Journal of Natural Gas Chemistry 13(2004)225–230

Kinetics of Methanol Carbonylation to Methyl Formate Catalyzed by Sodium Methoxide

Liang Chen[1*], Jianghong Zhang[2], Ping Ning[1], Yunhua Chen[1], Wenbing Wu[1]

1. Research Center of C1 Chemical Technology, Kunming University of Science and Technology, Kunming 650093, China

2. College of Science, Kunming University of Science and Technology, Kunming, 650093, China

[Manuscript received August 23, 2004; revised November 15, 2004]

Abstract: Kinetics of synthesis of methyl formate from carbon monoxide and methanol, using sodium methoxide as the catalyst and pyridine as the promoter in a batch reactor, was studied. Kinetic parameters such as the apparent reaction orders, the rate constant and the apparent activation energies were obtained. The experimental results showed that both the reaction orders with respect to CO and methanol equal to 1, the general reaction kinetic equation is $(-r)=-\mathrm{d}p(\mathrm{CO})/\mathrm{d}t=k\cdot p(\mathrm{CO})\cdot[\mathrm{MeOH}]$, and the rate constant is $k=8.82\times10^6\exp\,[-61.19\times10^3/(R\cdot T)]$ in the presence of pyridine. The apparent activation energies had decreased 6.44 kJ/mol and the rate constant had increased more than 1.5 times when pyridine was used as the promoter in the catalyst system.

Key words: carbon monoxide, pyridine, methanol, methyl formate, carbonylation, kinetics

1. Introduction

Methyl formate ($HCOOCH_3$) is an important and versatile chemical intermediate, which has been considered as one of the building-block molecules in C1 chemistry [1]. It demonstrates high reactivities for preparing formic acid [2–5], for isomerization of acetic acid [6], for producing acetic anhydride [7], for hydroesterification of alkenes [8] and for a variety of C1 chemicals [9] due to its aldehyde group, carboxyl group and active hydrogen. There are plenty of publications on methanol carbonylation for preparing methyl formate by different kinds of catalysts, such as copper-containing catalysts [10–15], Cu/SiO_2 catalysts [16], platinum group metal catalysts [17], ruthenium complex catalysts [18], anionic group VIII metal catalysts [19], epoxide–amine [20,21] catalysts, polymeric strongly basic resins catalysts [22], alkali metal methoxide [23–26], and so on. The commercial production of methyl formate *via* carbonylation of methanol and catalyzed by sodium methoxide (CH_3ONa) is effective in quite large scales [20].

However, carbon monoxide (CO) obtained from the tail gases of yellow phosphorous production contains some impurities such as carbon dioxide, water or phosphorous compounds like PH_3, which are particularly detrimental to the usual methyl formate synthesis catalyst (CH_3ONa) and must be totally removed before the reaction. Therefore, development of new catalytic systems for carbonylation of methanol into methyl formate which are less sensitive to CO impurities has important commercial importance. In this connection, the reaction system of liquid phase methanol carbonylation to methyl formate in the presence of a CH_3ONa catalyst and with pyridine as a promoter [23] is of great significance in the study of the kinetics of methyl carbonylation to methyl formate. In this work, the kinetics of methyl formate synthesis *via* carbonylation of methanol by using CH_3ONa as

---

[*] Corresponding author. Email: kmcexlc@yahoo.com.cn, Tel:+86 871 5173867, Fax: +86 871 5173867

This project was supported by Yunnan Science and Technology Cooperate Plan Foundation (99YT002) and Yunnan Nature Science Foundation (2003E0027M)

the catalyst and pyridine as the promoter was investigated.

2. Experimental

The carbonylation reaction of CO and methanol to methyl formate has been carried out previously by using CH_3ONa as the catalyst at a suitable temperature and pressure, and the reaction selectivity has been found to be almost 100% [27]. These previous research results [9,23] showed that no any other substances were found in the reaction product except the raw materials and the methyl formate product when MeONa was used as the catalyst and pyridine as the promoter at temperatures of 80–100 ℃ and pressures of 2.0–4.5 MPa. So it is evident that the reaction can be expressed as:

$$CH_3OH(l) + CO(g) \xleftrightarrow{\text{MeONa+pyridine}} HCOOCH_3 \quad (1)$$

2.1. Materials

The purities of the reactants were: carbon monoxide>99.9%; methanol, AR, $H_2O \leq 0.1\%$; Pyridine, AR. The sodium methoxide was prepared in our laboratory [9].

2.2. Methods

The procedure of methanol carbonylation to methyl formate is shown schematically in Figure 1.

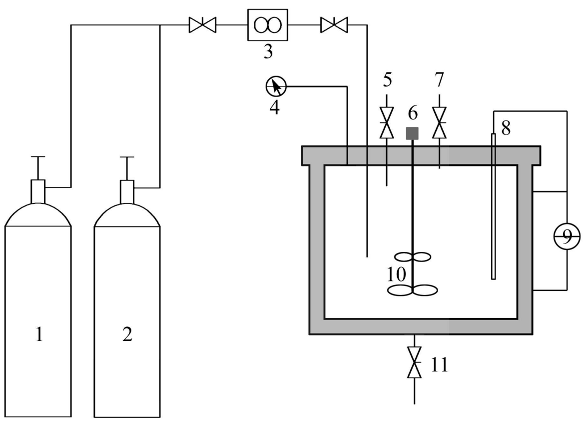

Figure 1. Schematic diagram of the apparatus unit for the synthesis of methyl formate

1—N_2 cylinder, 2—CO cylinder, 3—mass flow meter, 4—pressure gauge, 5—liquid inlet, 6—stirrer, 7—gas outlet, 8—indicating thermocouple, 9—autoclave controller, 10—autoclave, 11—liquid outlet

Method 1: A known amount of methanol, catalyst and the promoter agent(if need) were introduced into an autoclave, and then purged with CO gas at normal pressure. After heating the mixture to the required temperature, the autoclave was pressurized to the required pressure with CO as quickly as possible, then airproofed the autoclave and started stirring. The reaction was carried out at a constant temperature of the autoclave, and the system pressure decreased gradually as the reaction proceeded. The pressure of the reaction system was recorded every 1 minute.

Method 2: A known amount of methanol, catalyst and promoter agent were introduced into an autoclave, then stirring was started and the mixture heated. As soon as the liquid phase reached the required temperature, stirring was stopped, and CO gas was introduced into the autoclave until the required pressure was attained, then stirring was resumed. The reaction was carried out at constant temperature and pressure. When the reaction proceeded to a certain length of time, the autoclave was cooled, and both the liquid and gas products were analyzed by an HP1790 gas chromatograph.

3. Results and discussion

3.1. Reaction rate of methanol carbonylation

By using CH_3ONa as the catalyst and with no any promoters, the correlations of CO pressure and reaction time with different temperatures were shown in Figure 2.

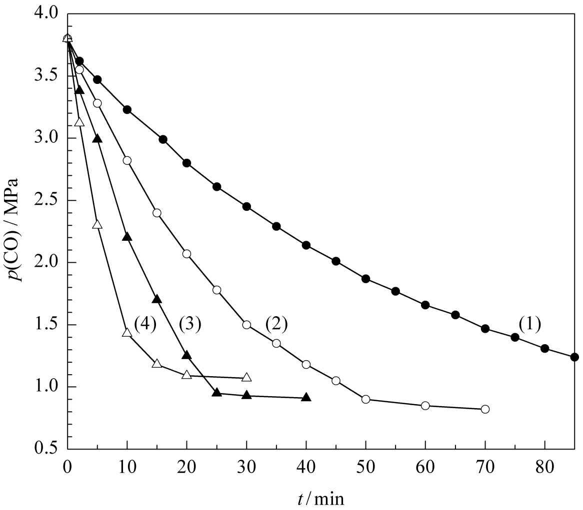

Figure 2. Effect of CO partial pressure on reaction time

(1) 60 ℃, (2) 70 ℃, (3) 80 ℃, (4) 90 ℃

It was proved that a higher temperature led to a faster reaction rate and a shorter equilibrium reaction time, but to a lower CO conversion owing to the exothermic effect of the reaction. However, because of the equilibrium restrain in a batch reaction, the reaction rate decreased very quickly, and the correlation curves exhibited the lowest points of no linearity. The fact was that the conversion of CO was approximately 40% at any temperature when the system pressure reached the lowest value, *i.e.*, methanol carbonylation to methyl formate is close to equilibrium at a 40% conversion of CO in a batch reactor. This result was consistent with that reported by Smathers [27].

3.2. Effect of CO partial pressure

Based on the reaction of Equation (1), the reaction rate was expressed as:

$$(-r) = \frac{-\mathrm{d}p(\mathrm{CO})}{\mathrm{d}t} = k \cdot [\mathrm{MeOH}]^{\alpha} \cdot p(\mathrm{CO})^{\beta} \qquad (2)$$

where p(CO) is the CO partial pressure (MPa), k is a rate constant (L/(mol·min)), [MeOH] is the concentration of liquid methanol (mol/L), and α and β are the reaction orders.

When this reaction was run according to Method 1, but without any promoters, it can be considered that the concentration of methanol was constant because of the large excess of methanol in the liquid phase. So it could be considered that only the partial pressure of CO was varying with the reaction time.

As shown in Figure 3, the natural logarithm of the CO partial pressure (ln$p$(CO)) versus the reaction time (t) showed good linearity at different temperatures when there was no promoter present.

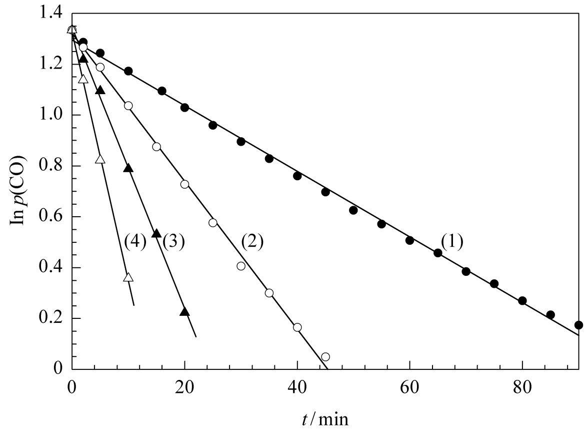

Figure 3. Relation between natural logarithm of CO partial pressure and reaction time

(1) 60 ℃, (2) 70 ℃, (3) 80 ℃, (4) 90 ℃

This indicated that the reaction was first order with respect to the partial pressure of CO from 60 to 90 ℃, *i.e.*, β=1. Therefore, the kinetic equation of methanol carbonylation to methyl formate could be represented as follows:

$$\frac{-\mathrm{d}p(\mathrm{CO})}{\mathrm{d}t} = k_0 \cdot p(\mathrm{CO}) \qquad (3)$$

From the linear slope in Figure 3, the rate constants (k_0) at different temperatures could be obtained, as listed in Table 1.

Table 1. Rate constants at different temperatures without any promoters

Temperature (℃)	k_0
60	0.0129
70	0.0291
80	0.0553
90	0.0978

3.3. Effect of temperature on rate constant

The kinetic curve of the natural logarithm of the rate constant (k_0) and the reciprocal of reaction temperature based on the data of Table 1 was shown in Figure 4.

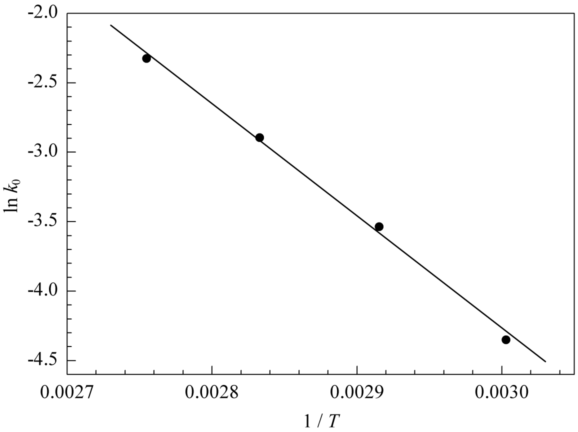

Figure 4. Relation between natural logarithm of the rate constant (k_0) and the reciprocal of reaction temperature

It can be seen that the plot exhibited a good linearity, *i.e.*,

$$\ln k_0 = \frac{-8135}{T} + 20.124 \qquad (4)$$

Based on Equation (4) and the Arrhenius equation ($k = A \cdot e^{-\Delta E/RT}$), the activation energy (ΔE_0) of methanol carbonylation to methyl formate by using sodium methoxide as the liquid phase catalyst and without any promoters was 67.63 kJ/mol, and the preexponential factor (A_0) was 9.96×10^6. These indicated that the reaction was operating in the kinetic region.

$$k_0 = 9.96 \times 10^6 \exp\frac{-67.63 \times 10^3}{R \cdot T} \qquad (5)$$

3.4. Effect of methanol concentration on the reaction

When running the reaction according to Method 2 for the preparation methyl formate, and by keeping the CO pressure and the CH_3ONa catalyst concentration constant, the effect of the methanol concentration on the reaction was shown in Figure 5. It can be seen that the plot ln$c$(MeOH) of versus reaction time (t) was linear. This indicated that the reaction rate with respect to methanol is first order, *i.e.*, α=1.

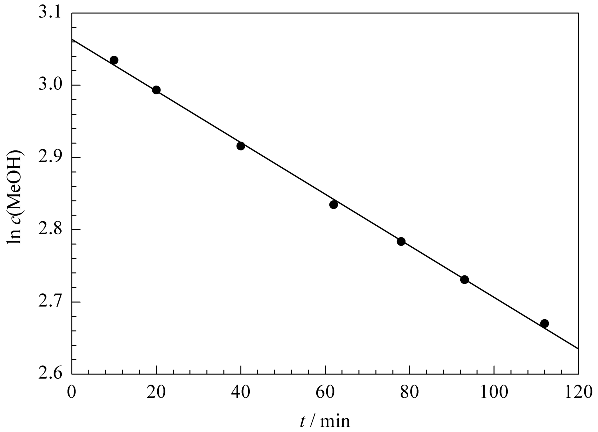

Figure 5. Relation between natural logarithm of MeOH concentration and reaction time

3.5. Effect of catalytic promoter on the reaction

At a partial pressure of 3.8 MPa CO, and with CH_3ONa of 0.4 mol/L and pyridine of 2 mol/L in the reaction liquid phase, the reaction was run according to Method 2 for the preparation of methyl formate, and the result of the effect of the promoter on the reaction was shown in Figure 6. The plot of the natural logarithm of CO partial pressure (ln$p$(CO)) versus reaction time (t) also showed good linearity at different temperatures in the presence of pyridine as the promoter.

The rate constant (k_1) could be obtained from the linear slope of Figure 6. Moreover, the relation of lnk_1 *vs* $1/T$ was presented in Figure 7. Then, from the linear slope of Figure 7 and the Arrhenius equation, the rate equations could be obtained for the reaction when there was pyridine present as a promoter, as expressed by Equations (6) and (7). The activation energy (ΔE_1) was 61.19 kJ/mol, and the preexponential factor (A_1) was 8.82×10^6.

$$\ln k_1 = \frac{-7359.8}{T} + 18.373 \qquad (6)$$

$$k_1 = 8.82 \times 10^6 \exp\frac{-61.19 \times 10^3}{R \cdot T} \qquad (7)$$

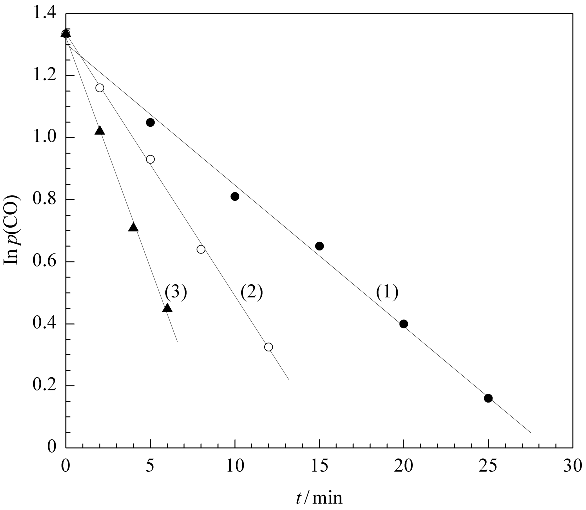

Figure 6. Relation between natural logarithm of CO partial pressure and reaction time with the presence of a promoter

(1) 70 ℃, (2) 80 ℃, (3) 90 ℃

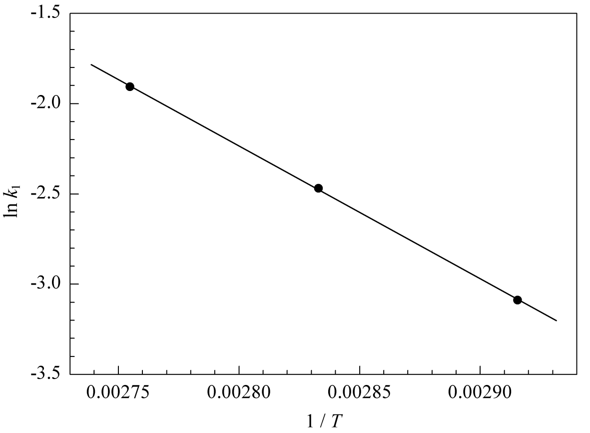

Figure 7. Relation between natural logarithm of rate constant (k_1) and reciprocal of reaction temperature with the presence of a promoter

By comparing these results with those of no promoters present (Equation 5), it can be found that the activation energy of methanol carbonylation to methyl formate in the presence of 2 mol/L pyridine in the liquid phase had decreased by 6.44 kJ/mol.

Comparison of the results indicating the effect of the pyridine promoter on the reaction rate and the activation energy was listed in Table 2. It was evident that pyridine accelerated the reaction of methanol carbonylation to methyl formate when added to the CH_3ONa catalyst system. At a pyridine concentration of 2 mol/L in the liquid phase and at temperatures of 60–80 ℃, the reaction rate constant increased 1.52–1.58 times, showing that pyridine had a good promoter function on the carbonylation reaction.

Table 2. Comparison of kinetic parameters with and without a promoter

		k_0 (Without pyridine)	k_1 (Pyridine of 2 mol/L)	k_1/k_0
Rate constant (L/(mol.min))	70 (℃)	0.0291	0.0456	1.58
	80 (℃)	0.0553	0.0846	1.53
	90 (℃)	0.0978	0.1487	1.52
Activation energy (ΔE)(kJ/mol)		67.63	61.19	ΔE_0-ΔE_1=6.44
A		9.66×10^6	8.82×10^6	—

4. Conclusions

(1) Kinetic study on methanol carbonylation to methyl formate in the presence of sodium methoxide catalyst and the pyridine promoter showed that the reaction orders of CO and methanol was found to be approximately 1 at the temperature range of 60 to 90 ℃ . The reaction equation can be described as $(-r)$= $-\mathrm{d}p(\mathrm{CO})/\mathrm{d}t=k\cdot[\mathrm{MeOH}]\cdot p(\mathrm{CO})$.

(2) The rate constants without or with pyridine in the sodium methoxide catalyst system can be described as $k_0=9.96\times10^6\exp[-67.63\times10^3/(R\cdot T)]$ and $k_1=8.82\times10^6\exp[-61.19\times10^3/(R\cdot T)]$. Adding 2 mol/L pyridine in the reaction liquid phase could cause the reaction rate constant to increase 1.52–1.58 times at temperatures of 60–80 ℃, and reducing the reaction temperature can give a better promoter effect on methanol carbonylation to methyl formate.

(3) The activation energy was found to be 67.63 kJ/mol without the promoter, but it was reduced to 61.19 kJ/mol in the presence of pyridine as the promoter. It was found that the reaction proceeded in the kinetic region. Compared with no any promoters, the activation energy decreased by 6.44 kJ/mol in the presence of 2 mol/L pyridine and at temperatures of 60–90 ℃.

References

[1] Lee J S, Kim J C, Kim Y G *et al.* *Applied Catalysis*, 1990, **57**(1): 1

[2] Leonard J D. USP 4 299 981. 1981

[3] Lynn J B, Homberg O A, Singleton A H. USP 3 907 884. 1975

[4] Hohenschutz H, Kiefer H, Schmidt J E. USP 5 206 433. 1993

[5] Li Zh F, Chen L, Zhang J H *et al.* *Tianranqi Huagong (Natural Gas Chemical Industry)*, 2002, **27**(3): 1

[6] Kawataka F, Shima Y, Nakamura K. USP 5 969 183, 1999

[7] Seuillet B, Castanet Y, Mortreux A *et al.* *Applied Catalysis A: General*, 1993, **93**(2): 219

[8] Yang X G, Zhang J Q, Liu Zh T. *Applied Catalysis A: General*, 1998, **173**(1): 11

[9] Zhang J H. [Master Thesis]. Kunming: Kunming University of Science & Technology, 2001

[10] Joerg K, Mueller F J, Irgang M *et al.* USP 5 194 675, 1993

[11] Chen Sh Ch, Cheng W J, Lin F Sh *et al.* USP 5 144 062, 1992

[12] Yoneoka M, Ikarashi T, Watabe K *et al.* USP 5 399 745, 1995

[13] Shreiber E H, Roberts G W. *Applied Catalysis B: Environmental*, 2000, **26**(2): 119

[14] Guerrero-Ruiz A, Rodriguez-Ramos I, Fierro J L G. *Applied Catalysis*, 1991, **72**(1): 119

[15] Minyukova T P, Simentsova I I, Khasin A V *et al.* *Applied Catalysis A: General*, 2002, **237**(1): 171

[16] Guerreiro E D, Gorriz O F, Larsen G *et al.* *Applied Catalysis A: General*, 2000, **204**(1): 33

[17] Aplin R P, Maitlis P M, Smith T A. USP 4 778 923, 1988

[18] Choi S J, Lee J S, Kim Y G. *Journal of Molecular Catalysis*, 1993, **85**(2): L109

[19] Chang B H, Grimm R A, Trivedi Bhupendra C. USP 4 661 623, 1987

[20] Gérard E, Götz H, Pellegrini S *et al.* *Applied Catalysis A: General*, 1998, **170**(2): 297

[21] Green M J. EP 0 104 875, 1988

[22] Di Girolamo M D, Lami M, Marchionna M *et al.* *Catalysis Letters*, 1996, **38**: 127

[23] Chen L. *Tianranqi Huagong (Natural Gas Chemical Industry)*, 2002, **27**(1): 14

[24] Ferdinand L, Arthur H, Jurgen D. USP 5 917 085, 1999

[25] Couteau W, Ramioulle J. USP 4 216 339, 1980

[26] Bai L, Zhao Y L, Hu Y Q *et al.* *J Nat Gas Chem*, 1996, **5**(3): 229

[27] Lee D S. USP 4 100 360, 1978