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Reaction Kinetics of Methanol Carbonylation to Methyl Formate Catalyzed by CH_3O^- Exchange Resin

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Abstract The carbonylation of methanol with CO using CH_3O^- exchange resin as a heterogeneous catalyst at temperatures near 350 K is examined systematically in an attempt to derive kinetic rate expressions for the reaction. The activation energies for the carbonylation and decarbonylation reactions are found to be 68 kJ/mol and 105 kJ/mol, respectively. The CH_3O^- exchange resin is also shown to suffer no degradation of catalytic activity upon repeated separation and re-use at 353 K.

Keywords Methanol carbonylation · Methyl formate · Methanol synthesis · CH_3O^- Exchange resin · Heterogeneous catalyst

1 Introduction

Methanol, an important raw material in many chemical processes, is mainly produced from CO and H_2 using copper-based catalysts such as $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ [1]. Gas-phase methanol synthesis using this approach is a well-established industrial reaction, and is known to be exothermic and thermodynamically unfavorable at higher temperatures [2–4]. Methanol can also be produced by a two-stage process in the liquid phase, involving the carbonylation of an alcohol to a formate, followed by hydrogenation to give the original alcohol together with methanol, [5] as described by

$$CO + ROH \rightleftarrows HCOOR \qquad \text{(Stage1)}$$

$$HCOOR + 2H_2 \rightarrow CH_3OH + ROH \qquad \text{(Stage2)}$$

This two-stage methanol synthesis proceeds at moderate temperatures and pressures in the liquid phase. The carbonylation of an alcohol to the corresponding formate is usually carried out in the presence of alkali metal alkoxides such as $NaOCH_3$, [6–8] amines, [9] transition-metal complexes, [10, 11] and basic resins [11–14]. Hydrogenolysis of the formate proceeds in the presence of a copper-chromite catalyst [15, 16].

A catalytic system consisting of an anion-exchange resin and Raney Cu catalyst suspended in methanol solution has been reported to afford methanol in 70% yield over 4 h at 393 K under 5.0 MPa syngas pressure [17]. It may be possible to apply such a heterogeneous catalyst system as an industrial processes. For development of a single low-temperature slurry-phase reactor based on this system, a kinetic expression of two-stage methanol synthesis will be highly useful.

In this work, the kinetics of methyl formate synthesis by methanol carbonylation using a CH_3O^- exchange resin is examined in an attempt to derive the relevant kinetic equations for methanol carbonylation over a representative solid catalyst. The use of a solid anion-exchange resin such as CH_3O^- would make the work-up procedure very simple. As the resin can be readily separated from the reaction mixture by filtration, the re-usability of the catalyst is also examined.

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2 Experimental

2.1 Catalyst Preparation

Cl^- anion-exchange resin (TSA1200) was obtained from Mitsubishi Chemical Co. Ltd. CH_3O^- exchange resin was prepared by a column-exchange operation as follows. To ensure complete preparation of the Cl^- exchange resin, 1,500 cm^3 of HCl solution (1.0 mol/L) was passed at 10 cm^3/min through a 3 cm-diameter column packed with 150 cm^3 of TSA1200. To promote exchange of Cl^- with OH^-, 3,000 cm^3 of NaOH solution (1.0 mol/L) was then successively passed through the column at the same flow rate (10 cm^3/min). The resin was then washed under running water until the pH of the flux solution reached 7.0. To further promote exchange between OH^- and CH_3O^- anions, 3,000 cm^3 of $NaOCH_3$ (1.0 mol/L) methanol solution was subsequently passed through the column at 1.5 cm^3/min. The final resin (TSA-CH_3O^-) was confirmed to have a CH_3O^- concentration of 0.54 mmol/cm^3.

2.2 Reaction Procedure

The reaction of methanol carbonylation was carried out using a 234 cm^3 magnetically stirred batch autoclave equipped with an internal thermocouple for temperature control. The TSA-CH_3O^- and methanol were introduced into the autoclave, and air in the autoclave was replaced by argon. The autoclave was then heated to the prescribed temperature while stirring the reactant and suspended catalyst. Stirring was stopped once the target temperature was reached, and CO was charged into the chamber to the prescribed pressure. The mixture was then stirred again to commence the reaction. The pressure drop was continuously monitored and samples of liquid and vapor phases were analyzed by gas chromatography using a CP-WAX 52 CB fused silica capillary column.

3 Results and Discussion

The carbonylation of methanol with CO over TSA-CH_3O^- was carried out in a methanol solution at 353 K. A large amount of methanol (2.47 mol, 100 cm^3) was used as both the reactant and the solvent for the reaction. In all the reaction experiments carried out in this study, methyl formate was the only detectable product. The CO pressure (P_{CO}) was calculated by taking the difference between the total pressure at any reaction time and the initial pressure of the reactor, then subtracting the methanol pressure.

Two examples of the drop in P_{CO} as a function of reaction time are shown in Fig. 1. In both cases, P_{CO} decreased to a similar constant value, despite the different concentrations of TSA-CH_3O^- employed (6.0×10^{-2} cm^3/cm^3, 1.5×10^{-1} cm^3/cm^3). However, with the lower concentration of catalysts, the reaction took longer to reach the constant pressure level. This result suggests that the carbonylation is a reversible reaction under the present reaction conditions. As the total pressure reached the constant value, the CO conversion was (80±1)%. The dissolution of CO into methanol has been confirmed to reach the equilibrium within one minute under the present conditions [6] i.e., the mass transfer of CO is not the rate determining process in the present reaction system. Thus, using the initial rate technique, the kinetic parameters for the forward reaction described by the reaction (1) are obtained.

$$CO + CH_3OH \rightleftarrows HCOOCH_3 \tag{1}$$

As shown in Fig. 2, the natural logarithm of P_{CO} displays good linearity with reaction time at the beginning of the reaction, indicating that the forward reaction rate (r_{forw}) for Eq. (1) (i.e., the rate of CO consumption) is first order with respect to P_{CO}, as expressed by

$$r_{forw} = -\frac{1}{RT}\frac{dP_{CO}}{d}t = k_2 P_{CO} \tag{2}$$

where R is the ideal gas constant and T is the reaction temperature.

The dependence of the forward reaction rate on the concentration of TSA-CH_3O^- at the same reaction temperature (353 K) is shown in Fig. 3. This relationship demonstrates that the rate of CO consumption is proportional to the concentration of TSA-CH_3O^-, confirming the first-order dependence of the reaction rate on the concentration of the catalyst, i.e.,

$$r_{forw} = k_3[TSA - CH_3O^-] \tag{3}$$

On the basis of Eqs. (2) and (3), r_{forw} can be expressed by

$$r_{forw} = k_4[TSA - CH_3O^-]P_{CO} \tag{4}$$

The concentration of CO in the liquid phase ([CO]) can be expressed according to Henry's law by

$$[CO] = \frac{\alpha}{RT}P_{CO} \tag{5}$$

where α is proportionality constant. Thus, r_{forw} can be expressed by

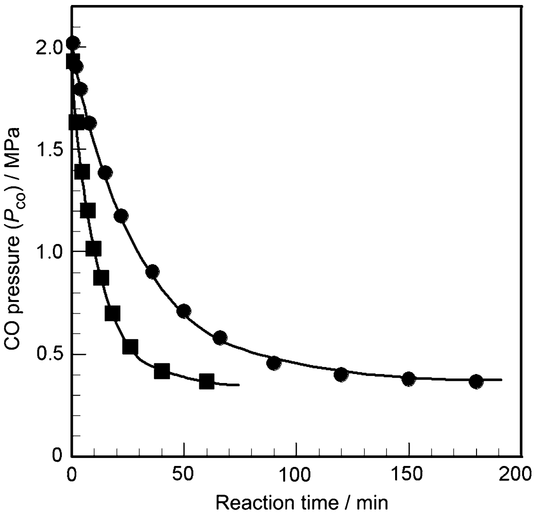

Fig. 1 Effect of CO partial pressure on reaction time (T = 353 K; $[CH_3OH]_0$ = 2.47 mol/L; PCO^0 = 5.0 MPa). (○) [TSA-CH_3OH] = 6.0 × 10^{-2} (cm^3/cm^3), (□) [TSA-CH_3OH] = 1.5 × 10^{-1}(cm^3/cm^3)

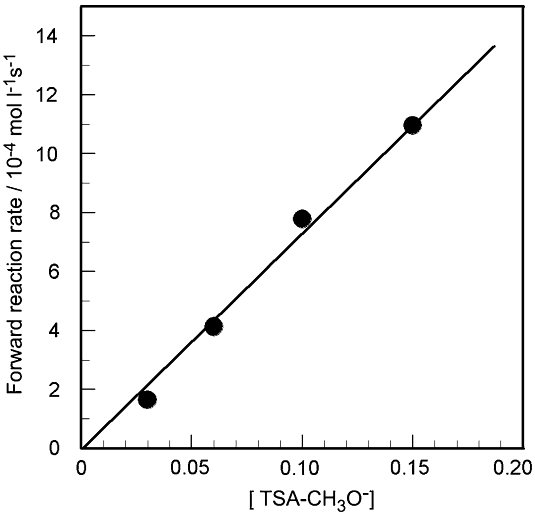

Fig. 3 Dependence of forward reaction rate on [TSA-CH_3O^-] (T = 353 K; $[CH_3OH]_0$ = 2.4 mol/L;Pco^0 = 50kPa)

$$r_{\text{forw}} = k_6[\text{TSA} - \text{CH}_3\text{O}^-][\text{CO}] \tag{6}$$

where

$$k_4 = \frac{\alpha}{RT}k_6$$

The effect of methanol concentration on the rate of the forward reaction was determined by carrying out the reaction in toluene as the solvent. The initial concentration of methanol ($[CH_3OH]_0$) in this case was 3.3 × 10^{-1} mol/L, and the initial CO pressure was 5.0 MPa. The concentration of CH_3OH in the liquid phase ($[CH_3OH]$) can be estimated at any reaction time by

$$[\text{CH}_3\text{OH}] = [\text{CH}_3\text{OH}]_0 - \left(\frac{P^0_{\text{CO}} - P_{\text{CO}}}{RT}\right)\frac{V_{\text{g}}}{V_{\text{l}}} \tag{7}$$

where PCO^0 is the initial partial pressure of CO in the gas phase, and V_g and V_l are the volumes of the gas phase and liquid phase. The natural logarithm of $[CH_3OH]$ also varies linearly with respect to reaction time (Fig. 4) at the beginning of the reaction. Thus, r_{forw} is also first order with respect to the concentration of methanol:

$$r_{\text{forw}} = k_8[\text{CH}_3\text{OH}] \tag{8}$$

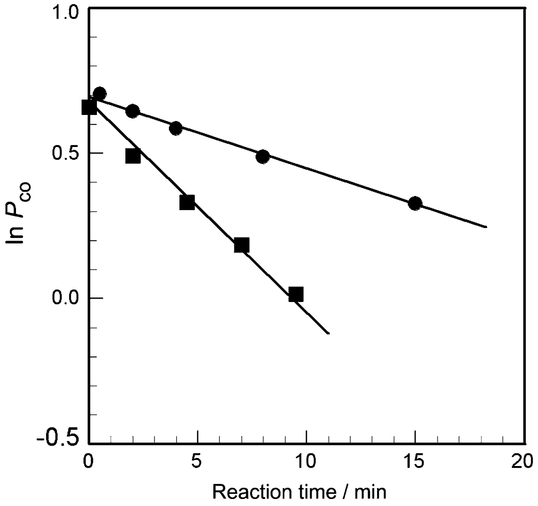

Fig. 2 Variation in natural logarithm of P_{CO} with respect to reaction time (T = 353 K; $[CH_3OH]_0$ = 2.47 mol/L; Pco^0 = 5.0MPa). (○) [TSA-CH_3OH] = 6.0 × 10^{-2}(cm^3/cm^3), (□) [TSA-CH_3OH] = 1.5 × 10^{-1}(cm^3/cm^3)

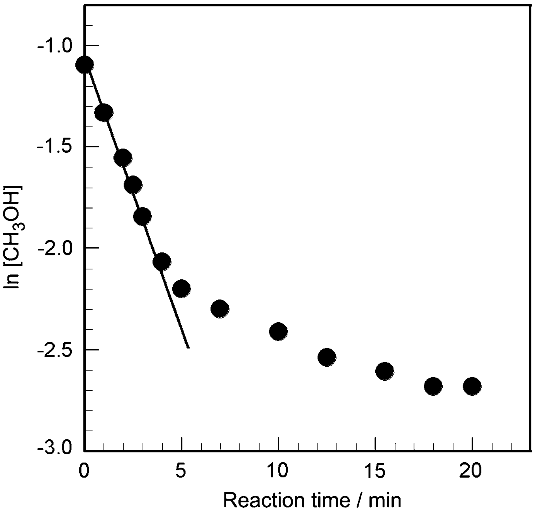

Fig. 4 Variation in natural logarithm of $[CH_3OH]$ with reaction time in toluene (T = 353 K; [TSA–CH_3O^-] = 3.0 × 10^{-2} (cm^3/cm^3); Pco^0 = 5.0 MPa; $[CH_3OH]_0$ = 3.3 × 10^{-1} mol/L)

On the basis of Eqs. (4) and (8), r_{forw} can be expressed by

$$\begin{aligned} r_{\mathrm{forw}} &= k_9[\mathrm{TSA-CH_3O^-}][\mathrm{CH_3OH}][\mathrm{CO}] \\ &= k_1\frac{\alpha}{RT}[\mathrm{TSA-CH_3O^-}][\mathrm{CH_3OH}]P_{\mathrm{CO}} \end{aligned} \tag{9}$$

Equation (9) can be derived from the following mechanism of the forward reaction:

$$\mathrm{TSA\text{-}CH_3O^-} + \mathrm{CO} \rightleftarrows \mathrm{TSA\text{-}CH_3OCO^-} \tag{10}$$

$$\mathrm{TSA\text{-}CH_3OCO^-} + \mathrm{CH_3OH} \rightarrow \mathrm{TSA-CH_3O^-} + \mathrm{HCOOCH_3} \tag{11}$$

where the rate-determining step is that expressed by Eq. (11).

If the order of the reverse reaction (decarbonylation reaction) with respect to the concentrations of $\mathrm{TSA\text{-}CH_3O^-}$ and methyl formate is assumed to be one, the total reaction rate for the carbonylation of $\mathrm{CH_3OH}$ with CO can be expressed by

$$\begin{aligned} r = {} & \left(k_1\frac{\alpha}{RT}[\mathrm{TSA-CH_3O^-}][\mathrm{CH_3OH}]P_{\mathrm{CO}}\right) \\ & -\left(k_{-1}[\mathrm{TSA-CH_3O^-}][\mathrm{HCOOCH_3}]\right) \end{aligned} \tag{12}$$

where k_1((mol/L)$^{-1}$ s^{-1}) and k_{-1} (s^{-1}) are the rate constants of the forward and reverse reaction, respectively, and $[\mathrm{HCOOCH_3}]$ is the concentration of methyl formate in the liquid phase.

The concentration of methyl formate can be calculated from P_{CO} as follows.

$$[\mathrm{HCOOCH_3}] = \frac{P^0_{\mathrm{CO}} - P_{\mathrm{CO}}}{RT}\frac{V_{\mathrm{g}}}{V_{\mathrm{l}}} \tag{13}$$

Thus, Eq. (12) can be re-expressed using Eqs. (7) and (13) as

$$\begin{aligned} r = {} & -\frac{1}{RT}\frac{\mathrm{d}P_{\mathrm{CO}}}{\mathrm{d}}t = k_1\frac{\alpha}{RT}[\mathrm{TSA\text{-}CH_3O^-}] \\ & \left\{[\mathrm{CH_3OH}]_0 - \left(\frac{P^0_{\mathrm{CO}} - P_{\mathrm{CO}}}{RT}\right)\frac{V_{\mathrm{g}}}{V_{\mathrm{l}}}\right\}P_{\mathrm{CO}} \\ & - k_{-1}[\mathrm{TSA\text{-}CH_3O^-}]\left(\frac{P^0_{\mathrm{CO}} - P_{\mathrm{CO}}}{RT}\right)\frac{V_{\mathrm{g}}}{V_{\mathrm{l}}} \end{aligned} \tag{14}$$

where we can define

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} \tag{15}$$

Integrating Eq. (15) then gives

$$\ln\left(\frac{X - Z\,P^0_{\mathrm{CO}} - P_{\mathrm{CO}} - \frac{X+Z}{2}}{X + Z\,P^0_{\mathrm{CO}} - P_{\mathrm{CO}} - \frac{X-Z}{2}}\right) = \lambda k_1 t \tag{16}$$

where

$$\begin{aligned} X &= RT\frac{V_{\mathrm{l}}}{V_{\mathrm{g}}}[\mathrm{CH_3OH}]_0 + \frac{RT}{\alpha K_{\mathrm{eq}}} + P^0_{\mathrm{CO}} \\ Y &= RT\frac{V_{\mathrm{l}}}{V_{\mathrm{g}}}P^0_{\mathrm{CO}}[\mathrm{CH_3OH}]_0 \\ Z &= (X^2 - 4Y)^{1/2} \\ \lambda &= \alpha RT\frac{V_{\mathrm{g}}}{V_{\mathrm{l}}}[\mathrm{TSA\text{-}CH_3O^-}]Z \end{aligned}$$

The value of α is assumed to be 0.154, as obtained by Tonner et al. [18] Eqs. (15) and (16) were used to obtain values for parameters k_1 and k_{-1} by nonlinear regression using the least-squares method. The mean values obtained for k_1 and k_{-1} were 2.7×10^{-3} (mol/L)$^{-1}$ s^{-1} and 1.4×10^{-3} s^{-1}, respectively, at 353 K. Reasonable fits of the kinetic model to the conversion data in Fig. 1 were obtained with these rate constants at 353 K, where the CO pressure (solid lines in Fig. 1) calculated by Eq. (16) is compared with the values obtained experimentally. The observed variation in CO pressure with reaction time is in close agreement with the CO pressure calculated by Eq. (16).

Investigation of the temperature dependence of k_1 and k_{-1} near 350 K revealed that k_1 decreases from 5.7×10^{-3} (mol/L)$^{-1}$ s^{-1} at 362 K, to 2.7×10^{-3} (mol/L)$^{-1}$ s^{-1} at 353 K, and 1.4×10^{-3}(mol/L)$^{-1}$ s^{-1} at 343 K, while values of 3.9×10^{-3}, 1.4×10^{-3} and 5.0×10^{-4} s^{-1} were obtained for k_{-1}. Because there has been no available literature data regarding kinetic parameter for the carbonylation of methanol with CO over heterogeneous solid catalysts, these values obtained for k_1 and k_{-1} will be valuable in modeling a single slurry-phase reactor for the low-temperature methanol synthesis. The Arrhenius plots indicate activation energies of 68 kJ/mol and 105 kJ/mol for the forward and reverse reactions, respectively. These values are comparable to the reported ones for dissolved alkali methoxide catalysts, [6, 19, 20] which are 67.7–70.7 kJ/mol for carbonylation and 92.1 kJ/mol for decarbonylation, suggesting the activated complex in the reaction with catalyst is the same as that with dissolved alkali methoxide catalysts, i.e. methoxycarbonyl anion.

3.1 Re-use of Catalyst

The $\mathrm{TSA\text{-}CH_3O^-}$ solid catalyst examined in this study can be readily separated from the reaction mixture by filtration and re-used without further modification of the used catalyst. The rate constants obtained for repeated re-use of the

Table 1 Recycling of TSA-CH_3O^- catalysis in methanol carbonylation with CO

Run no.	Rate constant of forward reaction: k_1((mol/L)$^{-1}$ s^{-1})	
	353 K	373 K
1	2.7×10^{-3}	6.6×10^{-3}
2	2.6×10^{-3}	5.8×10^{-3}
3	2.9×10^{-3}	5.3×10^{-3}
4	3.0×10^{-3}	–

catalyst in new reactions under the same conditions are listed in Table 1. The catalytic activity was fully retained even after 4 runs in reactions conducted at 353 K, whereas the activity decreased systematically with re-use at 373 K. The use of a solid catalyst such as CH_3O^- exchange resin substantially simplifies the work-up procedure compared to current industrial approaches.

4 Conclusion

CH_3O^- exchange resin was shown to be an effective re-usable heterogeneous catalyst for the carbonylation of methanol with CO at 353 K. The kinetic rate constants for carbonylation and decarbonylation determined in this study will be valuable in modeling the low-temperature synthesis of CH_3OH in a single slurry-phase reactor.

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