

Article

Process optimization study on the carbonylation of methyl acetate

Baohe Wang, Baomin Ge, Jing Zhu*, Lina Wang

Key Laboratory for Green Chemical Technology of Ministry of Education, Research and Development Center of Petrochemical Technology, Tianjin University, Tianjin 300072, China



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ABSTRACT

Acetic anhydride is the important organic chemical raw material, and is used widely in chemical industry, pharmaceutical industry, dyes, spices and other fields. In this paper, the process of carbonylation of methyl acetate in rhodium iodine catalyst system was studied, and the suitable reaction conditions were determined. At the same time, the kinetic model was established. The optimum reaction conditions were as follows: the reaction pressure was 5 MPa, the hydrogen content was 8%, the amount of iodomethane was 15%, the amount of lithium iodide was 3%, the reaction temperature was 150 °C and the reaction time is 3 h. Under the above reaction conditions, the selectivity of the reaction is close to 100% and the conversion is as high as 92%. The macroscopic kinetic model of the reaction was established in the temperature range of 120 °C–150 °C. The reaction is an irreversible reaction without the formation of by-products and the dynamic equation is also given in the Conclusions section.

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1. Introduction

Acetic anhydride has the appearance of colorless transparent liquid. It is slightly soluble in water and slowly hydrolyzed into acetic acid in water. Acetic anhydride is an important organic chemical raw material, and it has a very wide range of applications in cellulose synthesis, pharmaceutical synthesis and dye synthesis [1].

The industrial production methods of acetic anhydride [2] are mainly acetaldehyde oxidation co-production method, acetic acid cleavage method and carbonylation of methyl acetate method. The carbonylation of methyl acetate process has the advantages of short process, good product quality, low consumption and less waste. This paper mainly studies the carbonylation of methyl acetate in rhodium catalyst system.

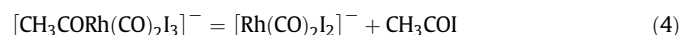
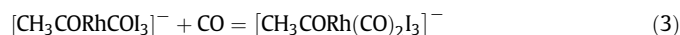
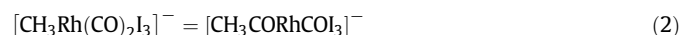
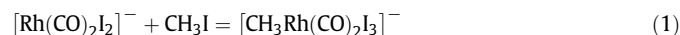
Inspired by the process of carbonylation of methanol [3–8], many researchers found that metal carbonyls have a significant catalytic effect on the carbonylation reaction [9–13]. The main point of the study was to select the main metal of the catalyst, followed by cobalt, then rhodium and many other metals. The BP company of British [14,15], the Estman company of United States [16,17], and the Chinese Academy of Sciences [18,19] all studied in-depth, and had their own characteristics.

BP Company has its own unique catalyst system and has been using the rhodium. This process needs a halide as a combined catalyst and an iodine salt as a stabilizer. Also, ruthenium as catalytic additives and quaternized amides such as *N,N*-diethylimidazolium iodide as stabilizers are added so that the reaction can proceed smoothly.

The amount of water is reduced by adding a small amount of acetic anhydride to the reaction system, so that the reaction tends to anhydrous process and by-products are greatly reduced.

On this basis, Estman Company also gradually adopted rhodium iodine catalyst system, in which rhodium as the main catalyst, iodomethane and iodine salt as co-catalysts. The iodine salt is basically composed by alkali metals and alkaline earth metal, it is not only able to provide a better rate of formation of acetic anhydride when adding raw material in a suitable range, but also to deduce the by-product of diethylene glycol diacetate during the reaction. $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is the catalytic activity center in the carbonylation of methyl acetate. Polichnowski [20] outlined his mechanistic study of the rhodium-catalyzed, iodide-promoted carbonylation of methyl acetate. The reaction mechanism of carbonylation of methyl acetate is shown in Fig. 1. (See Tables 1–5.)

The reaction processes are as follows:



In this catalytic cycle, the oxidation, addition, insertion, reduction and elimination of the reaction must be carried out under anhydrous conditions. Reaction (1–5) rate is slow. If LiI is added as the promoter,

* Corresponding author.

E-mail address: cj_zhu1975@tju.edu.cn (J. Zhu).

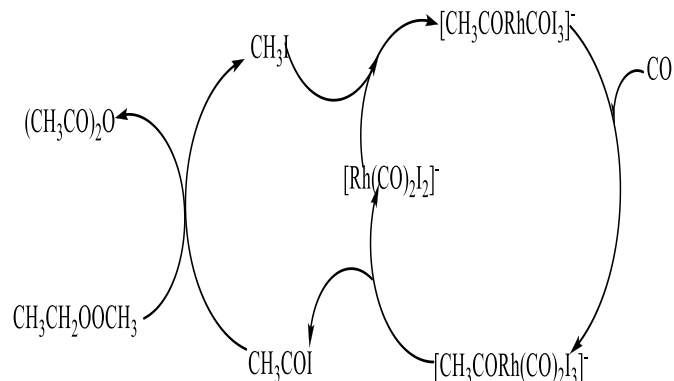
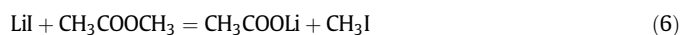


Fig. 1. Reaction mechanism of carbonylation of methyl acetate.

the following reactions can occur on the basis of the carbonylation of methyl acetate cycle:



With the help of the two fast reactions, the overall rate of carbonylation can be increased. Reaction mechanism is shown in Fig. 2. The general formula for the methylation of methyl acetate is:



Subsequently, the Company changed the catalyst system, using rhodium catalyst, methyl iodide, while *N, N*-diethyl imidazole iodide and lithium iodide mixture or a separate *N, N*-diethyl imidazole iodide were added. The results showed that the effect is not as good as the lithium iodide, because the amount of by-products did not decrease. So Estman Company finally chooses the catalyst system including methyl iodide, lithium iodide, and rhodium.

Many researchers have also developed different chelate rhodium complexes or rhodium-loaded catalysts [21,22] to increase the stability and longevity of the catalysts, but have failed to achieve industrial production. Therefore, the catalytic system of rhodium-iodomethane-metal iodide is still the traditional catalytic system used in industrial production.

Although the catalyst system has been well applied in the industry, the technological conditions of the catalytic system have not been studied in detail.

Industrial common rate equation [23] (subscript C represents acetic anhydride and A, B represent methyl acetate and CO, respectively) is as follows

$$r = \frac{dc_C}{dt} = -\frac{dc_A}{dt} = k'c_Ac_B$$

Zoeller [24] found that reaction rate was independent of the CO pressure and its concentration could be approximated to be constant when the total reaction pressure was above 3.0 MPa in carbonylation of methyl acetate catalyzed by $\text{RhCl}_3\text{-CH}_3\text{I-LiI}$. Therefore, the reaction pressure studied in our experiment was above 3.0 MPa.

In this paper, the optimum reaction conditions for the carbonylation of methyl acetate catalyzed by rhodium-iodomethane-lithium iodide

Table 1
Experimental data at 393 K

t/min	60	90	120	150
$\ln C_{A0}/C_A$	6.02×10^{-3}	0.1744	0.30	0.33

Table 2
Experimental data at 403 K

t/min	60	90	120	150	180
$\ln C_{A0}/C_A$	0.357	0.635	0.892	1.079	1.347

were studied. And on this basis, the kinetic equation of the reaction was deduced.

2. Experimental

2.1. Chemicals

Methyl acetate with purity $\geq 99\%$ was purchased from Tianjin Chemical Reagents Company. Lithium iodide with purity $\geq 99\%$ was purchased from Shanghai Zhong Li Chemical Reagents Company. RhCl_3 with purity ≥ 0.39 was purchased from Tianjin Chemical Reagents Wholesale Company. Hydrogen, nitrogen and carbon monoxide with purity $\geq 99.99\%$ were purchased from Tianjin Berkeley Gas Company.

2.2. Experiment

The reaction was carried out in a 500 ml zirconium autoclave, and the whole reaction apparatus were consisted of an electrical heater, an electric mixer, and a control-temperature equipment.

Rhodium catalyst, lithium iodide, methyl acetate, methyl iodide and acetic acid were added to the autoclave, and then hydrogen and carbon monoxide were added according to the partial pressure ratio. When the pressure was 2 MPa, the mixtures were heated to needed temperature. Next, carbon monoxide was added until the reaction pressure reached needed pressure. During the reaction, pressure and reaction temperature remain constant and take samples every 0.5 h. After a certain period of time, reaction was stopped when the pressure in autoclave no longer decreased. After cooling, the reaction product can be released from the discharge valve and then analyzed.

2.3. Analytical methods

Analytical Instruments: Fu Li 9790 Gas Chromatograph

Column: AC20, $\varnothing 0.22\text{mm} \times 30000\text{mm}$

Carrier gas: N_2 , $29.8\text{ ml} \cdot \text{min}^{-1}$; H_2 , $30\text{ ml} \cdot \text{min}^{-1}$; air, $300\text{ ml} \cdot \text{min}^{-1}$

Injection volume: $1\text{ }\mu\text{l}$

Column temperature: The temperature was raised to $40\text{ }^\circ\text{C}$ at a rate of $15\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and held for 6 min, then raised to $160\text{ }^\circ\text{C}$ at a rate of $15\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and held for 7 min.

Detector: FID

Detector temperature: $180\text{ }^\circ\text{C}$

Inlet temperature: $180\text{ }^\circ\text{C}$

Calculation method: Determination of acetic anhydride content by gas chromatography using area correction normalization

3. Results and Discussion

3.1. The effect of pressure

Pressure is an important factor affecting the carbonylation of methyl acetate. When the pressure is too low, the reaction cannot proceed.

Table 3
Experimental data at 413 K

t/min	30	60	90	120	150	180
$\ln C_{A0}/C_A$	0.041	0.499	0.916	1.386	1.76	2.302

Table 4
Experimental data at 423 K

<i>t</i> /min	30	60	90	120	150	180
$\ln C_{A0}/C_A$	0.2614	0.8	0.1347	1.419	2.04	2.526

When the pressure is too high, it is not conducive to the reaction. Therefore, the effect of pressure on the selectivity and conversion of the reaction was investigated.

The result is shown in Fig. 3. It can be seen that the conversion of methyl acetate increases with the increase of the pressure. When the pressure reaches 5 MPa, the conversion of methyl acetate reaches the maximum value. When the pressure exceeds 5 MPa, the conversion rate gradually decreased. However, when the pressure is less than 5 MPa, the reaction selectivity has a slight change, all close to 100%; when the pressure is more than 5 MPa, the selectivity of acetic anhydride changes greatly, reaching about 97%.

According to Henry's law, the saturated concentration of the gas in the liquid is proportional to the equilibrium pressure of the gas on the liquid surface at a certain temperature. The law shows that as the pressure increases, the more carbon monoxide dissolves in the reaction solution. However, it can be seen from the Fig. 3 that when the reaction pressure exceeds a certain value, the conversion and selectivity decrease. It is mainly because that the carbon monoxide pressure exceeds the amount of carbon monoxide required for the reaction and the remaining carbon monoxide participates in side reaction, thereby reducing the selectivity of the reaction. Therefore, the more suitable reaction pressure is 5 MPa, at which the reaction can achieve a higher conversion rate and a near 100% selectivity.

3.2. The effect of hydrogen partial pressure

Hydrogen is one of the important factors which maintain the activity of the catalyst, but this effect is limited, the appropriate amount of hydrogen can effectively promote the catalytic reaction, but excessive hydrogen is not conducive to the progress of the reaction. Therefore, the effect of hydrogen partial pressure on the selectivity and conversion of the reaction was investigated. The experimental result is shown in Fig. 4. It can be seen that when the partial pressure of hydrogen is 8%, the reaction has a high selectivity and conversion rate; When the partial pressure of hydrogen is less than 8%, the conversion of the reaction increases with the increase of the amount of hydrogen, and the selectivity of the reaction is above 99%; when the partial pressure of hydrogen is more than 8%, the conversion of the reaction decreases and the selectivity decreases significantly as the amount of hydrogen increases.

Under the condition of no hydrogen the reaction is in a state of balance, the conversion of the methyl acetate doesn't change; after adding the hydrogen, there is a sharp rise in the conversion of the methyl acetate, but then the conversion of methyl acetate drops with the increase of the amount of hydrogen. This phenomenon occurs because $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is the active center [20]. When no hydrogen is added, the rhodium compound in the reaction system is present as $[\text{Rh}(\text{CO})_2\text{I}_4]^-$ and only a small amount of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and the conversion of the reaction is very low. When the hydrogen is added, the rhodium compound in the reaction system is mainly in the presence of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, so that the conversion of the reaction increases abruptly. But when the hydrogen partial pressure exceeds a certain value, the excess hydrogen can promote the occurrence of side reaction,

Table 5
Arrhenius data at 393 K–423 K

T^{-1}/K^{-1}	0.00254	0.00248	0.00242	0.00236
<i>k</i>	0.00435	0.00808	0.01482	0.0216
$\ln k$	−5.438	−4.818	−4.212	−3.832

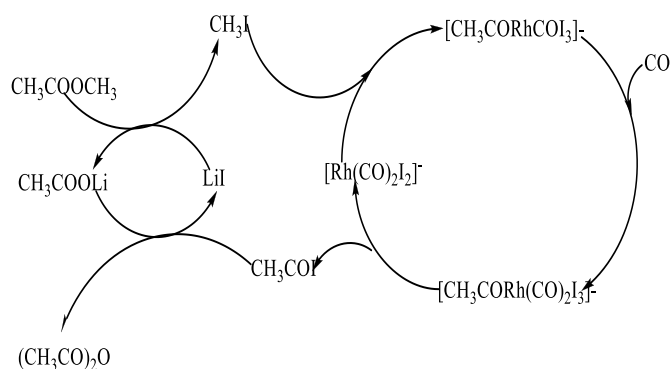


Fig. 2. Reaction mechanism of carbonylation of methyl acetate including alkali metal.

so that the selectivity of the reaction decreases. The possible side reaction is as follows: $(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{COOH}$.

It can be concluded that the presence of the appropriate amount of hydrogen can promote the carbonylation of methyl acetate and increase the conversion of the reaction. On the contrary, Excess hydrogen can hinder the reaction and reduce the selectivity of the reaction.

3.3. The effect of CH_3I addition

Methyl iodide as the co-catalyst plays an important role in the reaction. The experimental result is shown in Fig. 5. It can be seen that with the increase of the methyl iodide content, the conversion of the reaction gradually increases, and the selectivity of the reaction shows a decreasing trend. The suitable amount of CH_3I was 15%.

For the carbonylation of methyl acetate, halide is involved in the formation of acetyl iodide. Iodomethane and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ undergo the oxidative addition reaction to form acetyl iodide, which is a slow reaction [20]. When the iodine ion is present in large amount, the salt effect and the presence of coordination are more favorable for the formation and stabilization of the transition state, thus accelerating the reaction. When too much CH_3I is added, the remaining methyl iodide will participate in other reactions to generate by-products in later stage reaction, so that the selectivity of the reaction is reduced.

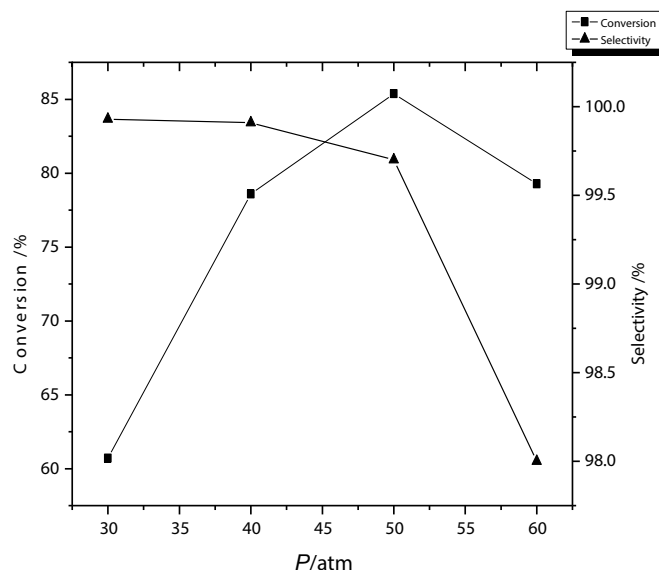


Fig. 3. Effect of the pressure on reaction. Conditions: $P_{\text{H}_2} = 8\%$, $W_{\text{CH}_3\text{I}} = 15\%$, $W_{\text{LiI}} = 3\%$, $T = 150^\circ\text{C}$, $t = 3\text{ h}$, $1\text{ atm} = 101325\text{ Pa}$.

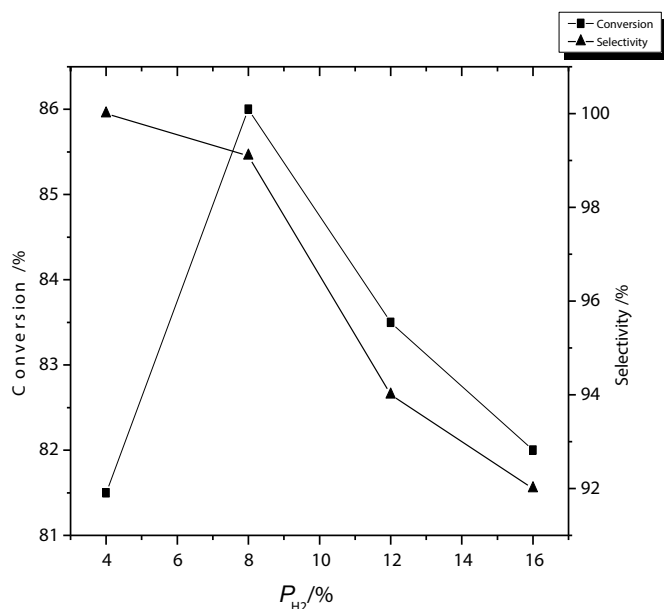


Fig. 4. Effect of the partial pressure of hydrogen on reaction. Conditions: $P_{CO} = 5$ MPa, $W_{CH_3I} = 15\%$, $W_{LiI} = 3\%$, $T = 150$ °C, $t = 3$ h.

3.4. The effect of LiI addition

The rhodium-iodine catalyst system use lithium iodide as a co-catalyst to improve the efficiency of the catalyst. The effects of the addition of LiI on the selectivity and conversion of the reaction were investigated. Fig. 6 shows that the conversion of the reaction increases with the increase of the amount of lithium iodide, but the selectivity of the reaction decreases with the increase of the amount of lithium iodide.

According to the researches of Luft *et al.* [25] and Polichnowski [20] and our experimental facts, it is believed that LiI has three important effects in the catalyst system: (1) Produce CH_3I .

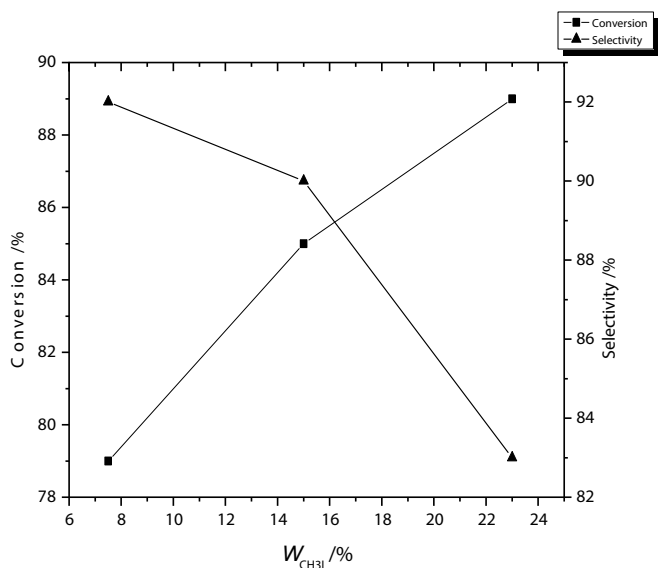
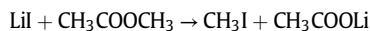


Fig. 5. Effect of the addition of CH_3I on reaction. Conditions: $P_{CO} = 5$ MPa, $P_{H_2} = 8\%$, $W_{LiI} = 3\%$, $T = 150$ °C, $t = 3$ h.

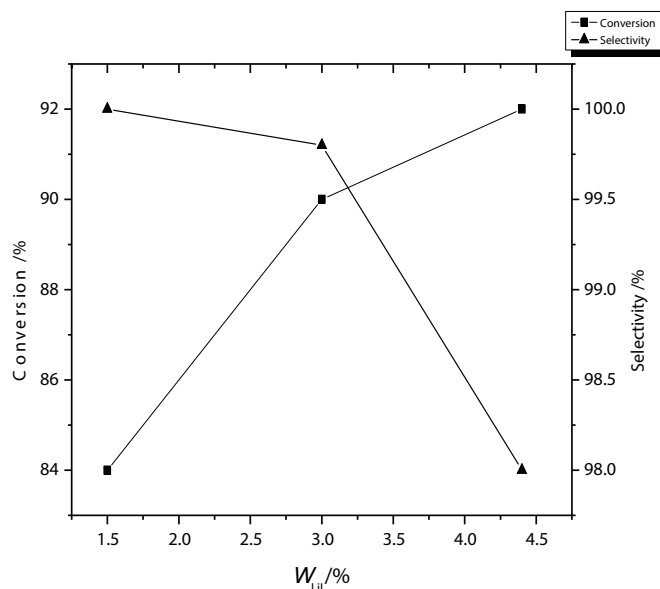


Fig. 6. Effect of the addition of LiI on reaction. Conditions: $P_{CO} = 5$ MPa, $P_{H_2} = 8\%$, $W_{CH_3I} = 15\%$, $T = 150$ °C, $t = 3$ h.

The rate control step of the catalytic cycling reaction is the oxidation addition of Rh and CH_3I , so LiI shows an important effect. (2) Produce $[Rh(CO)_2I_2]^-$. Studies have shown that [26] the oxidation addition step is nucleophilic reaction, $[Rh(CO)_2I_2]^-$ is active center. (3) Stabilize catalyst. The high concentration of LiI can maintain a high concentration of active species in the solution and reduce the precipitation of rhodium.

3.5. Effect of reaction temperature

Fig. 7 shows that in the low temperature range, between 120 °C and 150 °C, the conversion increases and the selectivity is close to 100%; in the high temperature range, between 160 °C and 190 °C, the conversion and selectivity decrease with the increase of temperature.

There are two reasons to explain the above experimental results. On one hand, it is universally known that gas solubility generally reduces with the increase of temperature. The solubility of CO and H_2 decreases at high temperature, so that the reactants are insufficient and the conversion of the reaction decreases. On the other hand, the high temperature will influence reaction pathways, some of the side reactions need to be carried out at higher temperatures, and when the

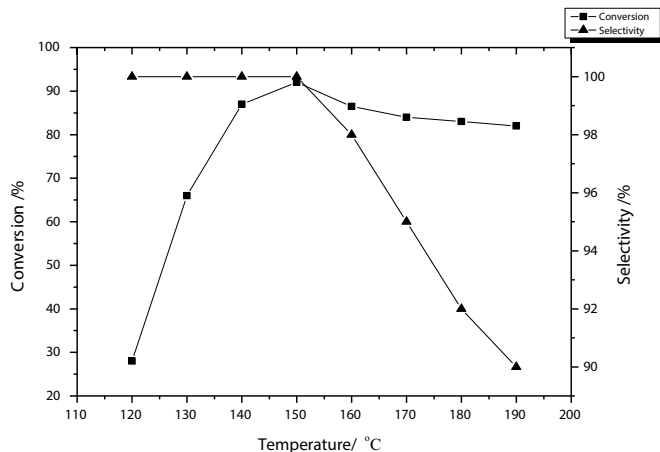


Fig. 7. Effect of reaction temperature on reaction. Conditions: $P_{CO} = 5$ MPa, $P_{H_2} = 8\%$, $W_{CH_3I} = 15\%$, $W_{LiI} = 3\%$, $t = 3$ h.

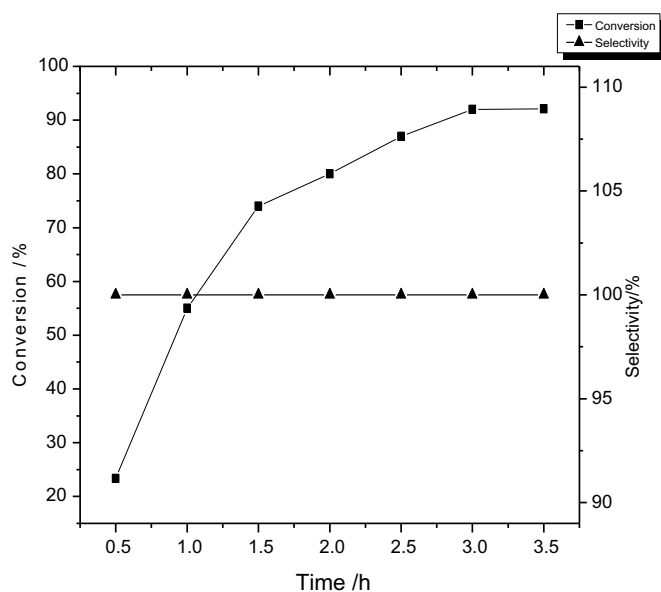


Fig. 8. Effect of reaction time on reaction. Conditions: $P_{CO} = 5 \text{ MPa}$, $P_{H_2} = 8\%$, $W_{CH_3I} = 15\%$, $W_{LiI} = 3\%$, $T = 150^\circ\text{C}$.

temperature is too high, the side reactions occur, resulting in the decrease of selectivity of the reaction.

3.6. Effect of reaction time

The Fig. 8 shows that the conversion of the reaction increases with the increase of the reaction time, but the selectivity of the reaction does not change with time. As time increases, the amount of consumed reactants is increasing, so the conversion of the reaction increases

4. Establishment of Dynamic Model

4.1. Curve fitting at 393 K–423 K and calculation of rate constant k

It can be seen from the Figs. 9–12 that $\ln(C_{A0}/C_A)$ is linearly related to the time, which indicates that the carbonylation of methyl acetate is

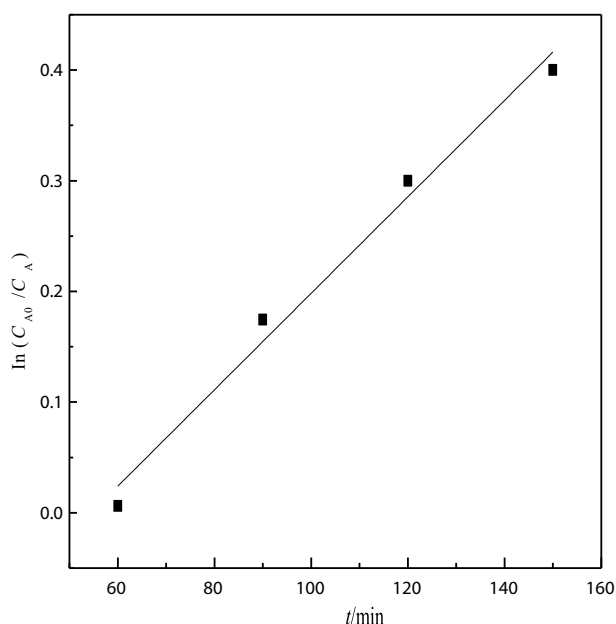


Fig. 9. $\ln(C_{A0}/C_A) - t$ at 393 K. ($Y = 0.00435X - 0.23576$, $R = 0.9754$).

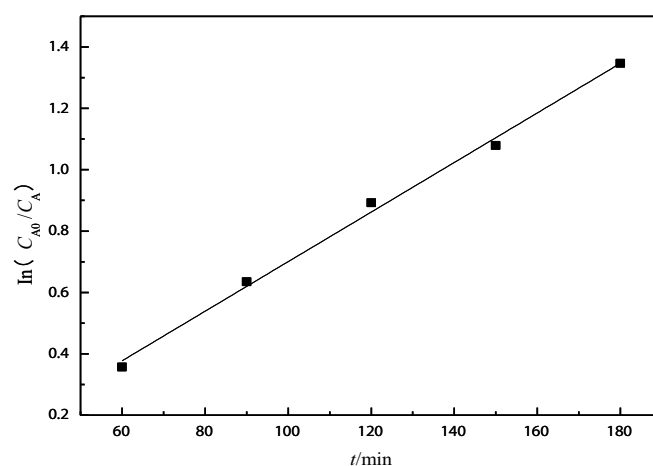


Fig. 10. $\ln(C_{A0}/C_A) - t$ at 403 K. ($Y = 0.00808X - 0.1076$, $R = 0.9886$).

consistent with the first order irreversible reaction model. It has a good agreement with our assumption

4.2. Reaction activation energy

According to the Arrhenius formula: $\ln k = -\frac{E_a}{RT} + \ln A$, we calculate the activation energy of the reaction. It can be seen from the Fig. 13, the reaction activation energy was $E_a = 75.159 \text{ kJ} \cdot \text{mol}^{-1}$.

5. Conclusions

By studying different reaction conditions of the process of carbonylation of methyl acetate in rhodium iodine catalyst system, the optimum reaction conditions were as follows: the reaction pressure was 5 MPa, the hydrogen content was 8%, the amount of iodomethane was 15%, the amount of lithium iodide was 3%, the reaction temperature was 150°C and the reaction time is 3 h. Under the above reaction conditions, the selectivity of the reaction is close to 100% and the conversion is 92%.

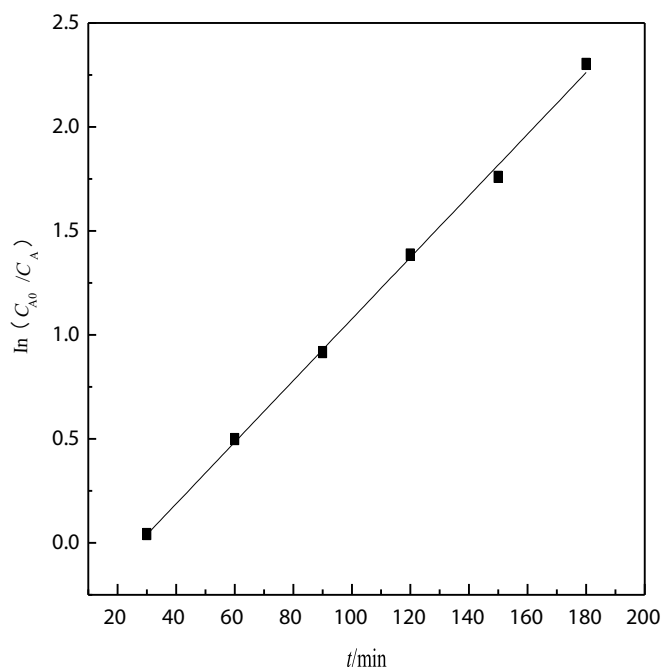


Fig. 11. $\ln(C_{A0}/C_A) - t$ at 413 K. ($Y = 0.01482X - 0.40513$, $R = 0.9988$).

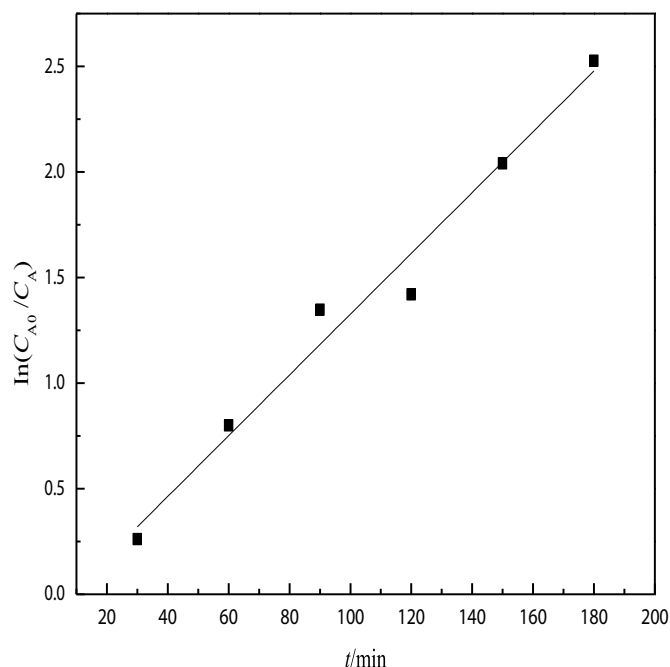


Fig. 12. $\ln(C_{A0}/C_A) - t$ at 423 K. ($Y = 0.0216X - 0.1126$, $R = 0.9984$).

The macroscopic kinetic model of the reaction was established in the temperature range of 120 °C–150 °C. The reaction is an irreversible reaction without the formation of by-products and the dynamic equation is $C_A = C_{A0}e^{-kt}$ ($k = 4.3 \times 10^7 \exp. (-9040/T)$), the activation energy $E_a = 75.159 \text{ kJ} \cdot \text{mol}^{-1}$.

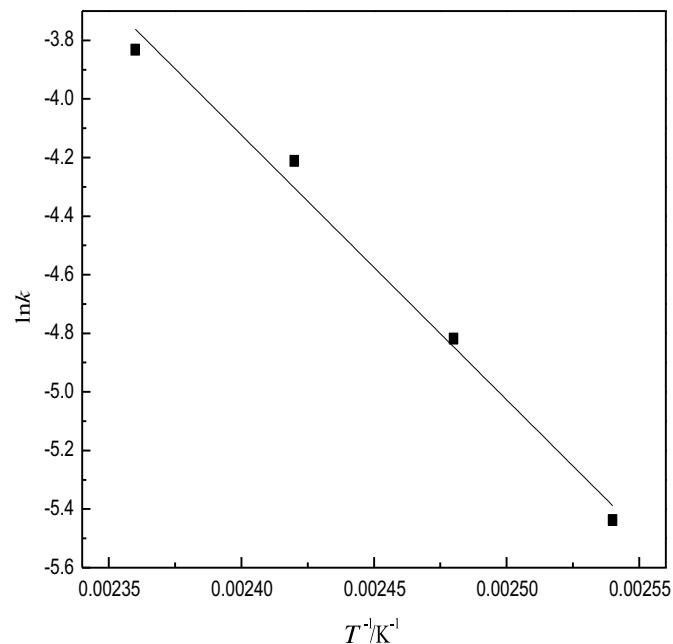


Fig. 13. Arrhenius curve of reaction rates for the carbonylation of methyl acetate. ($Y = -9040X + 17.5793$, $R = 0.9915$).

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