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Macro-Kinetics of Styrene Oxidation Catalyzed by Co^{2+}-Exchanged X[1]

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Abstract—The macro-kinetics and pathway of styrene oxidation catalyzed by Co^{2+}-exchanged X, using O_2 as oxidant, were investigated. The effects of external diffusion, internal diffusion, the styrene concentration, O_2 pressure, the catalyst concentration and the reaction temperature on the styrene oxidation reaction rate were examined. The results showed that the reaction rate of styrene oxidation was 0.19 order with respect to the styrene concentration, 0.64 order with respect to O_2 pressure, and zero to first order with respect to the different catalyst concentration. The calculated activation energy for this reaction was 13.79 kJ/mol. On the other hand, the three products in the styrene oxidation reaction were, respectively, used as the reactant to examine the reaction pathway of styrene oxidation. The results revealed that styrene oxidation reaction occurred as two parallel reactions. One was the production of styrene oxide and the other was the production of benzaldehyde and formaldehyde with former partially oxidized to benzoic acid and the latter mostly oxidized to CO_2 and H_2O.

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1. INTRODUCTION

Styrene oxide is a very important intermediate in the field of pharmacy, spicery, plasticizer, epoxy resin thinner, flavoring agent, etc. [1–3]. It is commercially produced by the direct epoxidation of styrene on organic peroxy acid catalysts or a chlorohydrin process [4]. The direct epoxidation of styrene with organic peroxy acids as catalysts has the advantages of short procedure and high yield. However, organic peroxy acids are unstable and have the danger of explosion. Meanwhile, they are difficult to be separated from the reaction stream. On the other hand, the process of chlorohydrin is long and produces wastewater. Nowadays, many researches are carried out to produce styrene oxide by oxidation of styrene with various oxidants, such as H_2O_2 [5–7], *tert*-butylhydroperoxide [1, 8, 9], NaClO [10], $NaIO_4$ [11]. It is quite desirable that oxygen is used as the oxidant for this reaction, which is beneficial in terms of safety, economy and environment.

The research work on the styrene oxidation reaction using oxygen as oxidant was focused on the development of the new catalysts. Various catalysts, such as Co-, Fe- and Mn-T(p-SO_3H)PP porphyrins [12], Salen-Mn(III) complex [13], manganese(III) complexes of Br_2Salen and (*tert*-butyl)$_4$Salen ligands catalysts [14], have been explored. In these catalytic systems, different initiators, such as *iso*-butyraldehyde [12, 13] and *tert*-butylhydroperoxide [14], which were expensive and difficult to be recycled, had to be used to obtain reasonable styrene conversions and styrene oxide selectivities. On the other hand, catalytic processes for styrene oxidation by oxygen without initiator were also explored using manganese porphyrin [15], $Cu_2(OH)PO_4$ [16], TiO_2/SiO_2 [17], etc. as the catalysts, only a low styrene conversion (<30%) was obtained. A $Mo^{VI}O_2$(L)–NaY composite catalyst with oxygen as the oxidant [18] exhibited 68% of styrene conversion and 100% of styrene oxide selectivity, however, the preparation procedures for the catalyst were complex.

Recently, a cheap Co^{2+}-exchanged faujasite was found to be an efficient catalyst for the epoxidation of styrene with oxygen under mild and simple reaction conditions. Styrene oxide was produced with 60% of selectivity, along with 40% of benzaldehyde selectivity and 40% of styrene conversion at 373 K for 4 h, with dimethyl formamide (DMF) as the solvent [19, 20]. We found that higher styrene conversion of 62.5% and styrene oxide selectivity of 57.1% could be achieved when a mixed solvent composed of DMF and dimethyl sulfoxide (DMSO) was used under similar reaction conditions [21]. In this paper, we reported the macro-kinetics of styrene oxidation with O_2 using Co^{2+}-exchanged X as the catalyst in the DMF/DMSO mixed solvent. Meanwhile, the styrene oxidation reaction pathway over Co^{2+}-exchanged X catalyst in the solvent was also investigated.

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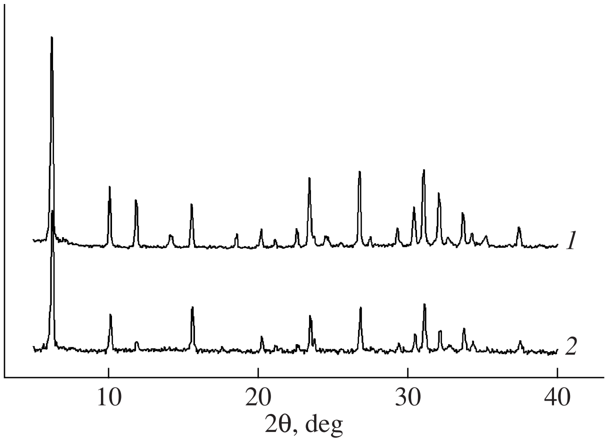

Fig. 1. XRD patterns of zeolite X (*1*) and Co^{2+}-exchanged X (*2*).

2. EXPERIMENTAL

2.1. Preparation of the Catalyst

Zeolite X was synthesized using sodium hydroxide and potassium hydroxide as the alkali source, sodium silicate as the silica source and sodium aluminate as the alumina source by the hydrothermal synthesis [22]. Briefly, the synthesis gel with a molar composition of $5.5\ Na_2O : 1.65\ K_2O : 1.0\ Al_2O_3 : 2.2\ SiO_2 : 122\ H_2O$ was prepared by adding suitable amount of the above reagents in water under vigorous stirring. After aging at 343 K for 3 h, it was transferred into a polypropylene bottle and crystallized at 369 K for 2 h. The final product was obtained after filtrating, washing with deionized water and drying at 373 K for 24 h.

Co^{2+}-exchanged X was prepared by first dispersing 1.0 g zeolite X in 30 ml 0.3 M $Co(NO_3)_2$ solution at 300 K with vigorous stirring for 24 h. After filtrating, the catalyst was thoroughly washed with deionized water to remove the adsorbed cobalt ion. The final catalyst was obtained after drying at 313 K in vacuum for 24 h. The cobalt content was found to be 8.4 wt %, as analyzed by an Inductively Coupled Plasma emission spectroscopy.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer with CuK_α radiation at 40 kV 30 mA. Scanning electronic micrograph (SEM) images were taken with a Philips-Quanta 200. An Optimv 2000DV Inductively Coupled Plasma emission spectroscopy was used to analyze the cobalt content in the catalyst.

2.3. Catalytic Reactions

The styrene oxidation reaction with O_2 was carried out in a 100 ml round-bottomed glass flask reactor connected with a condenser. In a typical reaction, a measured amount of catalyst was added to the reactor, which was precharged with desired amount of styrene and the mixed solvent (volume ratio of DMF to DMSO of 82.5 : 17.5) at the desired temperature. O_2 was bubbled into the reaction solution. The mixture was vigorously stirred with a magnetic stirring bar during the reaction. After reaction for a period of time, the catalyst was filtered off, and the liquid organic products were quantified with a gas chromatograph (GC) equipped with a quartz capillary column (PEG–20M, 0.25 mm × 30 m) and a flame ionization detector (FID). The formaldehyde in the products was detected with a high performance liquid chromatography (Agilent 1100). A C_{18} column was used with the mobile phase of 0.06 mol l^{-1} phosphoric solution (pH 2.5)-acetonitrile (volume ratio of phosphoric solution to acetonitrile of 50 : 50), at a detection wavelength of 336 nm with the column temperature of 303 K. The corrected area normalization method was used for the quantitative analysis.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalyst

Figure 1 shows the XRD patterns of zeolite X and Co^{2+}-exchanged X. It can be seen that zeolite X before and after the ion-exchange kept pure faujasite structure. The XRD peak intensity was decreased for Co^{2+}-exchanged X, compared to as-synthesized zeolite X. This phenomenon is the same as that reported in literature [23–25].

Figure 2 shows the SEM pictures of zeolite X and Co^{2+}-exchanged X. It can be seen that the morphology of zeolites were round in shape, with a particle size of 2–5 μm. The morphology and the particle size of zeolite X did not change before and after the ion-exchange.

3.2. Blank Test and the Elimination of Internal and External Diffusions

To examine the styrene oxidation reaction without a catalyst, the reaction was carried out by adding 6 ml of styrene and 30 ml of mixed solvent in a 100 ml round-bottomed glass flask, and bubbling oxygen at a rate of 3 ml/min into the solution. The reaction temperature was 373 K and the reaction time was 2 h. The experimental results showed that the conversion of styrene was only 3.3%, indicating that the styrene oxidation reaction was very slow without a catalyst.

The effect of external diffusion on the reaction could be eliminated by increasing the speed of agitation. Fig. 3 illustrates the results of styrene oxidation with oxygen using Co^{2+}-exchanged X as the catalyst at various agitation speeds. As can be seen from Fig. 3, the agitation speed had a strong influence on the rate of styrene oxidation reaction. The conversion of styrene increased with the increase of the agitation speed when the agitation speed was increased from 80 to 800 rpm. Further increase of the agitation speed from 800 to

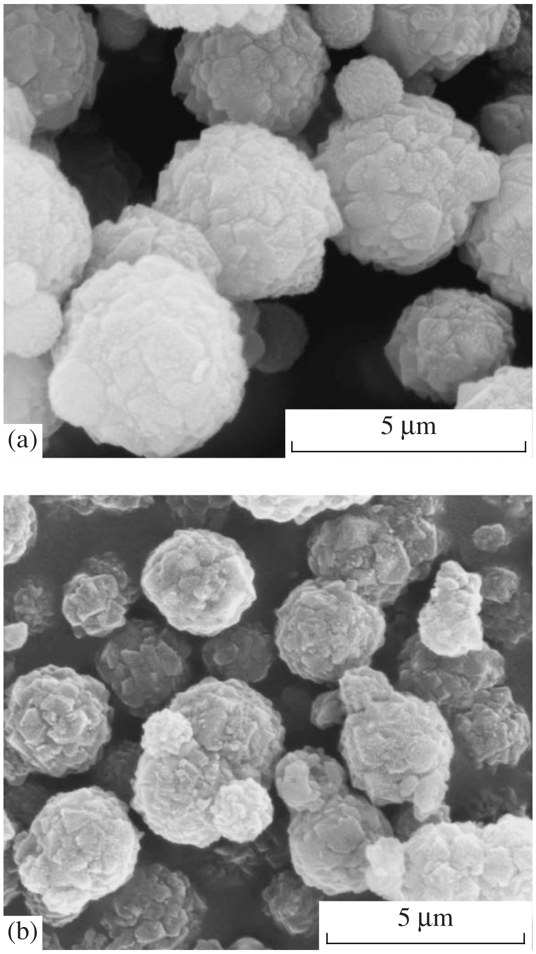

Fig. 2. SEM images of zeolite X (a) and Co^{2+}-exchanged X (b).

1200 rpm did not lead to the increase of the styrene conversion, indicating that the effect of external diffusion on this reaction had been eliminated. Therefore, the agitation speed was kept at 800 rpm during the reaction.

The effect of internal diffusion could be eliminated by changing the particle size of the catalyst. In general, the effect of internal diffusion on the reaction was less when the size of catalyst was quite small. As can be seen from Fig. 2, the particle size of the catalyst ranged from 2 to 5 μm. Therefore, it was very difficult to investigate the effect of internal diffusion on the reaction using the method of decrease the catalyst size. However, we can judge the effect of internal diffusion on the reaction by this formula:

$$\Phi = \frac{rd_p^2}{4C_sD_e} < 1/|n|, \qquad (1)$$

where, r is the reaction rate (mol min^{-1} l^{-1} g cat), d_p is the particle size (cm) of the catalyst, C_s is the reactant concentration (mol l^{-1}), D_e is the diffusion coefficient (cm^2 min^{-1}) of the reactant in the solvent. Their orders were 10^{-3}, 10^{-4}, 1, and 10^{-5}, respectively. Accordingly, the value of Φ was about 10^{-6}, which is far less than $1/|n|$. It is known that the effect of the internal diffusion on the reaction order n can be ignored when $\Phi < 1/|n|$ [26], where, n is the reaction order. Therefore, the effect of internal diffusion on this reaction was thought to be eliminated under our experimental conditions.

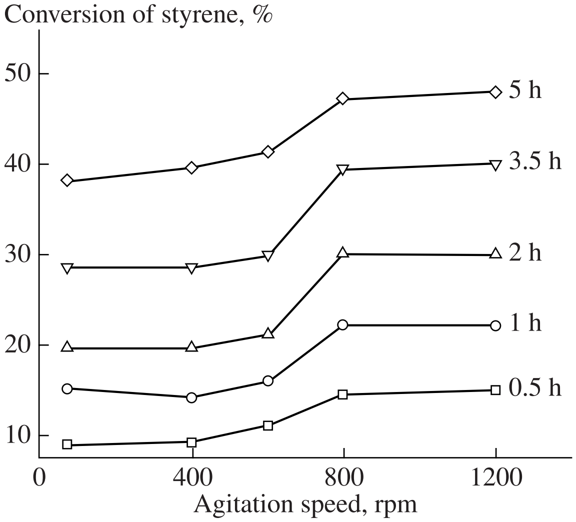

Fig. 3. The effect of agitation speed on styrene oxidation reaction at different reaction time. Reaction conditions: styrene, 6 ml; mixed solvent, 30 ml; Co^{2+}-exchanged X, 1.0 g; reaction temperature, 373 K; flow rate of O_2, 3 ml/min; atmospheric pressure.

3.3. Effect of the Reaction Time

Figure 4 shows the effect of the reaction time on the styrene oxidation with oxygen using Co^{2+}-exchanged X catalyst. As can be seen from Fig. 4, the styrene conversion increased very sharply in the initial 6 h and slightly changed after 6 h. At the same time, the selectivity of benzaldehyde almost unchanged while that of styrene oxide slightly decreased with the increase of the reaction time, suggesting that longer reaction time was favorable for the formation of benzaldehyde, which probably due to benzaldehyde was further oxidized to benzoic acid.

3.4. Effect of the Catalyst Concentration

To determine the reaction order n, the catalyst concentration was systematically varied, whereas the other reaction conditions were kept constant. The results are shown in Fig. 5. In the reaction, the styrene conversion was used to calculate the reaction rate as:

$$r_{\text{styrene}} = \frac{C_{\text{styrene}} - C_{\text{styrene},\,t}}{t} = \frac{C_{\text{styrene},\,0}X_{\text{styrene}}}{t}, \qquad (2)$$

where, r_{styrene} is the styrene reaction rate (mmol l^{-1} h^{-1}), $C_{\text{styrene},0}$ is the styrene concentration (mmol l^{-1}) before

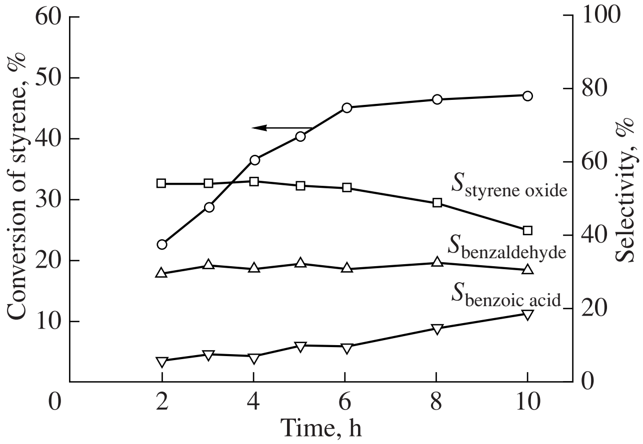

Fig. 4. Effect of the reaction time on styrene oxidation reaction. Reaction conditions: styrene, 6 ml; mixed solvent, 30 ml; Co^{2+}-exchanged X, 1.0 g; reaction temperature, 373 K; flow rate of O_2, 3 ml/min; atmospheric pressure.

the reaction, $C_{\text{styrene},t}$ is the styrene concentration (mmol l^{-1}) after the reaction, X_{styrene} is the conversion of styrene (no unit), and t is the reaction time (h).

As can be seen from Fig. 5, the reaction rate was very slow when no catalyst was used, while it was rapidly increased with the increase of the catalyst concentration. The reaction rate was found to be linear with the catalyst concentration in the range of 0–18.2 g/l. Therefore, the reaction order was first order with respect to the catalyst concentration. The reaction rate was slowly increased when the catalyst concentration was in the range of 18.2–27.2 g/l. In this case, the reaction order was between zero and first order with respect to the catalyst concentration. When catalyst concentration was more than 27.2 g/l, the reaction rate was independent on the catalyst concentration, i.e., the catalyst concentration had no influence on the reaction rate. Consequently, the reaction order was zero to the catalyst concentration in this case.

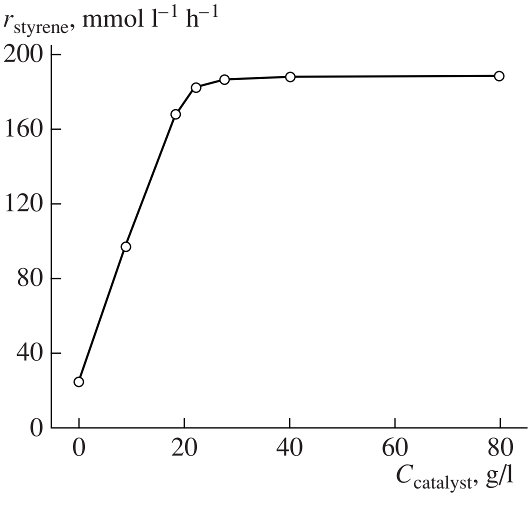

Fig. 5. Effect of the catalyst concentration on reaction rate. Reaction conditions: styrene, 6 ml; mixed solvent, 30 ml; reaction temperature, 373 K; reaction time, 2 h; flow rate of O_2, 3 ml/min; atmospheric pressure.

3.5. Effect of the O_2 Pressure

The effect of oxygen pressure on the reaction rate was studied at the pressure range (real) of 0.1–0.18 MPa and the temperature of 373 K with a fixed amount of catalyst. The results were presented in Fig. 6. The reaction rate was calculated as 0.64 order to oxygen pressure, indicating that the styrene oxidation reaction order was 0.64 with respect to the oxygen pressure.

In the gas-liquid-solid three-phase reaction system, the higher the gas pressure, the more gas would dissolve in the liquid, which would result in a higher reaction rate. However, higher oxygen pressure led to the decrease of styrene oxide selectivity, while gave rise to the increase of the benzaldehyde selectivity and benzoic acid selectivity, indicating that high O_2 pressure is favorable for the formation of benzaldehyde and benzoic acid.

3.6. Effect of the Styrene Concentration

The effect of the styrene concentration on the oxidation reaction rate was shown in Fig. 7. The styrene oxidation rate was analyzed using STATISTICA and the results indicated that the styrene oxidation reaction order was 0.19 with respect to the styrene concentration. Meanwhile, the selectivity of styrene oxide, benzaldehyde and benzoic acid kept unchangeable with the increase of styrene concentration.

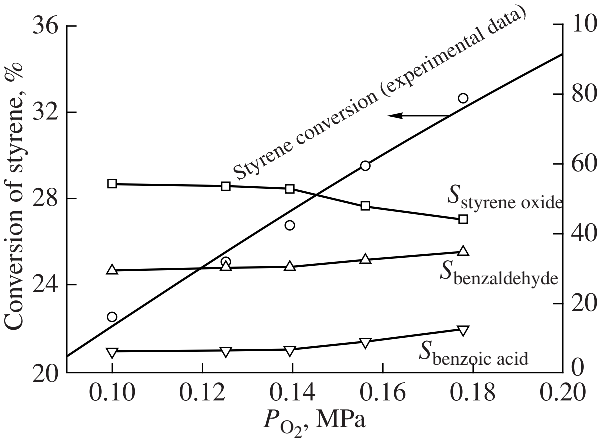

Fig. 6. Effect of the oxygen pressure on styrene oxidation reaction. Reaction conditions: styrene, 6 ml; mixed solvent, 30 ml; Co^{2+}-exchanged X, 1.0 g; reaction temperature, 373 K; reaction time, 2 h; flow rate of O_2, 3 ml/min.

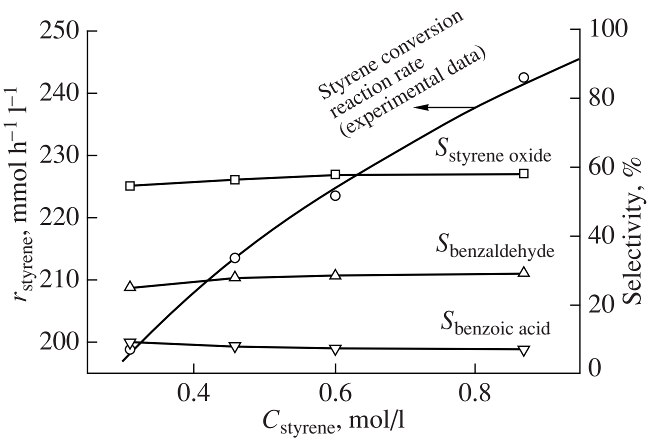

Fig. 7. Effect of the styrene concentration on reaction rate. Reaction conditions: styrene, 6 ml; Co^{2+}-exchanged X, 1.0 g; reaction temperature, 373 K; reaction time, 2 h; flow rate of O_2, 3 ml/min; atmospheric pressure.

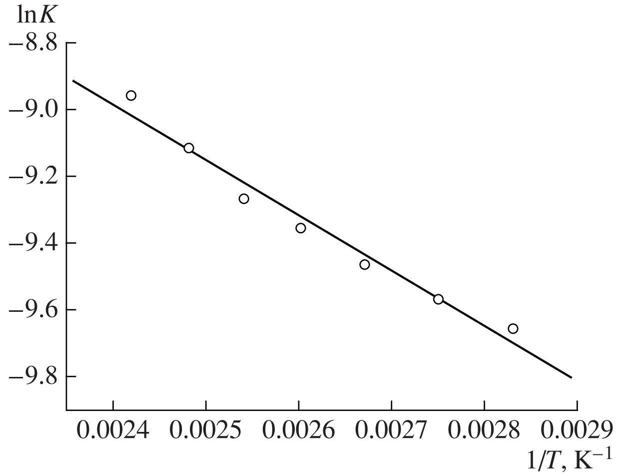

Fig. 8. Effect of reaction temperature on apparent rate constant.

3.7. Effect of Reaction Temperature

Table shows the effect of the reaction temperature on the styrene oxidation reaction. As expected, the styrene conversion increased at higher temperatures. Meanwhile, both the selectivity of styrene oxide and benzaldehyde decreased with the increase of the reaction temperature, and thereby, more benzoic acid and other impurity were produced at higher temperatures, as indicated by GC analysis results.

Figure 8 shows the Arrhenius plot of the reaction date (table). It can be seen that $\ln K$ had very good linear relation to $1/T$. From Fig. 8, the calculated apparent activation energy E_a was 13.79 kJ/mol and the frequency factor was 6.73×10^{-3} l h^{-1} g^{-1} kPa^{-1}.

From the above results, the macro-kinetic equation of styrene oxidation reaction could be expressed as:

when $C_{Catalyst} < 18.2$ g/l,

$$r = 6.73 \times 10^{-3}\exp(-13790/RT)C_{Catalyst}P_{O_2}^{0.64}C_{Styrene}^{0.19}; \quad (3)$$

when 18.2 g/l $< C_{Catalyst} < 27.2$ g/l,

$$r = 6.73 \times 10^{-3}\exp(-13790/RT)C_{Catalyst}^{0-1}P_{O_2}^{0.64}C_{Styrene}^{0.19}; \quad (4)$$

when $C_{Catalyst} > 27.2$ g/l,

$$r = 1.83 \times 10^{-1}\exp(-13790/RT)P_{O_2}^{0.64}C_{Styrene}^{0.19}; \quad (5)$$

the units of r, $C_{Catalyst}$, P_{O_2}, and $C_{Styrene}$ are mmol l^{-1} h^{-1}, g l^{-1}, kPa, and mol l^{-1}, respectively.

3.8. The Styrene Oxidation Pathway

From Fig. 4 we knew that the main products for styrene oxidation reaction were styrene oxide, benzaldehyde and benzoic acid. In order to elucidate the reaction pathway, the three products were, respectively, used as the reactant and the reaction was carried out following the same conditions as those of styrene oxidation mentioned above. When styrene oxide was used as the reactant, no product was found after the reaction, indicating that styrene oxide did not further react in the styrene oxidation reaction. When benzaldehyde was used as the reactant, benzoic acid was found to be the only product and the amount of benzoic acid increased with the increase of the reaction time. No styrene oxide was detected. When benzoic acid was used as the reactant, no product was found. For the formation of benzaldehyde and formaldehyde in the styrene oxidation reaction, Haber et al. [12] thought that it resulted from the oxidative cleavage of C=C in styrene. We could not detect formaldehyde by GC, so we used high performance liquid chromatography and found that there was a trace amount of formaldehyde in the styrene oxidation reaction products. Since the amount of formaldehyde did not match the amount of the formed benzaldehyde, we assumed that formaldehyde either was oxi-

Effect of the reaction temperature on styrene oxidation reaction

Temperature, K	Styrene conversion, %	Selectivity, %		
		styrene oxide	benzaldehyde	benzoic acid
353	13.7	60.3	38.0	0.8
363	15.0	59.2	38.9	0.9
373	16.6	59.9	35.9	1.8
383	18.5	59.9	36.4	2.1
393	20.2	59.0	31.0	4.0
403	23.5	57.2	30.6	6.1
413	27.5	57.1	30.9	6.1

Note: Reaction conditions: styrene, 10 ml; mixed solvent, 20 ml; Co^{2+}-exchanged X, 1.6 g; reaction time, 2 h; flow rate of O_2, 3 ml/min; atmospheric pressure.

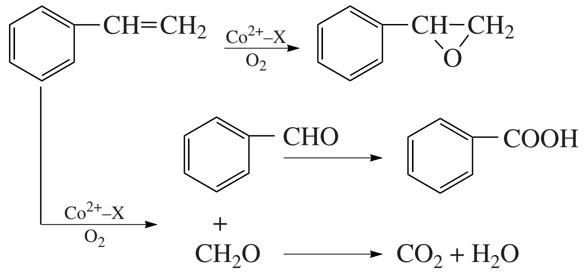

Fig. 9. The pathway of styrene oxidation reaction.

dized or escaped from the reaction system with the unreacted oxygen. Thereafter, we introduced the tail gas into water to trap the possibly escaped formaldehyde. However, no formaldehyde was detected in the water after the reaction. When we introduced the tail gas into a clear $Ca(OH)_2$ solution, the $Ca(OH)_2$ solution became turbid in a short time. The deposit was proved to be $CaCO_3$ by XRD, indicating that there contained CO_2 in the tail gas. When we added a little dry $CuSO_4$ crystal into the styrene oxidation reaction mixture, the color of $CuSO_4$ crystal changed from grey to sky-blue after shaking, suggesting that there was water in the reaction mixture. From the above results, we concluded that most of formaldehyde was oxidized to CO_2 and H_2O.

Therefore, the styrene oxidation reaction pathway could be expressed as two parallel reactions, as shown in Fig. 9. One was the oxidation of styrene to styrene oxide, the other was the oxidative cleavage of styrene into benzaldehyde and formaldehyde, with benzaldehyde partially oxidized to benzoic acid and formaldehyde mostly oxidized to CO_2 and H_2O.

4. CONCLUSIONS

Co^{2+}-exchanged X was applied to the styrene oxidation reaction with oxygen as the oxidant. It was found that the effect of external diffusion on the reaction was eliminated when the agitation speed was more than 800 rpm. The effect of internal diffusion on the reaction would be ignored since the particle size of the catalyst was very small. The macro-kinetics was investigated as that the reaction rate of styrene oxidation was 0.64 order with respect to oxygen pressure, 0.19 order with respect to styrene concentration, and zero to first order with respect to the different catalyst concentration. The calculated activation energy for this reaction was 13.79 kJ/mol. The styrene oxidation reaction pathway could be expressed as two parallel reactions. One was the oxidation of styrene to styrene oxide; the other was the oxidative cleavage of styrene into benzaldehyde and formaldehyde, with benzaldehyde partially oxidized to benzoic acid and formaldehyde mostly oxidized to CO_2 and H_2O.

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