

# Epoxidation of allyl chloride with molecular oxygen and 2-ethyl-anthrahydroquinone catalyzed by TS-1

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Received 13 September 2004; received in revised form 4 November 2004; accepted 4 November 2004

Available online 22 December 2004

## Abstract

The production of epichlorohydrin with hydrogen peroxide is an environmentally benign process, but the relatively high cost of hydrogen peroxide prevents it from being commercialized. In the present work, the production of epichlorohydrin by epoxidation of allyl chloride with molecular oxygen in the presence of 2-ethyl anthrahydroquinone using TS-1 as the catalyst was studied. The catalysts after reaction were characterized with FT-IR and TGA. The reaction results showed that the heterogeneous reaction could be carried out under mild conditions, and the addition of methanol solvent could increase the yield of the product. It was found that the concentration of 2-ethylanthrahydroquinone in the working solution should not be too high, otherwise, it would decrease the yield of the product. The product and unreacted reactants could be separated simply by distillation.

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**Keywords:** Epoxidation; Allyl chloride; Molecular oxygen; Alkyl anthrahydroquinone; TS-1

## 1. Introduction

Epichlorohydrin (ECH) is an important chemical intermediate with wide applications. The high temperature chlorination of propylene is the main method for the production of epichlorohydrin in the present manufacture. This process has several demerits: it needs excessive chloride and a relatively high-energy expenditure, and produces several byproducts. At the same time, there is serious environmental pollution besides the strict demand for the high purity of propylene and high quality of other materials.

Hydrogen peroxide is widely accepted as a green oxidant, as it is easy to handle, relatively non-toxic and breaks down readily in the environment to benign byproducts [1]. In recent years, the epoxidation of olefins with hydrogen peroxides as oxidant has attracted more and more researchers [2–12]. However, the relatively high cost of hydrogen peroxide has prevented the commercialization of these processes. A

method to solve the problem is to generate hydrogen peroxide in situ. In the selection of an in situ generation method, the anthraquinone route is favored by various reasons. It is already proven on a commercial scale. Now, over 98% of hydrogen peroxide in the world is produced by anthraquinone route. Several literatures have devoted to an integrated process for the epoxidation of propylene involving autoxidation of an alkyl anthrahydroquinone [13–16], but little for allyl chloride. And some parameters, such as the effect of methanol and the initial concentration of anthrahydroquinone, were not investigated. Xi and coworkers [17] had tried to epoxidize allyl chloride with molecular oxygen at 35 °C using 2-ethylanthrahydroquinone (HEAQ) as recyclable reductant and  $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3[\text{PW}_4\text{O}_{16}]$  as a homogeneous catalyst. In their work, the epichlorohydrin was obtained by the reaction of the hydrogenated working solution and  $\text{O}_2$ , followed by the reaction of the resulting  $\text{H}_2\text{O}_2$  with allyl chloride. The two-stage process is relatively complex.

In the present work, the epoxidation of allyl chloride (ALC) with molecular oxygen and HEAQ catalyzed by TS-1 in one reactor was investigated. The 2-ethyl anthraquinone

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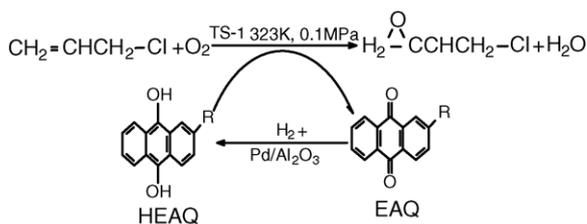


Fig. 1. Epoxidation of allyl chloride with molecular oxygen in the presence of an alkyl anthraquinone.

could be recycled as shown in Fig. 1. The effects of methanol, the initial concentration of HEAQ in the working solution and the effect of epoxide impurities to the hydrogenation of the working solution were studied.

## 2. Experimental

### 2.1. Materials

Unless specially mentioned, the chemicals used in this work were at least of the C.P. grade and were used as received. The TS-1 catalyst was provided by Research Institute of Petroleum Processing of SINOPEC, China, synthesized by a hydrothermal method according to the published procedures [18]. The working solution (120 g 2-ethyl anthraquinone dissolved in 750 cm<sup>3</sup> C<sub>9</sub> aromatics and 250 cm<sup>3</sup> trioctyl phosphate (TOP)) was provided by ChangZhou Nitrogen Fertilizer Company. The hydrogenated anthraquinone solution was obtained through the hydrogenation of the dried working solution at 60 °C in a three-phase fixed-bed reactor with commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The concentration of HEAQ was determined by iodimetric titration.

### 2.2. General procedure for epoxidation of allyl chloride with O<sub>2</sub>

The epoxidation reaction of allyl chloride was carried out in a glass semi-batch reactor with an electromagnetic stirrer. The reaction temperature was controlled at 50 °C by circulating water in the jacket outside the reactor. Allyl chloride, hydrogenated anthraquinone working solution and TS-1 were firstly charged into the reactor, and then O<sub>2</sub> was supplied with a rate of 20 cm<sup>3</sup> min<sup>-1</sup> to the reactor using a needle valve. The reaction was maintained at the reaction temperature with vigorous stirring for 2 h. The concentrations of H<sub>2</sub>O<sub>2</sub> and ECH in samples of the products were determined by iodimetry and gas chromatography (HP 4890, FID, OV-101 column, 25 m) with an internal standard method, respectively. The yield of the product was calculated based on allyl chloride.

### 2.3. Characterization of the catalysts

The recycled TS-1 sample was treated by washing with tributyl phosphate and drying before characterization. The

residues on the TS-1 catalysts were subjected to FT-IR and TG analyses. TG analysis was performed on the TA-50 Shimadzu Thermogravimetric Analyzer to study the mass loss of the catalysts at 15 °C min<sup>-1</sup> heating rate from room temperature to 800 °C under a oxygen rate of 30 cm<sup>3</sup> min<sup>-1</sup>. FT-IR spectra of the samples pressed with KBr in the framework region (400–4000 cm<sup>-1</sup>) were recorded at room temperature with a MAGNA-IR 560 spectrometer.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 2 shows the FT-IR spectra of the fresh and recycled TS-1 samples. The absorption bands at 1220, 1100, 960, 550 and 450 cm<sup>-1</sup> are characteristics of the TS-1 catalyst. The recycled TS-1 catalyst shows a series of strong absorption bands from 2870 to 3000 cm<sup>-1</sup>. The stretching bands at 2962 and 2875 cm<sup>-1</sup> can be assigned to the methylic C–H, and the one at 2934 cm<sup>-1</sup> to C–H bond of methylene. This revealed that some substances with these groups existed on the catalyst. The bands from 1000 to 1700 cm<sup>-1</sup> except for the characteristic bands of TS-1 can be assigned to anthraquinone derivatives [19]. The band near to 700 cm<sup>-1</sup> can be assigned to the stretching vibration of C–Cl, which indicated that allyl chloride maybe existed in TS-1.

The TGA profiles show at least three distinct stages of weight loss as shown in Fig. 3. A weight loss due to the desorption of water amounting to 2.5% was observed between room temperature and 200 °C. The stage of 200–350 °C, corresponding to a weight loss of 22%, can be ascribed to working solution and allyl chloride deposited on the surface of TS-1. The weight loss of 2.5% from 400 to 600 °C can be assigned the loss of allyl chloride which diffused into the pores of TS-1. The TG analyses of TS-1, treated by working solution and allyl chloride, respectively, were made in order

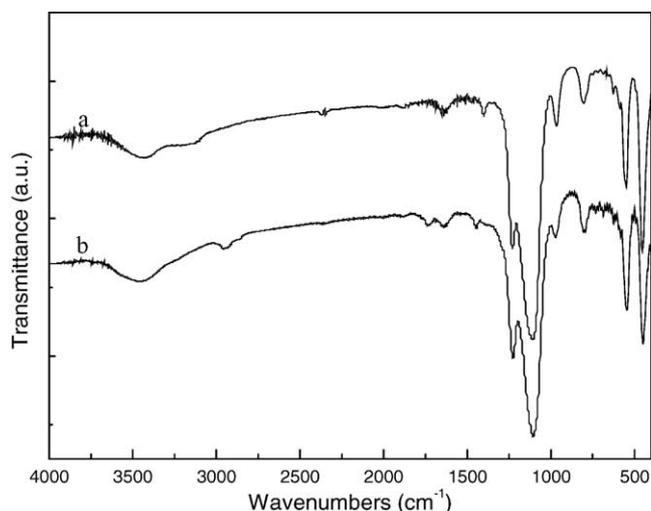


Fig. 2. FT-IR spectra of the fresh (a) and the recycled (b) TS-1.

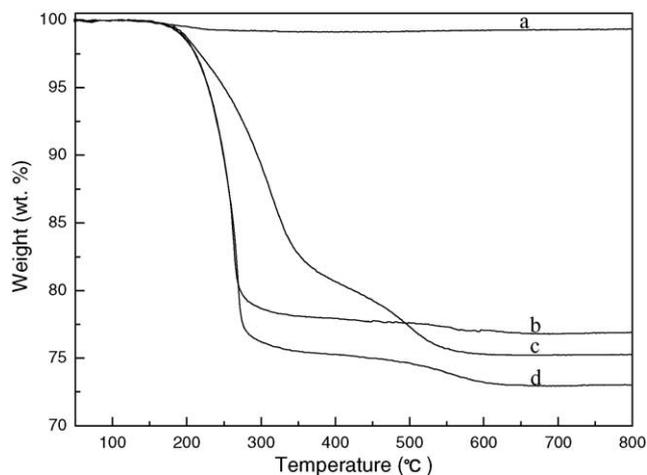


Fig. 3. TGA profiles of different TS-1 samples: (a) fresh TS-1; (b) TS-1 treated by working solution; (c) TS-1 treated by allyl chloride; (d) recycled TS-1.

to certify the above assignments. The results are shown as b and c in Fig. 3. The two samples of b and c had dramatically weight loss at the stage of 200–350 °C. From 400 to 600 °C, the c sample had a significant weight loss while the b sample had little weight loss. This indicates that the anthraquinone derivatives can only be deposited on the surface of TS-1, while allyl chloride can diffuse into the pore of TS-1 where the active sites for the epoxidation reaction are located. The experimental results of FT-IR and TGA indicate that TS-1 is suitable for the catalytic reaction and the anthraquinone working solution had no influence on its catalytic performance.

### 3.2. Influence of methanol solution on the epoxidation

The solubility of allyl chloride in the working solution was evaluated in the preliminary experiments in order to eliminate the mass transfer problem associated with the presence of different liquid phases. Allyl chloride and the working solution could mix at a volume ratio of 1 to 1, which primarily shows that allyl chloride is miscible with the working solution in the experiment. The epoxidation reaction was carried out by direct addition of allyl chloride and oxygen into the hydrogenated working solution. In our experiments, it was observed that no other products were obtained except epichlorohydrin. So the yield of epichlorohydrin was taken as the parameter to evaluate the reaction. The results are shown in Table 1. The results indicate that the anthraquinone route is intrinsically suitable for being used with titanium silicates-1 having MFI structure. The TS-1 catalyst significantly maintained high activity in the ALC/O<sub>2</sub>/HEAQ system. The moderate operating temperature in the autoxidation step for anthrahydroquinone makes it suitable for the epoxidations of allyl chloride.

For the epoxidation of propylene, the alcoholic solvents have a positive effect on the reaction [20]. The effects of the solvents on the epoxidation of allyl chloride with 30% H<sub>2</sub>O<sub>2</sub> over TS-1 were also investigated in our work. The results are

Table 1  
Epoxidation of allyl chloride with molecular oxygen

Molar ratio <sup>a</sup>	Epichlorohydrin yield (%)		
	No methanol solvent	Addition of methanol	
		0.15 mol L <sup>-1</sup> HEAQ	0.2 mol L <sup>-1</sup> HEAQ
0.75	15.5	17.0	19.0
1	12.0	24.9	11.4
3	5.5	17.7	8.0

Reaction conditions: TS-1 catalyst; 323 K; the rate of O<sub>2</sub> = 20 cm<sup>3</sup> min<sup>-1</sup>; 2 h.

<sup>a</sup> The molar ratio of ALC and anthrahydroquinone.

shown in Table 2, from which it can be seen that methanol is the best solvent. It was considered that the alcoholic solvents promoted the formation of active species, the five-membered framework Ti cyclic species (as shown in Fig. 4) [21]. In the epoxidation reaction, the alcohol solvent functioned not only as a solvent for the reaction but also as a co-catalyst and took part in the reaction. Compared with ethanol and propanol, methanol, because of its smaller molecular size, easily enters into the channel of TS-1 catalyst. So the effect of methanol on the epoxidation of allyl chloride with molecular oxygen and HEAQ was investigated. The results (see Table 1) show that the yields of epichlorohydrin with methanol as solvent are distinctly higher than those in the absence of methanol. The difference might be attributed to the different types of solvent. TOP was the solvent for the reaction system when methanol was not added. Methanol is a protic solvent while TOP is a nonprotic solvent. In the reaction, the quantity of methanol was relatively small. Compared with TOP, the role played by methanol was primarily as a co-catalyst. Under this condition, the better yield of the product could be obtained when the initial molar ratio of HEAQ and allyl chloride was 1 to 1. The high molar ratio was unfavorable to increase the

Table 2  
Epoxidation of allyl chloride with H<sub>2</sub>O<sub>2</sub> catalyzed by TS-1

Solvents	Reaction time (min)	Based on allyl chloride	
		Conversion (%)	Yield (%)
Methanol	30	55.0	54.5
Ethanol	30	22.4	21.2
<i>n</i> -Propyl alcohol	30	0.9	0.7
2-Propanol	30	35.1	33.1
Nitrile	30	0.0	0.0

Reaction conditions: 323 K; solvent: ALC; H<sub>2</sub>O<sub>2</sub> = 10:1:1 (mol); catalyst concentration, 10 g L<sup>-1</sup>.

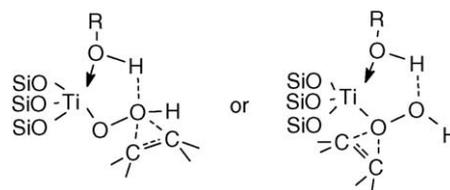


Fig. 4. The active species and epoxidation mechanism.

yield of epichlorohydrin and excessive allyl chloride would enhance the energy expenditure in the following separation processes.

### 3.3. Influence of the initial concentration of anthrahydroquinone

The effect of the initial concentration of anthrahydroquinone in the working solution on the epoxidation is also shown in Table 1. The experimental results indicate that the higher anthrahydroquinone concentration in the working solution could not give higher yield of ECH except below the initial molar ratio of 1 to 1 for allyl chloride and HEAQ. The higher the initial concentration of HEAQ in the working solution was, the more viscous the working solution was. The transport of oxygen is the key step for the oxidation of anthrahydroquinone, which is first order with respect to oxygen and is independent of the concentration of HEAQ [22]. So it is considered that the viscous hydrogenated working solution restrained the transport of oxygen and then the oxidation of the anthrahydroquinone to produce  $H_2O_2$ . Therefore, the initiation of the epoxidation reaction was restricted.

### 3.4. Influence of epoxide impurities on the hydrogenation of 2-ethylanthraquinone

After epoxidation reaction, the mixture was transferred into a phase separator to discharge the water, and then to the distiller. After two distillations, the ECH product was obtained from the top tower, and the remainder of ALC and methanol was recycled after distillation again, and the working solution was recycled to hydrogenation reactor. The epoxidation of allyl chloride with molecular oxygen using the above hydrogenated working solution was repeated and similar results were obtained, indicating that trace amounts of epoxide and methanol had not negative effects on the hydrogenation of 2-ethylanthraquinone.

The effects of components of the working solution such as TOP, anthraquinone, anthrahydroquinone and  $C_9$  aromatics on the epoxidation reaction with 30% hydrogen peroxide as oxygen source were also studied under the same reaction conditions. It was found that most of the components of the working solution had not appreciable influence on the epoxidation of allyl chloride and the stability of TS-1. The average pore diameter of TS-1 is 0.55 nm, where Ti-sites locate, while the cross-section of 2-ethylanthraquinones is larger than 0.6 nm. The small channel of this catalyst prevents the diffusion of 2-ethylanthraquinones molecules onto, and only allyl chloride, the in situ generated  $H_2O_2$  and methanol solvent can reach, the active Ti-sites.

From the experiments described above, we proposed an integration process flow sheet as shown in Fig. 5. It includes an oxidation reactor, in which the epoxidation of allyl chloride with molecular oxygen in the presence of HEAQ is carried out, and the units for splitting and recovering the methanol and unreacted allyl chloride, purifying the ECH, and regen-

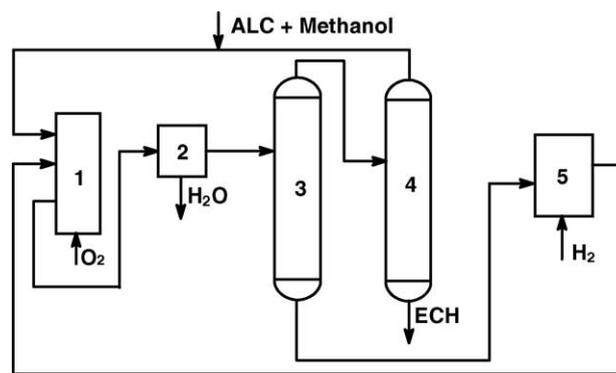


Fig. 5. Proposed process flow sheet for ECH production: (1) oxidation reactor; (2) splitter; (3) distillation column; (4) distillation column; (5) hydrogenation reactor for the working solution.

erating the oxidized working solution. The separation of the mixture has also been simulated with Pro-II software. Under the reaction conditions of the initial molar ratio of ALC and HEAQ at 1:1, the theoretical plates for the distillation column (3) and (4) are 7 and 12. These results will be published in the near future.

## 4. Conclusions

The epoxidation of allyl chloride with molecular oxygen could be effectively carried out under mild conditions in the presence of anthrahydroquinone working solution. The production of epichlorohydrin can be obtained in the absence of methanol solvent. The addition of methanol to the reaction system increased the yield of epichlorohydrin. The increase of HEAQ concentration in the working solution increased the viscosity of the working solution, restrained the mass transfer, and therefore, disfavored the epoxidation reaction. The product and reactants could be separated from the reaction system by distillation. The size of the anthraquinone molecules is larger than the channel of TS-1, therefore it has no effect on the stability of TS-1.

## Acknowledgements

The financial support of State Key Fundamental Research Project of China (Grant No. G2000048005) and the PhD Special Foundation of the Ministry of Education (Grant No. 20030056035) are greatly appreciated.

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