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Synthesis of dimethyl carbonate from methanol and carbon dioxide using potassium methoxide as catalyst under mild conditions

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The direct synthesis of dimethyl carbonate (DMC) from methanol and carbon dioxide using potassium methoxide as a catalyst in the presence of CH_3I was investigated. The results showed that CH_3OK is an effective catalyst; the raised yield (16.2%) and high selectivity (100%) of DMC formation under mild conditions were achieved. The effect of the reaction conditions, such as reaction temperature, pressure of carbon dioxide, the molar ratio of potassium methoxide to methanol and the amount of methyl iodide, on the reaction is discussed. The roles of the potassium methoxide and methyl iodide were explored, that is, the former acts as a catalyst, and the latter does as a promoter to the formation of DMC from CH_3OH and CO_2. In addition, the reaction mechanism was proposed according to the results obtained in the catalytic reaction.

KEY WORDS: dimethyl carbonate; carbon dioxide; methanol; methyl iodide; potassium methoxide.

1. Introduction

Dimethyl carbonate (DMC) is an important carbonylating and methylating reagent as a green chemical substituting dimethyl sulfate and phosgene, which are corrosive and toxic agents; an intermediate for higher carbonates and carbamates [1] as well as a promising octane enhancer [2]. The widely used method for its preparation in industry is the oxidative carbonylation of methanol by carbon monoxide and oxygen with copper (II) and/or palladium (II) catalysts [3]. It is expensive to use CO as a raw material, accompanied by a potential explosion and poison hazard. Recently, the utilization of carbon dioxide, a readily available, inexpensive and environmentally acceptable starting material, as the raw material of DMC synthesis has been attempted.

Carbon dioxide is one of the greenhouse gases causing global warming and an alternative source of carbon with most abundant reserves. Synthesis of chemicals using carbon dioxide as raw material will alleviate global climate change, extend the carbon resources and promote sustainable development of chemical industry. However, this chemical process is still underdeveloped due to the fact that CO_2 is highly thermodynamically stable and kinetically inert. The problem of CO_2 activation is a permanent challenge for the chemist to 'force' this molecule into selective reactions under mild conditions. Therefore, the investigation on the synthesis of DMC from carbon dioxide and methanol has highly important practical and academic significance.

In the past several decades, much attention has been paid to the organotin-catalyzed formation of DMC from CO_2. The first report was proposed by Japanese groups [4,5]. Kizlink *et al.* have improved the catalytic activities of this reaction, but a high turnover number (TON) is still not achieved [6–8]. The DMC preparation from CO_2 and methanol using zirconia and modified zirconia, such as H_3PO_4/ZrO_2 and CeO_2–ZrO_2, as catalysts was investigated by Tomishige and co-workers [9–11]. Although the selectivity of DMC over these catalysts was very high (ca. 100%), unfortunately the methanol conversion was very low (less than 1%). Zhao *et al.*, reported that metal acetate effectively catalyzed the preparation reaction of DMC from carbon dioxide and methanol [12], the yield of DMC is 796 mol%/mol-cat (3.2 mol%) at pressure of 9.3 MPa; Fujimoto and Arai *et al.*, reported the synthesis of DMC in the presence of base K_2CO_3 and methyl iodide under milder conditions [13,14], although the methanol conversion was higher, the yield was still very low (less than or about 4%). Sakakura *et al.* applied an organotin catalyst to the synthesis of DMC from orthoester [15] and acetals [16], the yield of DMC reported in these systems was higher (58–70%), and however, these systems have disadvantages of the high cost of the starting materials and the difficulty in the catalyst-product separation due to the homogeneous nature of the catalyst. So the direct synthesis of DMC from methanol and carbon dioxide is still far from satisfactory due to the difficulty in the activation of carbon dioxide, deactivation of the catalysts induced by water formation in reaction process.

In our present investigation, we first report the synthesis of dimethyl carbonate from methanol and carbon

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dioxide using potassium methoxide as catalyst in the presence of methyl iodide under mild conditions. The results showed that the high selectivity (ca. 100%) and raised yield (16.2%) of DMC was achieved, which is the highest yield and selectivity among the results reported.

2. Experimental

All experiments were carried out in a stainless steel reactor with inner volume of 500 mL provided with a mechanical stirrer and an electric heater. The catalyst CH_3OK was prepared by following process: metal potassium (0.051 mol) was cut into small pieces and carefully added piece-by-piece in the reactor with a known amount of anhydrate methanol, CH_3OK was formed by the violent reaction of potassium and methanol at room temperature. Then, CH_3I was put into the reactor. After being purged three times with CO_2, the reactor was pressured to a known pressure and heated to the desired reaction temperature with stirring. After the required time, the liquid phase was cooled, sampled and analyzed by GC and GC–MS. The yield was calculated on the basis of methanol and turnover number was done on the molar amount of DMC formation per mole catalyst.

3. Results and discussion

3.1. Characteristics of the reaction system

The reaction between CO_2 and methanol was carried out in the presence of CH_3OK and methyl iodide. The experimental results are summarized in table 1. The catalyst CH_3OK displays high activity and selectivity for the preparation of DMC under milder conditions, and shows the highest yield of DMC to be 16.2% with the selectivity of 100% in entry 5. In addition, no by-product was detected by GC and GC–MS for all experiments, which present a striking contrast between CH_3OK and K_2CO_3 catalysts [13,14]. The reaction such as this higher yield is very rare in the preparation of DMC from CO_2 and methanol.

The amount of DMC formed increases in proportion with the molar ratio of potassium methoxide to the methanol rising (table 1). At the molar ratio of 0.051/0.85 and 0.051/1.10, amount of DMC formation is 0.069 and 0.071 mol, respectively. Continuous increase in molar ratio results in a slight decrease of DMC yield to 14.1% (Entry 10). However, the molar amount of DMC formed is more than that produced by complete conversion of CH_3OK as a reactant to DMC. The turnover number of DMC formation based on the amount of CH_3OK reaches 1.35, showing that the potassium methoxide acts as a catalyst in the DMC synthesis reaction.

Similar experiments were carried out with respect to methyl iodide. The amount of DMC formed increase with amount of CH_3I, and then the yield and amount of DMC slightly falls (Entry 1–6). Although the amount of DMC formed is almost equal to that of CH_3I used (Entry 2–4). In fact, the amount of DMC formed exceeds the consumed amount of CH_3I, because a certain amount of CH_3I was detected in the mixture solution at the end of the reaction (about 0.02 mol). This result indicates that CH_3I acts as a promoter, at least partly as a promoter. It is very different from the result reported by Fujita and co-workers [14]. In that work, the synthesis of DMC was carried out from methanol and CO_2 in the presence of K_2CO_3 and CH_3I. The amount of DMC formation was less than that of CH_3I used in the synthetic reaction; therefore, CH_3I may be a reactant and not a promoter in the system containing K_2CO_3. Under the same conditions, CH_3ONa also have activity for the synthesis of DMC (Entry 11), but its activity is lower than that of CH_3OK. The difference in the reactivity between them could be well ascribed to different basicities induced by different sizes of alkali metal ions.

To investigate the deactivation, the catalyst was extracted by distillation under vacuo at the end of

Table 1

The results of DMC synthesis from CO_2 and CH_3OH in the presence of CH_3OK and CH_3I

Entry	Cata. (mol)	CH_3OH (mol)	CH_3I (mol)	T (°C)	P (MPa)	Time (h)	DMC (mol)	Yield (%)
1	K(0.051)	0.85	0	80	7.3	10	0.0006	0.1
2	K(0.051)	0.85	0.016	80	7.3	10	0.018	4.2
3	K(0.051)	0.85	0.032	80	7.3	10	0.041	9.7
4	K(0.051)	0.85	0.048	80	7.3	10	0.049	11.6
5	K(0.051)	0.85	0.08	80	7.3	10	0.069	16.2
6	K(0.051)	0.85	0.128	80	7.3	10	0.052	12.2
7	K(0.051)	3.66	0.08	80	7.3	10	0.0063	1.5
8	K(0.051)	1.46	0.08	80	7.3	10	0.029	6.8
9	K(0.051)	1.10	0.08	80	7.3	10	0.071	12.8
10	K(0.051)	0.61	0.08	80	7.3	10	0.043	14.1
11	CH_3ONa (0.051)	0.85	0.048	80	7.3	10	0.011	2.6
12	Reused	0.85	0.048	80	7.3	10	0.023	5.4

reaction and then reused for the next run. It was found that the activity of the reused catalyst was negligible (Entry 12). Thus, it was concluded that the catalyst was deactivated in the course of the reaction. The reason of this deactivation could be explained by XRD pattern of the reused catalyst. In the XRD pattern, KI and $KHCO_3$ were found; this finding showed that some of the catalyst was converted into KI and $KHCO_3$. However, the detailed reason for the deactivation of catalyst need to be further investigated.

3.2. *Effect of reaction conditions*

Figure 1 illustrates the effect of CO_2 pressure upon the yields of DMC in the presence of CH_3OK. As the pressure of CO_2 increases, the yield of DMC shows two maxima near 2.0 and 7.3 MPa. This phenomenon is very similar to that in Arai's work, in which two maxima appeared near 4.5 and 8 MPa using K_2CO_3 as catalyst. The results in figure 1 also indicate that higher CO_2 pressures are not required for the DMC synthesis and supercritical condition is not appreciable for this reaction. The higher yield of DMC is achieved within 1.5–2.0 MPa. It has been rarely reported that, when CO_2 is used as a solvent or a reactant, reaction rates are maximal near the critical pressure of CO_2 (7.3 MPa) [12–14]. And at low pressures of CO_2, liquid and gaseous CO_2 coexists in the reactor. With increase in the CO_2 pressure, the amount of liquid phase increases. Probably, the increase in the amount of the liquid should arise from absorption of CO_2 into the liquid. So the increase in the yield of DMC observed upto 2.0 MPa should be ascribed to the absorption of CO_2, since the change in the amount of liquid is negligible in the range of 0–2 MPa. However, the decrease in the DMC yield observed in the region of CO_2 pressure from 2.0 to 7.3 MPa and beyond 7.3 MPa would result from the dilution effect, because the amount of liquid phase increases in greater rate with increase in the pressure from 2 to 7.3 MPa and beyond 7.3 MPa [14].

The effect of reaction temperature on the yield of DMC at the initial pressure of 1.2 MPa is shown in figure 2. The yield rises from about 6% to 13% in the range from 60 to 80 °C, subsequently exhibiting a very little decrease (figure 2). The reaction is accelerated at higher temperature, which shortens the time reaching thermodynamic equilibrium. On the other hand, when raising temperature or heating up may not be propitious to the formation of DMC, because this synthetic reaction is an exothermic ($\Delta H = -15.51$ KJ/mol) [17]. Thus, the change in the yield of DMC with the temperature increase shown in figure 2 may have to do with the mutual action of the kinetics and thermodynamics. And figure 3 shows yield-time profile of the reactions. The DMC yield increases with time and the increase in the yield between 6 and 10 h is not evident. These results mean that the rate of DMC formation decreases with time, which could be ascribed to the reaction equilibrium achieved.

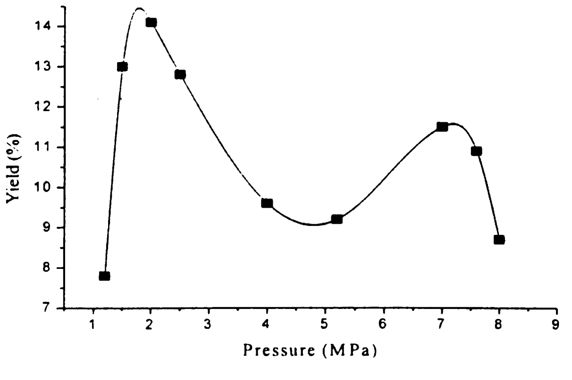

Figure 1. The effect of pressure on the yield of DMC. *T*: 80 °C, CH_3OK/CH_3OH: 3/50 (mol), CH_3I: 0.048 mol, time: 6 h.

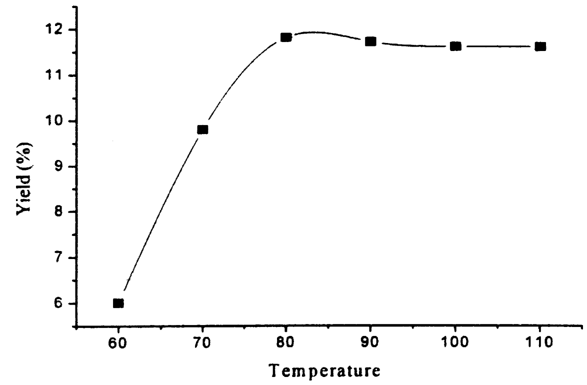

Figure 2. The effect of temperature on the yield of DMC *P*: 2 MPa, time: 6 h, CH_3OK/CH_3OH: 3/50 (mol), CH_3I: 0.048 mol.

3.3. *Reaction kinetics and mechanism*

It was understood from the above discussion that the pressure or concentration of CO_2 in the liquid played an important role for the reaction. When a plot of ln (C_0/C) versus reaction time was made, this plot shows excellent linearity (where C_0 is the initial pressure and C is the instantaneous pressure of CO_2 at some moment).

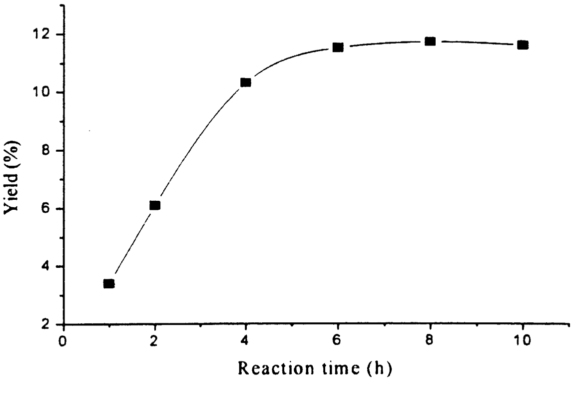

Figure 3. The effect of reaction time on the yield of DMC *T*: 80, *P*: 2 MPa, K/CH_3OH: 3/50 (mol/mol), CH_3I: 0.048 mol.

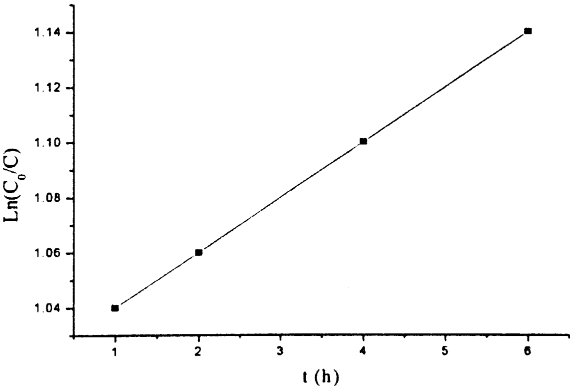

Figure 4. Plot of $\ln(C_0/C)$ versus reaction time (h).

Reaction is clearly first order in CO_2 (figure 4). First-order rate constant calculated from the plot is $k_{353\ K} = 0.0192\ h^{-1}$. Similarly, the rate constants at the different temperatures, such as 60, 70 and 85 °C were obtained, and a plot of ln k versus $1/T$ (K) also shows a good linearity (figure 5). The activation energy of the reaction was calculated by the linear slope, $E_a = 28.93$ KJ/mol.

The reaction mechanism of DMC synthesis in the presence of K_2CO_3 as catalyst proposed by Fang and Fujimoto [13] is shown as follows:

$$\text{Base} + CH_3OH \rightarrow CH_3O^- + \text{H---Base} \quad (1)$$

$$CH_3O^- + CO_2 \rightarrow [CH_3OCOO]^- \quad (2)$$

$$[CH_3OCOO]^- + CH_3I \rightarrow CH_3OCOOH_3 + I^- \quad (3)$$

$$I^- + \text{H---Base}^+ \rightarrow HI \quad (4)$$

$$HI + CH_3OH \rightarrow CH_3I + H_2O \quad (5)$$

This network involves the activation of methanol, carbon dioxide insertion and the production of dimethyl carbonate. Among them, the basicity of catalyst is very important to the activation of methanol, that is, the stronger the basicity is, the higher the concentration of CH_3O^- formation. However, when using CH_3OK as catalyst in this investigation, the higher yield of DMC was obtained due to the stronger basicity of catalyst CH_3OK than that of K_2CO_3, therefore, this finding further verifies the validity of the above mechanism.

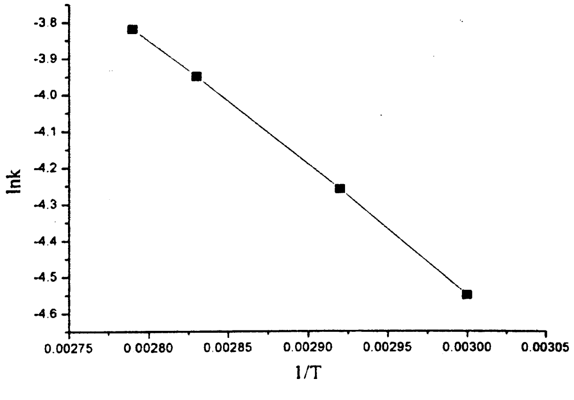

Figure 5. Plot of ln k versus $1/T$ (K) for the reaction at 333, 343, 353 and 358 K.

4. Conclusion

The synthesis of DMC from Methanol and CO_2 in the presence of CH_3OK and CH_3I was carried out under mild conditions; high yield (16.2%) and selectivity of 100% were achieved. Investigation results show that CH_3OK is an efficient catalyst; CH_3I is a promoter to the formation of DMC from CH_3OH and CO_2.

In contradistinction to the Refs. [13,14], four noteworthy features were found in the above investigations, first, we utilize the different catalytic system, the strong base catalyst CH_3OK substitutes K_2CO_3; second, the reaction conditions are more mild, especially at lower pressure of 2 MPa, the higher yield of DMC can be achieved; third, high selectivity of 100% was achieved, which is significant for the industrial product; fourth, the reaction mechanism proposed in the literature [13] was further validated by this experimental result.

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