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# Chlorohydrination of Allyl Chloride with HCl and H<sub>2</sub>O<sub>2</sub> to Produce

# Dichloropropanols Catalyzed by Hollow Titanium Silicate Zeolite

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In global, over 95% of epichlorohydrin is commercially manufactured via chlorohydrination route with hazard  $Cl_2$  as raw material, which brings serious operation and pollution problems. Herein, we describe a novel  $Cl_2$ -free process for synthesizing dichloropropanols from allyl chloride with  $H_2O_2$  and HCl catalyzed by hollow titanium silicate zeolite under mild conditions. High conversion and overall dichloropropanol selectivity exceeding 95% are simultaneously achieved, and the heterogeneous catalyst is ultra stable and easy to be reused. Comprehensive experiment and spectroscopic results infer that Lewis acidity of framework Ti species is synergistic with Brönsted acidity of HCl to accelerate the epoxidation of allyl chloride and ring-opening of epoxy groups.

**D**ichloropropanols (DCPs) are key precursors for synthesizing epichlorohydrin (ECH), which is widely used for commercial production of epoxy resins, surfactants, pharmaceuticals and plasticizers.<sup>[1,2]</sup> Nowadays, over 95% of ECH is prepared by combining the chlorohydrination of allyl chloride (AC) with Cl<sub>2</sub> to produce DCPs (including 1,3-DCP and 2,3-DCP) and dehydrochlorination of DCPs with Ca(OH)<sub>2</sub> in industry, as shown in Scheme.1(A).<sup>[3,4,5]</sup> It is theoretically estimated that about 0.64kg gaseous Cl<sub>2</sub> is consumed per kilogram of DCPs, with the formation of 0.3kg HCl waste. Obviously, it entails many serious disadvantages, including low atom utilization efficiency, high waste generation, and high energy consumption. <sup>[6,7]</sup> Especially, to reduce the formation of trichloropropane (TCP), Cl<sub>2</sub> should be diluted by large amount of H<sub>2</sub>O, giving birth to large amount of harmful sewage and ultra-low DCPs concentration (<4%). Although several alternative green approaches has been explored, i.e. glycerol chlorination, <sup>[8,9]</sup> the epoxidation of AC catalyzed by Ti-containing zeolites <sup>[10,11,12]</sup> and heteropolycompounds<sup>[13]</sup>. These novel processes are still far beyond commercialization at large scale, owing to the complex

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operation, high energy consumption, and poor catalyst stability. TS-1 zeolite with MFI topology has been widely used in the field of the ketone ammoximation,<sup>[14,15]</sup> phenol hydroxylation<sup>[16,17]</sup> and the epoxidation of allylic compounds (allyl alcohol, allyl chloride, mutually alcohol, crotyl alcohol, and 1-butene-3-ol), propylene and natural compounds (limonene).<sup>[18,19,20,21,22,23,24,25]</sup> However, TS-1 shows low catalytic performance (AC conversion<50%) in the direct epoxidation of AC to synthesis ECH, due to the electron-withdrawing effect of chloride group on C=C bonds (Fig. S1).<sup>[26,27]</sup> During direct epoxidation, we also observed that the polymerization of AC easily occurred, which causes the blocking of micropores. Moreover, huge methanol solvent is needed, increasing the solvolysis of ECH and the energy consumption for solvent separation. <sup>[28,29]</sup> Therefore, to develop an environmental friendly process to produce DCPs is still a tremendous challenge facing green manufacturing of ECH in industry.

Herein, inspired by the elementary steps of chlorohydrination process and catalytic oxidation mechanism of TS-1/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O system,<sup>[3,30,31]</sup> an efficient chlorohydrination route to produce DCPs from AC catalyzed by hollow titanium silicate (HTS) zeolite, with HCl and H<sub>2</sub>O<sub>2</sub> as reactants, has been developed (Scheme.1B). HTS zeolite is prepared via the post synthesis of traditional TS-1 with organic template under hydrothermal conditions. The chlorohydrination reaction was carried out at low temperature, with continuous stirring in a three-necked reactor. Over 85.0% conversion of AC is observed, with 87.8% selectivity of 1,3-DCP and 1.7% selectivity of 2,3-DCP, respectively (Fig.1). Importantly, there is almost no TCP observed, and the DCPs concentration is over 20%, thus this approach shows much greater advantages than traditional routes. And to our best knowledge, it is the first time to synthesize DCP from AC with inorganic H<sub>2</sub>O<sub>2</sub> and HCl under the impact of framework Ti species of TS-1 zeolite.

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## (A) Traditional chlorohydrination route

(B) Novel chlorohydrination route catalyzed by HTS zeolite



Scheme.1 Comparison of the industrial chlorohydrination process and the novel method for production of dichloropropanol (A) Industrial Cl<sub>2</sub> route, (B) Novel Cl<sub>2</sub>-free method



Fig.1 Chlorohydrination of allyl chloride with H<sub>2</sub>O<sub>2</sub> and HCl catalyzed by different Ti-containing catalysts under the same conditions

Our experiments display that HTS zeolite is the best one among different Ti-containing catalysts we tested (Fig.1 and Fig.S2). In principle, HOCl and/or the chloronium ion species derivated from

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Cl<sub>2</sub> are considered as the chemical intermediates of the chlorohydrination process.<sup>[32,33]</sup> while TCP is produced from the direct chlorination of AC with gaseous Cl<sub>2</sub>. Apparently, low AC conversion (<5%) and high TCP selectivity (>14%) are observed over amorphous TiO<sub>2</sub> (A-TiO<sub>2</sub>), amorphous TiO<sub>2</sub>-SiO<sub>2</sub> (A- TiO<sub>2</sub>-SiO<sub>2</sub>), crystalline TiO<sub>2</sub> (including Anatase, Rutile, and Brookite), owing to the diffusion limitation inside condensed phase (Fig.S3 and Table S1). In addition, when enhancing the accessibility of octahedral Ti specie, far higher AC conversion (>45%) and TCP selectivity (>65%) are coinstantaneously found over soluble TiCl<sub>4</sub> and TiO<sub>2</sub>/S-1, while no TCP has been detected in blank test. It suggests the octahedral Ti species (Fig.S4) favor the generation of Cl<sub>2</sub> and then accelerates the direct chlorination of AC in organic phase, similarly as the  $Cl_2$ chlorohydrination reaction we have done. However, interestingly, both TS-1 and HTS show high total selectivity (>90%) of 1,3-DCP and 2,3-DCP under the same reaction conditions. It indicates that isolated tetrahedral framework Ti species acted as Lewis acid sites (Fig.S5) are prominently helpful for the efficient transformation of AC to DCPs through this improved chlorohydrination route. In addition, HTS presents significantly higher AC conversion (85%) than TS-1 (49%), which is attributed to the better mass diffusion performance within hollow cavities of zeolite (Fig.S6).<sup>[34,35]</sup>

In contrast to the industrial chlorohydrination route, ECH and 3-chloride-1, 2-propylene glycol (3-CPG) are achieved in novel route, especially in low HCl/H<sub>2</sub>O<sub>2</sub> region, via the epoxidation of AC catalyzed by tetrahedral framework Ti species and hydrolytic ring-opening of ECH with H<sub>2</sub>O, respectively. Consequently, we can observe that increasing reaction temperature doesn't enhance the AC conversion, but it can significantly improve the selectivity of 3-CPG and DCP at the same time (Fig.S7), without the detection of ECH at relative high temperature (40-50°C). It is inferred that H<sub>2</sub>O and HCl are competitive to react with the epoxy groups of ECH, which further verifies the existence of ECH-intermediated pathway (Fig.S8). Moreover, when H<sub>2</sub>O is replaced by other organic solvents (such as methanol and acetone), it causes a sudden drop of AC conversion from 67.3% (in water) to 31.3% (in methanol) and 11.4% (in acetone), respectively (Fig.S9). Meanwhile, no 3-CPG is formed in organic solvent systems, which is ascribed to the inhibition of hydrolysis reaction of epoxy groups with H<sub>2</sub>O. Interestingly, few amount of 1,3-dichloroacetone (4.31%) was formed in methanol system, which is explained by the deep oxidation of 1,3-DCP by HTS/H<sub>2</sub>O<sub>2</sub> system. According to these results, we confirm that the formation of ECH and DCPs

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proceeds via the epoxidation of AC and the addition reaction of HCl to ECH, respectively, due to the high reactivity of epoxide group in acidic conditions.

On the other hand,  $Cl_2$  has been characterized as a major intermediate in this route by UV-Raman spectroscopy (of 325nm irradiation wavelength) (Fig.S10). Thus, the other plausible mechanism involves the electrophilic addition of activated Cl species to the C=C bonds of AC molecules as industrial chlorohydrin approach (Fig.S11). As the H<sub>2</sub>O<sub>2</sub> solution is continuously added, the activated Cl species (including HOCl and Cl<sub>3</sub><sup>-</sup>) are gradually generated, and then they readily react with AC to produce DCPs, rather than dissolve in organic phase, owing to only trace TCP detected. However, when reduces the catalyst amount, the selectivity of TCP surprisingly becomes higher, almost as high as that catalyzed by octahedral Ti species (Fig.S12). That is because, if there are no enough active sites for generating DCPs, the activated Cl species cannot be readily consumed, then they will diffuse into the organic phase in the form of Cl<sub>2</sub> to accelerate the formation of TCP. That is why TCP selectivity becoming higher as a function of the increasing of HCl concentration, owing to the decreasing of H<sub>2</sub>O content (Fig.2A). Hence, it is of great importance to match the AC conversion and the formation of Cl<sub>2</sub> to enhance the selectivity of DCPs in this route.

To further identify which pathway mainly occurred, the ring opening reaction of ECH with aqueous HCl catalyzed by HTS was carried out, with high yield of 1,3-DCP (86.32%)(Fig.S13). Meanwhile, it is observed that the major product is 2,3-DCP (>90% selectivity) for chlorohydrin route in both our lab and industry (Table S2). As previously mentioned, the major product is 1,3-DCP isomer (>90% selectivity in Fig.2A) in our novel route. Therefore, we infer that DCPs are preferentially generated via the addition of HCl to epoxy groups of ECH, rather than the direct electrophilic addition of HOCl to AC molecules.<sup>[7]</sup> Particularly, in the case of high catalyst amount, the AC conversion and DCPs yield are closely relevant with the increasing of HCl amount. It suggests that the addition of HCl to ECH catalyzed by H<sup>+</sup> ions can promote the epoxidation reaction equilibrium by consuming ECH. As a consequence, there is a synergy between the Lewis acid sites (framework Ti species) and Brönsted acid sites (H<sup>+</sup>) to enhance the formation rates of ECH and DCPs.



**Fig.2 Catalytic performance of HTS zeolite in chlorohydrination of allyl chloride**: A) Effect of HCl concentration on the allyl conversion and product selectivity; B) The conversion of allyl chloride and product distribution in the reuse experiments for 6 times under the same conditions.

Except for the high AC conversion and product selectivity, HTS zeolite shows more promising stability than TS-1 in this route (Fig.2b), which is of great importance for heterogeneous catalysis in industry. <sup>[36,37]</sup> The reuse tests were carried out under optimized reaction parameters for six times, without calcination treatment to remove the deposited organic compounds. It is clearly

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found that catalyst still remains as high catalytic activity as the fresh one after the sixth recycle, with >95% AC conversion and >98% DCP selectivity. Moreover, HTS zeolite has been deeply soaked by 10 wt% HCl solution for three months at room temperature under static state, to examine its stability (Fig.S14). The acid treated HTS were found to remain as reactive as fresh HTS, almost with the same AC conversion and product selectivity. After that, both reused HTS and acid treated HTS zeolites were investigated by multiple characterization methods, such as XRD, BET and TEM (Fig.S15). And there are almost no changes in physiochemical properties observed, which is accorded to its excellent resistibility of tetrahedral framework Si and Ti atoms to  $H_2O$  and HCl molecules, without the hydrolysis of T-O-Si bonds (T=Si or Ti) under acidic conditions. At the same time, both TS-1 and HTS zeolites show high reusability and regeneration in other catalytic oxidation reactions, carried out by EniChem and SINOPEC, respectively. <sup>[38,39]</sup>

When substituted olefins are introduced as substrates, it is observed that olefin conversion and alcohol selectivity are significantly decreasing along with the increasing of molar size (see Table 1). Notably, no alcohol product is detected for cyclooctene, whereas large amount of chloride substituted products are generated, attributing to the direct chlorination with Cl<sub>2</sub>. That is because cyclooctene is too large in size to diffuse into the micropores of TS-1 zeolite, thus it preferentially reacts with Cl<sub>2</sub> in organic phase.<sup>[4]</sup> Consequently, it further indicates that this improved chlorohydrination route majorly focuses on the epoxidation of AC with H<sub>2</sub>O<sub>2</sub> and electrophilic addition of HCl to epoxy groups in the presence of Lewis acid (framework Ti species) and Brönsted acid sites, rather than the traditional chlorohydrin route (Fig.S16).

**Table 1. Substrate scope for catalytic chlorohydrination of substituted olefins over HTS zeolite.** The reactions were carried out in a three-necked bottom flask at 30°C, with drop-wise adding of H<sub>2</sub>O<sub>2</sub> solution within 30 minutes.

Substrates	Products % Yield	%Conversion	Time	%Selectivity for		
			(h)	1	2	3
CI		99.81	2	98.7	0.68	0

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	$ \begin{array}{c}                                     $	99.99	2	86.28	13.72	0
$\bigcirc$	$ \begin{array}{c}     OH & CI \\     OH &$	30.78	2	56.09	38.08	5.83
$\bigcirc$	$\bigcirc \bigcirc $	7.53	2	55.92	6.92	37.16

From the viewpoint of industrial application, this Cl<sub>2</sub>-free chlorohydrination route is quite available to be carried out at large scale, just like those commercial processes catalyzed by HTS zeolite we have done.<sup>[40,41]</sup> Summarily, this process is of high DCPs yield and ultra-long catalyst lifetime, without the formation of low value-added TCP byproduct. Additionally, there are no organic solvents needed, which means it is not necessary to take extra energy consumption for solvent separation. More importantly, the route we report here provides a novel viewpoint to catalytically covert olefins to high valued chlorohydrins by rational blending the solid Lewis acid and liquid Brönsted acid sits, according to their instinct characteristics of chlorohydrination reactions.

reactions.

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