

Epoxidation of allyl chloride with H₂O₂ on Ti-ZSM-5 prepared by the isomorphous substitution

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The epoxidation of allyl chloride with H₂O₂ on Ti-ZSM-5 prepared by isomorphous substitution of HZSM-5 with TiCl₄ gas was studied. The results show that Ti-ZSM-5 has a high catalytic efficiency for the epoxidation of allyl chloride. The H₂O₂ utilization reaches 99.50% when the allyl chloride/H₂O₂ molar ratio is > 1. The effect of solvent species, catalyst concentration, H₂O₂ and allyl chloride concentration and reaction temperature on the epoxidation was investigated simultaneously. It is found that methanol is the best solvent for the reaction. The reaction rate equation with $v = k[\text{Cat.}][\text{H}_2\text{O}_2]^{1/2}[\text{C}_3\text{H}_5\text{Cl}]$ and the apparent activation energy with $E_a = 63.462 \text{ kJ/mol}$ are obtained according to the kinetics study.

Keywords Ti-ZSM-5, epoxidation of allyl chloride, epichlorohydrin (ECH), reaction kinetics, reaction mechanism

Introduction

Epichlorohydrin (ECH) is an important organic intermediate in the industry of epoxy resin, synthetic plycerine and chlorohydrin rubber so on. The high temperature chlorination of propylene is the main method for producing epichlorohydrin in the present manufacture. This process has several demerits: it needs excessive chlorine and a great deal of energy, and produces several by-products. And at the same time, there is the serious environmental pollution besides the strict demand for the purity of propylene and the quality of materials of reactors. In the recent years, several transition-metal-oxides-catalyzed epoxidations of olefins with hydrogen peroxides as oxidant, especially Ti-Si molecular sieves (TS)-catalyzed epoxidation, have attracted more and more researchers.¹⁻³ The TS/H₂O₂ process exhibits some remarkable behaviors with higher utilization and selectivity

of H₂O₂ under the mild reaction conditions and with less environmental pollution,^{4,7} thereby it could be applied to the epoxidation of allyl chloride to epichlorohydrin. However, few papers on the epoxidation of allyl chloride with H₂O₂ catalyzed by Ti-ZSM-5 have been reported.

In this paper, the epoxidation of allyl chloride with H₂O₂ catalyzed by Ti-ZSM-5 was studied. At the same time, the effect of solvent, catalyst, H₂O₂, allyl chloride amount and reaction temperature on the epoxidation of allyl chloride was investigated. The kinetics and mechanism of this reaction were also discussed.

Experimental

Preparation and characterization of catalyst

Ti-ZSM-5 was synthesized by the reaction of HZSM-5 with gaseous TiCl₄ in a quartz reactor under N₂ at 773 K for about 40 h. After completion of the reaction, the product was purged with N₂ at 773 K for 3—4 h and cooled down.

The Ti content of Ti-ZSM-5 being 2.60 mol% was analyzed by hydrogen peroxide color comparimetry on a 751G spectrophotometer.

X-Ray diffraction was performed with a D/Max-γA using Cu K_α radiation, the sample was run within the range of 0—90° for 2θ. The pattern of Ti-ZSM-5 showed the presence of orthorhombic MFI-type structure. No other phases were detected by XRD.

The skeletal IR spectra of Ti-ZSM-5 in the range of 400—1600 cm⁻¹ was recorded with a Nicolet 200SXV FT-IR spectrometer using KBr wafer technique. It exhibited an adsorption band at 975 cm⁻¹ which was absent in

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HZSM-5, indicating the insertion of titanium into the framework of molecular sieves.^{4,6}

Diffuse reflectance UV-vis spectra were obtained on a Hitachi UV-340 spectrometer. The pattern of Ti-ZSM-5 showed only a band at 220 nm which was assigned to the isolated framework titanium in the tetrahedral coordination,⁵ and no other bands were detected.

Epoxidation of allyl chloride

The epoxidation of allyl chloride was carried out in a 50 mL round-bottomed flask equipped with a condenser, a magnetic stirrer and a thermometer. Catalyst, solvent, allyl chloride and H₂O₂ aqueous solution (31.67 mol%) with the desired amounts were added into the reactor. The reaction was performed under the ambient atmosphere. Aliquots were removed at the different time intervals, the liquid mixture was separated from catalyst and analyzed using a 102G series gas chromatography fitted with a thermal conductivity detector and Porapak Q column (1.5 m × 3 mm I. D.). The analyzing conditions were the column temperature of 503 K and the carrier gas of H₂.

Kinetics study

The calculation of reaction initial rate (v_i): (1) function of $f(c)-t$ can be obtained by computer from the experimental curve of ECH concentration $f(c)$ against time (t), and the derivation of the function can obtain v_i when $t = 0$; (2) At $t = 0$, make a tangent line on the curve about the concentration of ECH against

time, and thus its slope is v_i . The v_i results obtained from the above two methods are unanimous.

Kinetic equation: Suppose that the kinetics equation is:

$$v = kC_1^{n_1}C_2^{n_2}C_3^{n_3} \quad (1)$$

In the experiment, C_1 , C_2 and C_3 in Eq. (1) represent the concentration of catalyst, H₂O₂ and allyl chloride, respectively. The concentration of H₂O₂ and allyl chloride is kept constant, then the Eq. (1) can be simplified to the following:

$$v = k'C_1^{n_1} \quad (2)$$

So the reaction order with catalyst n , can be obtained by the slope of a straight line, which a plot of $\ln v$ against $\ln C_1$ should give. From the same method, n_2 and n_3 in Eq. (1) can be calculated, and then the reaction kinetics equation can also be obtained.

Results and discussion

Activity evaluation of Ti-ZSM-5

The activities of Ti-ZSM-5 in the epoxidation of allyl chloride were investigated under the following conditions: temperature 318 K, allyl chloride 2 mL, H₂O₂ solution 1.00 mL or 1.60 mL, solvent methanol, the total volume of reaction system 15 mL, and stirred vigorously. The results were listed in Table 1.

Table 1 Activities of Ti-ZSM-5 in the epoxidation of allyl chloride with H₂O₂

Ti-ZSM-5 (g/L)	C ₃ H ₅ Cl (mol/L)	H ₂ O ₂ (mol/L)	C ₃ H ₅ Cl/H ₂ O ₂ molar ratio	t (min)	C ₃ H ₅ Cl conversion (%)	H ₂ O ₂ utilization ratio (%)
0	1.63	0.62	2.63	180	0.00	0.00
2	1.63	0.62	2.63	180	13.75	36.16
8	1.63	0.62	2.63	180	37.63	98.97
8	1.63	1.00	1.63	270	61.04	99.50

From Table 1, it was found that allyl chloride can not be epoxidized by H₂O₂ when there was no Ti-ZSM-5 as catalyst in the reaction system. And the C₃H₅Cl conversion and H₂O₂ utilization rose on abruptly with the increasing amount of Ti-ZSM-5. When the amount of Ti-

ZSM-5 was increased to 8 g/L, the C₃H₅Cl conversion and H₂O₂ utilization ratio reached 61.04% and 99.50% respectively after 270 min reaction, showing a high efficiency of Ti-ZSM-5 for the epoxidation of allyl chloride with H₂O₂ as an oxidant.

Effect of solvent on the epoxidation of allyl chloride

Dimethyl formamide (DMF), tetrahydrofuran (THF), acetone, ethyl alcohol and methanol were used as solvent for the epoxidation of allyl chloride with aqueous H_2O_2 , respectively, and the results were shown in Table 2. Although all of them are proper solvent for both allyl chloride and aqueous H_2O_2 to form a homogeneous phase, the epoxidation of allyl chloride did not occur when DMF or THF was used as a solvent. This is probably due to the titanium peroxocomplex (Ti—OOH), which was formed from Ti-ZSM-5 and H_2O_2 , is very unstable in the presence of DMF or THF, causing H_2O_2 to decompose over the surface of Ti-ZSM-5 quickly. Acetone is an aprotic solvent, and can not coordinate with Ti—OOH species to form an active intermediate compounds, so the activity of the epoxidation reaction was low. The protic solvents such as methanol and ethyl alcohol are easy to form active intermediate.^{5,6,8,9} But the epoxidation proceeded more efficiently when methanol was used as a solvent than ethyl alcohol. This can be contributed to steric hindrance, small bulk of molecule was beneficial to the effective collision between C_3H_5Cl and the active intermediate compound.

Table 2 Effect of solvent on the epoxidation of allyl chloride with H_2O_2

Solvent	C_3H_5Cl conversion (mol%)	H_2O_2 utilization ratio (mol%)
DMF	0.00	0.00
THF	0.00	0.00
Acetone	31.57	51.62
Ethyl alcohol	27.81	45.62
Methanol	47.65	78.17

C_3H_5Cl : 1.63 mol/L; H_2O_2 : 1.00 mol/L; Ti-ZSM-5: 8 g/L; Reaction temperature: 318 K; Reaction time: 60 min.

Relationship between the reaction rate and catalyst concentration

Table 3 shows the effect of the catalyst amount on the epoxidation of allyl chloride under the fixed concentration of C_3H_5Cl and H_2O_2 with methanol as a solvent. It can be found from Table 3 that the C_3H_5Cl conversion and H_2O_2 utilization increase with the increasing amount of Ti-ZSM-5. When the Ti-ZSM-5 concentration is 8 g/L, H_2O_2 utilization can reach 98.97%.

Table 3 Effect of catalyst amount on the epoxidation of allyl chloride

Ti-ZSM-5 (g/L)	C_3H_5Cl conversion (mol%)	H_2O_2 utilization ratio (mol%)
0	0.00	0.00
2	13.75	36.16
4	21.47	56.47
6	27.89	73.35
8	37.63	98.97

C_3H_5Cl : 1.63 mol/L; H_2O_2 : 0.62 mol/L; Solvent: methanol; Reaction temperature: 318 K; Reaction time: 180 min.

The relationship between the reaction rate v_i and the catalyst concentration [Cat.] is shown in Fig. 1. It can be observed from Fig. 1 that $\ln v_i$ with $\ln[\text{Cat.}]$ exhibits a linear relationship and the slope of the straight line is $n_1 = 1.0$, which indicates the epoxidation reaction of allyl chloride is a first order dependence on the catalyst concentration.

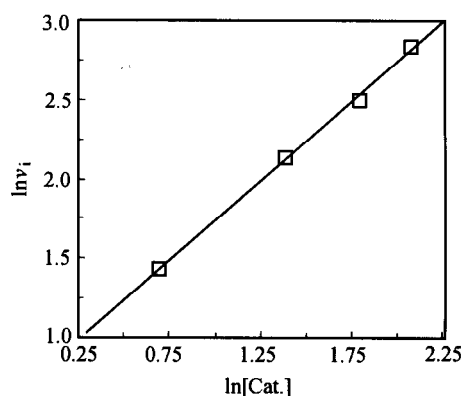


Fig. 1 Relationship between $\ln v_i$ and $\ln[\text{Cat.}]$.

Relationship between reaction rate and H_2O_2 concentration

The effect of H_2O_2 concentration on the epoxidation of allyl chloride is shown in Table 4. It is observed that the C_3H_5Cl conversion increased with the increasing H_2O_2 concentration.

The relationship of the epichlorohydrin (ECH) concentration and reaction time was recorded in Fig. 2 under the different H_2O_2 concentrations. From Fig. 2, the relationship between $\ln v_i$ and $\ln[H_2O_2]$ was obtained and shown in Fig. 3. It can be observed that a good linear relationship exists in the H_2O_2 concentration range of 0.10 to 1.73 mol/L ($-2.30 \leq \ln[H_2O_2] \leq 0.55$).

and the slope of straight line is $n_2 = 0.5$, suggesting a 0.5 order dependence on the H_2O_2 concentration for the epoxidation of allyl chloride.

Table 4 Effect of H_2O_2 concentration on the epoxidation of allyl chloride

H_2O_2 (mol/L)	$\text{C}_3\text{H}_5\text{Cl}/\text{H}_2\text{O}_2$ (molar ratio)	$\text{C}_3\text{H}_5\text{Cl}$ conversion (mol%)
0.30	5.45	18.24
0.40	4.08	23.92
0.62	2.63	29.63
1.00	1.63	35.03
1.73	0.94	44.33

$\text{C}_3\text{H}_5\text{Cl}$: 1.63 mol/L; Ti-ZSM-5: 8 g/L; Solvent methanol; Reaction temperature: 318 K; Reaction time: 60 min.

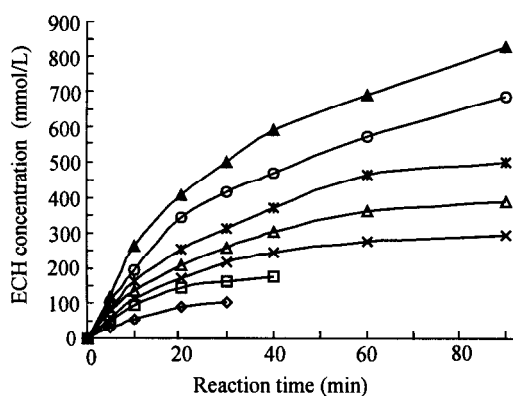


Fig. 2 Relationship between ECH concentration and reaction time under the different H_2O_2 concentration (H_2O_2 concentration: \diamond 0.10 mol/L, \square 0.20 mol/L, \times 0.30 mol/L, \triangle 0.40 mol/L, $*$ 0.62 mol/L, \circ 1.00 mol/L, \blacktriangle 1.73 mol/L; reaction temperature: 318 K, $[\text{C}_3\text{H}_5\text{Cl}] = 1.63$ mol/L, $[\text{Cat.}] = 8$ g/L).

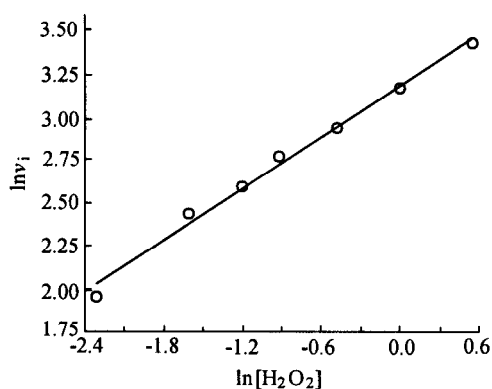


Fig. 3 Relationship between $\ln v_i$ and $\ln[\text{H}_2\text{O}_2]$.

Relationship between the reaction rate and allyl chloride concentration

The effect of allyl chloride concentration on the epoxidation of allyl chloride is shown in Fig. 4. From Fig. 4 it is found that the concentration of the epichlorohydrin increases with the increasing concentration of allyl chloride in the same reaction time. The relationship between $\ln v_i$ and $\ln[\text{C}_3\text{H}_5\text{Cl}]$ is also linear as shown in Fig. 5 and the slope n_3 is 1 when $[\text{C}_3\text{H}_5\text{Cl}] \leq 1.63$ mol/L ($\ln[\text{C}_3\text{H}_5\text{Cl}] \leq 0.49$), indicating a first order reaction. But when $[\text{C}_3\text{H}_5\text{Cl}] \geq 1.63$ mol/L ($\ln[\text{C}_3\text{H}_5\text{Cl}] \geq 0.49$), the relationship is not linear, indicating epoxidation reaction deviates from a first order reaction.

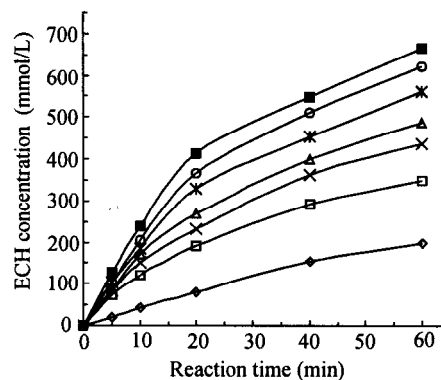


Fig. 4 Relationship between the ECH concentration and time under the different allyl chloride concentration ($\text{C}_3\text{H}_5\text{Cl}$ concentration: \diamond 0.33 mol/L, \square 0.65 mol/L, \times 0.98 mol/L, \triangle 1.31 mol/L, $*$ 1.63 mol/L, \circ 2.45 mol/L, \blacksquare 3.27 mol/L; reaction temperature: 318 K, $[\text{H}_2\text{O}_2] = 1.00$ mol/L, $[\text{Cat.}] = 8$ g/L).

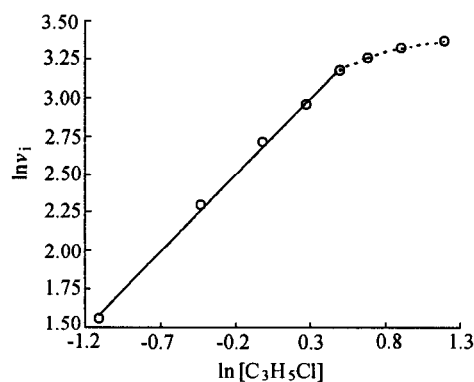


Fig. 5 Relationship between $\ln v_i$ and $\ln[\text{C}_3\text{H}_5\text{Cl}]$.

From the above experimental results the reaction kinetics equation can be obtained as follows:

$$v = kC_1^{n_1}C_2^{n_2}C_3^{n_3} = k[\text{Cat.}][\text{H}_2\text{O}_2]^{1/2}[\text{C}_3\text{H}_5\text{Cl}] \quad (3)$$

Effect of reaction temperature on the reaction rate

The epoxidation reaction rate at the different reaction temperature was tested against the H_2O_2 concentration, keeping the allyl chloride and catalyst concentration fixed. The epoxidation reaction rate v_i is plotted against the corresponding $[\text{H}_2\text{O}_2]^{1/2}$ value (See Fig. 6). There is a linear relationship between v_i and $[\text{H}_2\text{O}_2]^{1/2}$

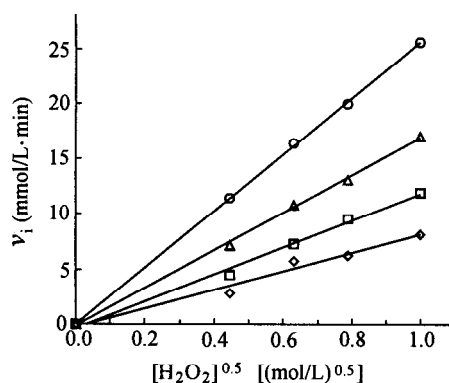


Fig. 6 Relationship between v_i and $[\text{H}_2\text{O}_2]^{1/2}$ at the different reaction temperature (Reaction temperature: \diamond 304 K, \square 308 K, \triangle 313 K, \circ 318 K; $[\text{C}_3\text{H}_5\text{Cl}] = 1.63$ mol/L, $[\text{Cat.}] = 8$ g/L).

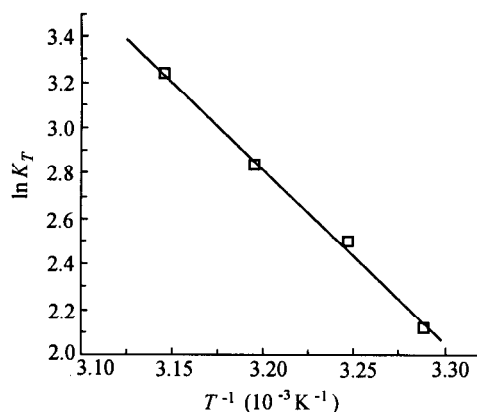


Fig. 7 Relationship between $\ln K_T$ and T^{-1} .

at the different reaction temperature, which is in agreement with the results obtained above. Moreover, the slope of every straight line represents the apparent rate constant, namely K_T under the corresponding reaction temperature. According to Arrhenius law, $\ln K_T$ is plotted against T^{-1} , and then a straight line is obtained (See Fig. 7). The slope of the straight line is $k = -E_a/R = -7.633 \times 10^3$ K, suggesting the apparent activation energy of the reaction is $E_a = 63.462$ kJ/mol.

Reaction mechanism of the allyl chloride epoxidation

Based on the Rideal-Freundlich mechanism, reaction rate can be expressed as follows:

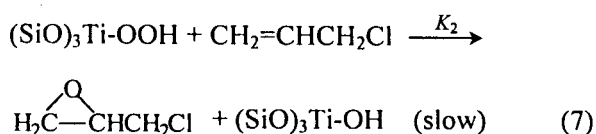
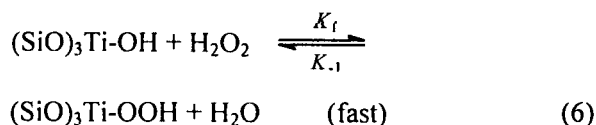
$$v = kN_{\text{total}}P_A P_B \quad (4)$$

We suppose that the adsorption heat decreases with the increasing $\ln \theta_A$ value, according to Freundlich formula, $\theta_A = KP_A^{1/n}$. Then the Eq. (4) can be changed into the following equation:

$$v = k'N_{\text{total}}P_A^{1/n}P_B \quad (5)$$

From the above experimental results, when n is 2, the equation of $v = k'N_{\text{total}}P_A^{1/2}P_B = kC_1C_2^{1/2}C_3 = k[\text{Cat.}][\text{H}_2\text{O}_2]^{1/2}[\text{C}_3\text{H}_5\text{Cl}]$ is in agreement with kinetics Eq. (3). So the mechanism of the epoxidation process can be deduced as follows:

The framework Ti in the tetrahedral coordination is the active center. In the process, H_2O_2 is first adsorbed on the surface of the molecular sieves and then interacts with the framework Ti to form titanium peroxocomplex Ti—OOH species, an active intermediate, which can carry out the surface reaction with the substrates to form the products. So the epoxidation reaction process can be expressed as follows:



From the results in Fig. 5, the epoxidation reaction deviates from the above reaction mechanism and the reaction order is lower than 1, when the concentration of allyl chloride is higher than 1.63 mol/L.

Conclusions

1. In the epoxidation reaction of allyl chloride with H_2O_2 , Ti-ZSM-5, which is prepared by the gas-solid isomorphous substitution, exhibits higher catalytic activity with the allyl chloride conversion and H_2O_2 utilization being 61.04% and 99.50%, respectively.

2. Methanol, a protic solvent with a smaller bulk, is the best reaction medium.

3. The kinetics equation in the Ti-ZSM-5-catalyzed epoxidation of allyl chloride can be expressed as the following:

$$v = k[\text{Cat.}][H_2O_2]^{1/2}[C_3H_5Cl]$$

The apparent activation energy is $E_a = 63.462$ kJ/mol.

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