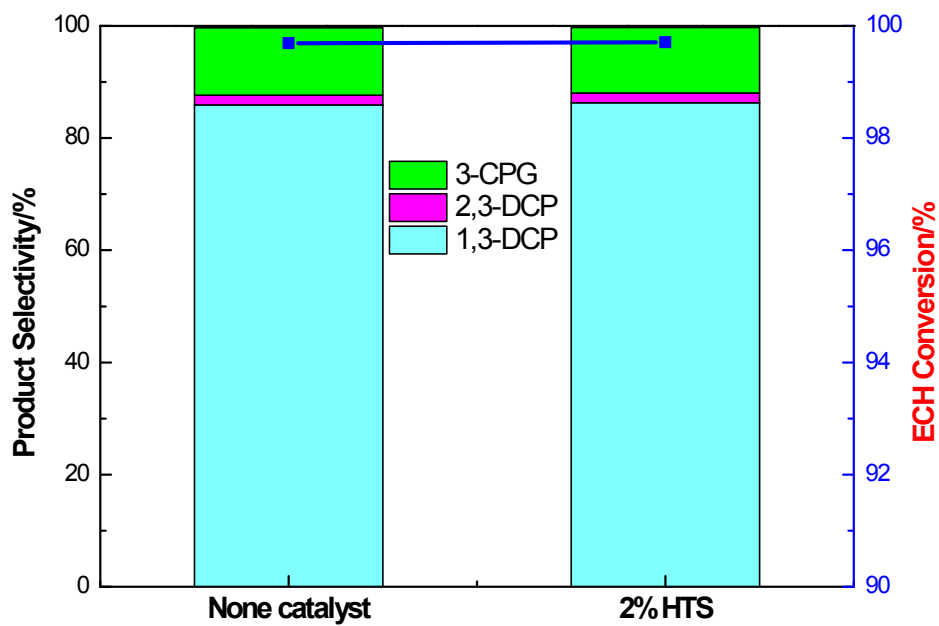


Fig. S13 Conversion and product selectivity of ring-opening reaction of ECH with aqueous HCl solution with and without HTS zeolite catalyst

Table S2 Conversion and product selectivity in AC chlorohydration with Cl₂ in the absence or presence of HTS zeolite catalyst

Catalyst	Mass of H ₂ O/ g	Mass of HCl/g	Flow rate of 1% Cl ₂	Conv. AC/%	S _{1,3-DCP} /%	S _{2,3-DCP} /%	S _{TCP} /%
None	100	0	0.5	0.13	0	100	0
None	100	0	0.5	0.44	8	91.44	0.56
None	90	10	0.5	0.73	20.49	79.35	0.16
HTS	100	0	0.5	0.61	11.11	86.76	2.14
HTS	90	10	0.5	0.53	14.73	81.72	3.55

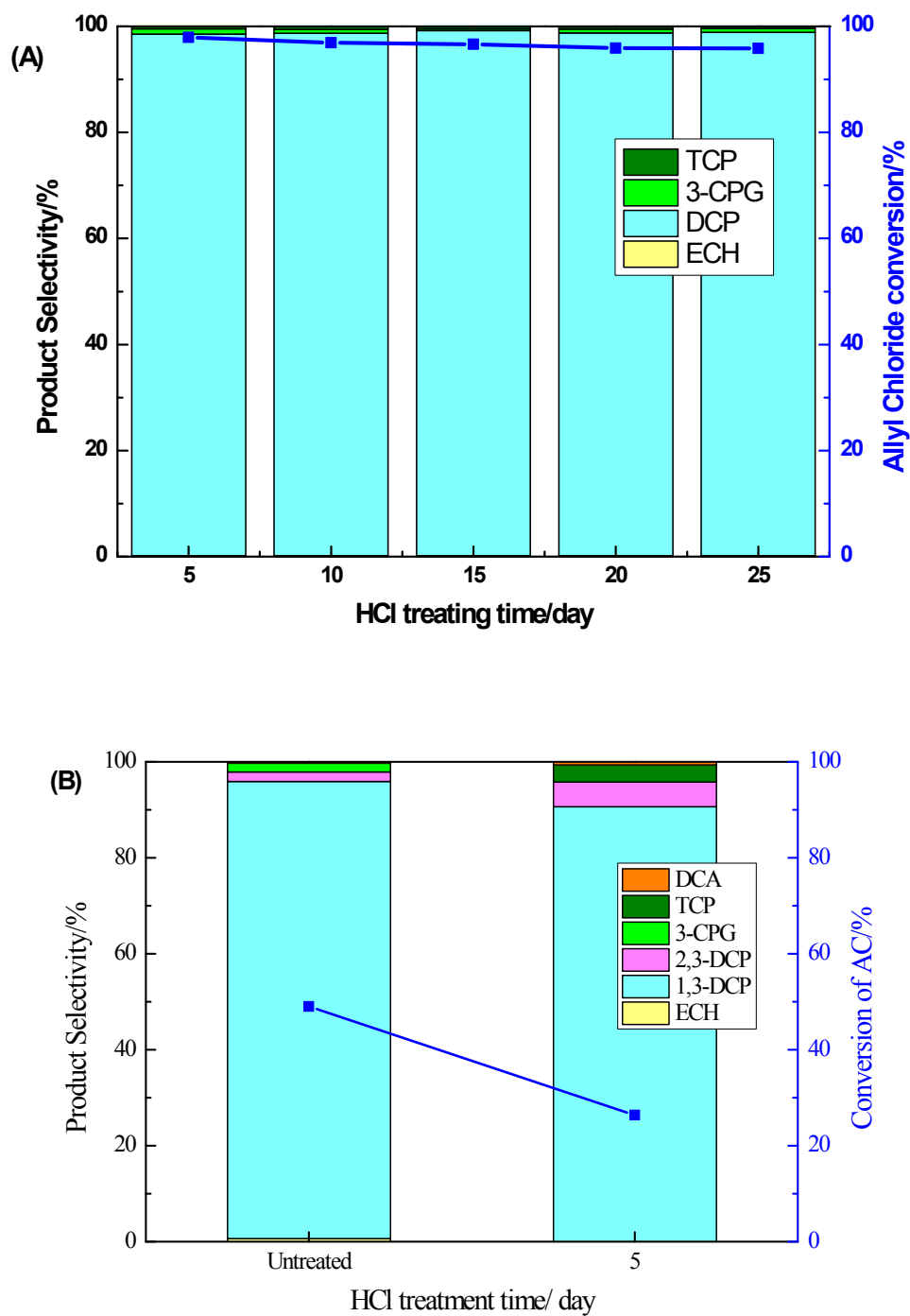
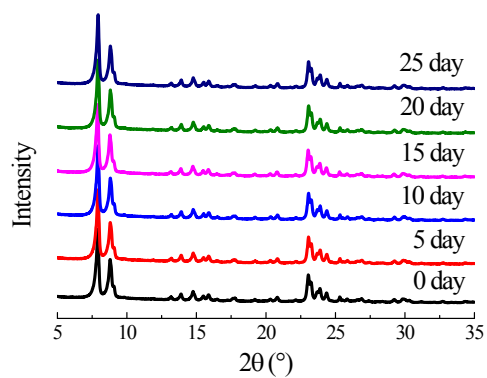


Fig. S14 Catalytic performance of acid-treated HTS (A) and TS-1 (B) zeolites in chlorohydration of AC with HCl and H₂O₂ under optimized conditions



Sample	XRF, %		R.C., %
	SiO ₂	TiO ₂	
0day	93.5	6.24	100.00
5day	93.6	6.11	100.55
10day	93.3	6.08	101.38
15day	93.0	6.03	99.59
20day	93.0	6.11	101.38
25day	-	-	100.69

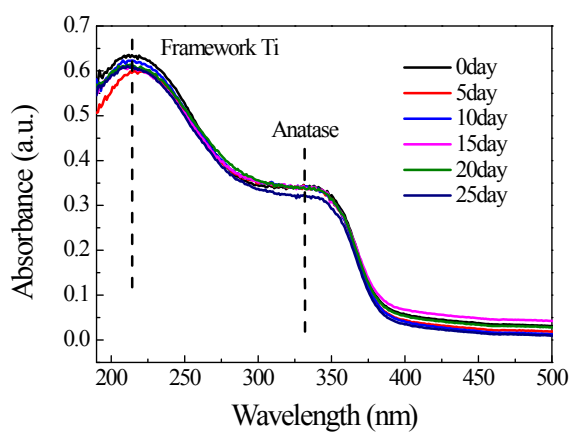


Fig. S15 Characterization of acid-treated HTS zeolites with different treatment time

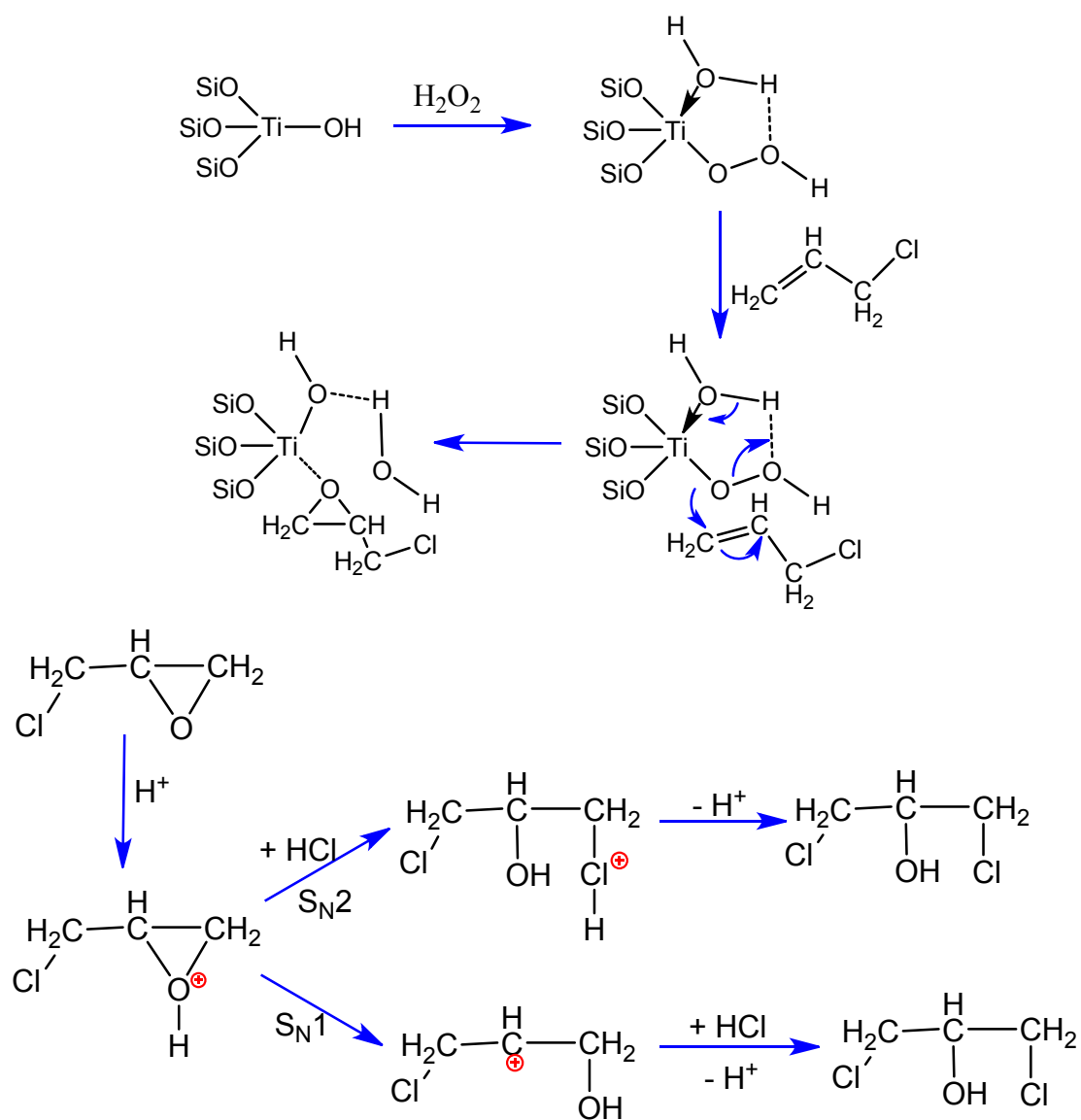


Fig. S16 Proposed mechanism of novel chlorohydration of AC with HCl and H_2O_2 catalyzed by HTS zeolite