Pseudo-homogenous Kinetics Model for the Synthesis of Dimethyl Carbonate from Urea and Methanol with Heterogeneous Catalyst

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Abstract. The synthesis of dimethyl carbonate (DMC) from urea and methanol includes two main reactions: one amino of urea is substituted by methoxy to produce the intermediate methyl carbamate (MC) which further converts to DMC via reaction with methanol again. In a stainless steel autoclave, the kinetics of these reactions was separately investigated without catalyst and with Zn-containing catalyst. Without catalyst, for the first reaction, the reaction kinetics can be described as first order with respect to the concentrations of methanol and methyl carbamate (MC), respectively. For the second reaction, the results exhibit characteristics of zero-order reaction. Over Zn-containing catalyst, the first reaction is neglected in the kinetics model since its rate is much faster than second reaction. After the optimization of reaction condition, the macro-kinetic parameters of the second reaction are obtained by fitting the experimental data to a pseudo-homogenous model, in which a side reaction of DMC synthesis is incorporated since it decreases the yield of DMC drastically at high temperature. The activation energy of the reaction from MC to DMC is 104 KJ/mol while that of the side reaction of DMC is 135 KJ/mol.

Introduction

Dimethyl carbonate (DMC), as an important green chemical raw material, has attracted much attention in recent years [1]. The DMC synthesis techniques reported mainly consist of phosgenation of methanol, oxidative carbonylation of methanol, ester exchange, esterification of carbon dioxide methanol and etc. But all of them suffer from corresponding shortcomings such as poisonous, easy explosion, reaction course complex and extremely low conversion. A route of the DMC synthesis from urea and methanol was developed presently for low cost and facile separation of production. In this synthesis approach, urea reacted with methanol to produce intermediate methyl carbamate (MC), which further converted to DMC by reaction with methanol. Besides, byproduct N-methyl methyl carbamate (NMMC) was produced via the reaction of DMC and MC, which was a main side reaction of this route [2].

For the above DMC synthesis route, many compounds such as K_2CO_3, CH_3ONa and CaO could be used as catalyst, but the DMC yield was far from satisfactory [3]. Among all catalysts, zinc compounds were considered as the best catalysts for their innocuity, high selectivity and conversion [4, 5]. Furthermore, comparing to metal oxides with either strong acidity or basicity, they did not promote the thermal decomposition of DMC [2, 6]. In the reaction of urea and diol, zinc compounds also showed excellent catalytic performance [7]. Based on these previous research [8,9], a new Zn-containing industrial heterogeneous catalyst has been developed by our group, which showed excellent catalytic activity[10].

Up to now, the kinetics about this DMC synthesis route, which could provide useful information for further investigations of the simulation and design of DMC synthesis reactor, has been rarely reported. In a previous work, the activation energy 110 KJ/mol for the reaction of urea to MC without catalyst was determined by using pseudo-first-order model [11]. Whereas, the further research of kinetics for the reaction of MC to DMC without catalyst was not performed. There are a few

contributions focused on the kinetics study of DMC synthesis by using a coupling reagent or homogenous catalyst [12, 13]. In Sun's work, taking organotin as homogenous catalyst and high boil electron donor solvent as a co-catalyst, the activation energies for the reactions of urea to MC and MC to DMC were found to be 98.1 KJ/mol and 107 KJ/mol, respectively [13]. However, the kinetics study with heterogeneous catalyst was scarce.

In the present work, the kinetics research of DMC synthesis from urea and methanol was carried out in a batch reactor without catalyst, and then with the Zn-containing heterogeneous catalyst devised by our research team. Kinetics experiments without catalyst were performed in two independent steps, the reactions of urea to MC and MC to DMC. The activation energies and preexponential factors were obtained by the linear regression of experimental data according to the model derived from reaction expressions. On the Zn-containing heterogeneous catalyst, the reaction time, temperature and other reaction factors were investigated firstly to find out the optimal reaction conditions. Then, the macro kinetics parameters and activation energy were estimated by the use of Matlab Optimization Toolbox.

Experimental

Urea, methanol, MC, DMC, isopropyl alcohol all are commercial reagents, the mass purities of the reagents are greater than 99.9%. Catalyst was prepared according to the patent [10]. DMC was synthesized in a 350mL autoclave reactor with a reflux column under the assigned conditions. The temperature was controlled by a PID temperature controller with a heater percent power adjustment that controlled the reactor temperature error less than 1K. Reactant and catalyst were put into autoclave first, and then were rapidly heated to the desired temperature with stirring. Methanol in experiment not only was reactant, but also was solvent. After the reaction temperature was steady, sample was fetched at interval and the corresponding sampling time was recorded. Some residual liquid of last time sampling in the sample pipe was thrown out before the next sampling. The products were determined by gas chromatogram configured with the GDX-203 column and thermal conductivity detector (TCD) using isobutyl alcohol as internal standard. Because urea can not be analyzed by gas chromatogram due to the decomposition at high temperature, its concentration was got by the equilibrium of materials.

Results and discussion

Kinetic model and parameter estimation without catalyst

Because the yield of MC could reach 95% before the appearance of DMC in our experiments, i.e., the reaction rate of MC synthesis was much faster than that of the following DMC synthesis. The kinetics experiments without catalyst were performed in two isolated steps for simplification

In the first step, MC synthesis from urea and methanol, the concentration of MC over time were measured at several fixed temperatures (403-433 K). Sampling began when stable temperature was reached, and stopped once DMC appeared. The concentration curves of MC over time are shown in Figure 1(A). It was not unexpected to observe that the concentration of MC was positively correlated with the reaction time, and increased faster as the increase of temperature. For instance, the MC concentration in solution after certain time at different temperatures ranked this order: 433K > 423K > 413K > 403K. At given temperature, the production rate of MC at the initial period of experiment was faster than that at the latter period. Thus, according to reaction expression (1), the reaction model equations were described as follows:

$$\frac{\mathrm{d}C_{mc}}{\mathrm{d}t} = k \cdot C_{urea} \cdot C_{me} \tag{1}$$

In this equation, C_{mc}, C_{urea} and C_{me} are the molar concentration of MC, urea and methanol in solution at a given time, respectively; t is reaction time; k is reaction rate constant. According to equilibrium of materials, equation (1) could be changed to

$$\frac{\mathrm{d}C_{mc}}{\mathrm{d}t} = k \cdot (C_{urea0} - C_{mc}) \cdot (C_{me0} - C_{mc}) \tag{2}$$

In this equation, C_{urea0} and C_{me0} are the initial molar concentration of urea and methanol. Equation (3) was got by integrating Equation (2)

$$(\ln\frac{C_{me0} - C_{mc}}{C_{urea0} - C_{mc}} - \ln\frac{C_{me0} - C_{mc0}}{C_{urea0} - C_{mc0}}) / (C_{me0} - C_{urea0}) = kt \tag{3}$$

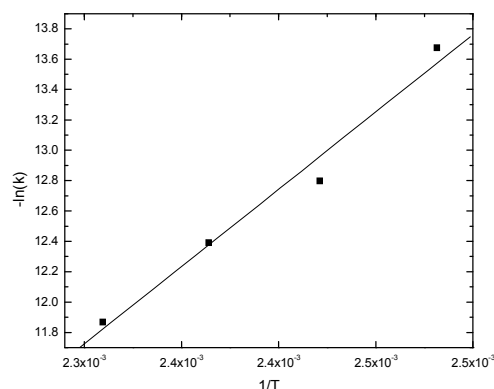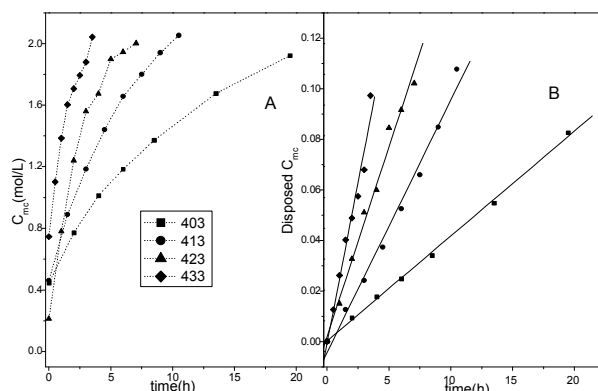A plot of Equation (3) right versus reaction time gives a straight line with the slope of k (see Figure 1(B)).

Figure 1. MC concentration profile at different temperatures. A, C_{mc} versus time; B, Right of Equation (3) versus time

Figure 2. Arrhenius plots for the synthesis of MC

The rate constants k for the MC synthesis computed by linear regression at every temperature is listed in Table 1. They are 1.15, 2.77, 4.15, 7.01 (E-6 $L \cdot mol^{-1} \cdot s^{-1}$) for 403, 413, 423, 433K, respectively. The linear correlation coefficients R all are close to 1. This result showed that rate constants increased with the increasing temperatures.

In Figure 2, the negative logarithm of rate constant is plotted against the reciprocal temperature. Based on the four runs of the present study shown in this figure, the kinetics activation energy was determined to be 84.7KJ/mol and the preexponential factor was evaluated as 1.20 E+6 $L \cdot mol^{-1} \cdot s^{-1}$ (see Table 1).

Table 1 Kinetics parameters and correlation coefficient for the synthesis of MC

Temperature (K)	Rate constant	R square
403	1.15 E-6	0.999
413	2.77 E-6	0.994
423	4.15 E-6	0.994
433	7.01 E-6	0.987
Activation energy	Preexponential factor	R square
84.7KJ/mol	1.20 E+6 $L \cdot mol^{-1} \cdot s^{-1}$	0.989

In the second step, DMC synthesis directly from MC and methanol, kinetics studies were performed over a temperature range of 453-483 K. At these high temperatures, urea could convert to MC completely in a short time. Thus, after urea has converted completely, we began to withdraw sample at intervals and corresponding sampling time were recorded. The DMC concentration profile versus time at different temperatures is illustrated in Figure 3.

It was clear that the concentration of DMC was in a good linear correlation with time; this indicated that the synthesis of DMC from MC and methanol was a zero-order reaction as shown in the model equation (4),

$$\frac{\mathrm{d}C_{dmc}}{\mathrm{d}t} = k \tag{4}$$

The reaction rate constants k for the DMC synthesis from MC at different temperatures obtained by linear fitting are shown in Table 2: 1.65, 2.97, 4.01, 5.93 (E-6 $mol \cdot L^{-1} \cdot s^{-1}$) for 453, 463, 473, 483 K, respectively.

Table 2 Kinetics parameters and correlation coefficient for the synthesis of DMC

Temperature(K)	Rate constant	R square
453	1.65 E-6	0.999
463	2.97 E-6	0.999
473	4.01 E-6	0.997
483	5.93 E-6	0.997
Activation energy	Preexponential factor	R square
75.3 KJ/mol	8.12 E+2 $mol \cdot L^{-1} \cdot s^{-1}$	0.992

From the results of Figure 4, which is plotted with the same way of Figure 2, we could deduce that the reaction activation energy was 75.3 KJ/mol and preexponential factor was 8.12 E+2 $mol \cdot L^{-1} \cdot s^{-1}$ (see Table 2).
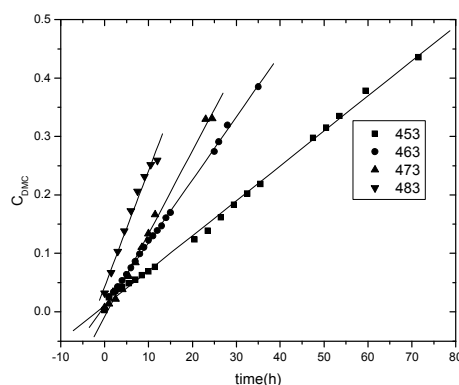

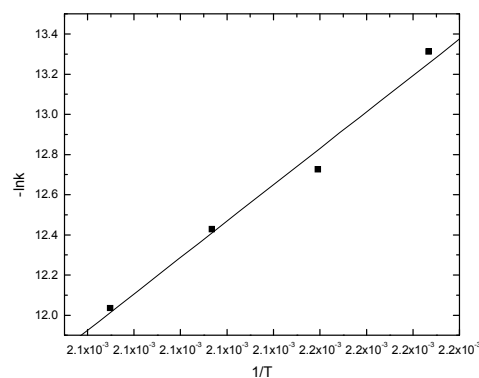Figure 3. DMC concentration profile at different temperatures

Figure 4. Arrhenius plots for the synthesis of DMC

By comparing with the kinetics parameters of second step, we found that the activation energy of the first step was a little higher (84.7 KJ/mol vs. 75.3 KJ/mol). However, its preexponential factor was much larger (1.20 E+6 $L \cdot mol^{-1} \cdot s^{-1}$ vs. 8.12 E+2 $mol \cdot L^{-1} \cdot s^{-1}$), and thus its reaction rate constant at the same temperature was about 10 times of that of the second step. In other words, according to the equation (1) and (4), the rate of MC formation is about 200 times of the rate of MC consume.

Kinetic model and parameter estimation over Zn-containing catalyst after the optimization of reaction condition

The external diffusion resistance can be eliminated by accelerating stirring speed. The stirring speed 1000 rpm adopted in the experiment was fast enough to eliminate external diffusion resistance, i.e., the DMC yield did not change with the further increase of stirring speed. The inner diffusion resistance decreases with the reduction of catalyst diameter. Figure 5(A) shows that the DMC yield approximately keeps stabilization by taking the catalyst whose diameter is less than 80 μm, that is to say, the inner diffusion has been efficiently eliminated.

The effect of catalyst loading is shown in Figure 5(B). It was found that the DMC yield increased sharply as the increase of catalyst amount till the maximum value 11.3%, and then began to decrease when the catalyst amount was more than 3.00g. This could be attributed to the side reaction of MC and DMC, which was also accelerated as the increase of catalyst amount.

With the increase of methanol/urea molar ratio, the yield of DMC passed through a maximum 12.5% at a methanol/urea molar ratio of 10, as can be seen in Figure 5(C). When the molar ratio was less than 10, the urea concentration was so high that cause the decomposition of urea via unclear route, which resulted in low DMC yield. When the molar ratio was more than 10, the DMC yield fell slightly. This may be attributed to the slower reaction rate with the decline of urea concentration.

Figure 5(D) demonstrates the DMC yield increased with the increase of temperature and decreased rapidly after 473 K. In theory, high temperature was benefit for the synthesis of DMC because this reaction was an endothermic reaction. However, the high temperature also accelerated the side reaction rate.

Figure 5(E) illustrates the effect of reaction time on the yield of DMC. The DMC yield increased at the first 12 h. At the same time, the side reaction increased gradually, which led to the consumption rate of DMC faster than the forming rate. At last, the DMC yield declined after 12 h.
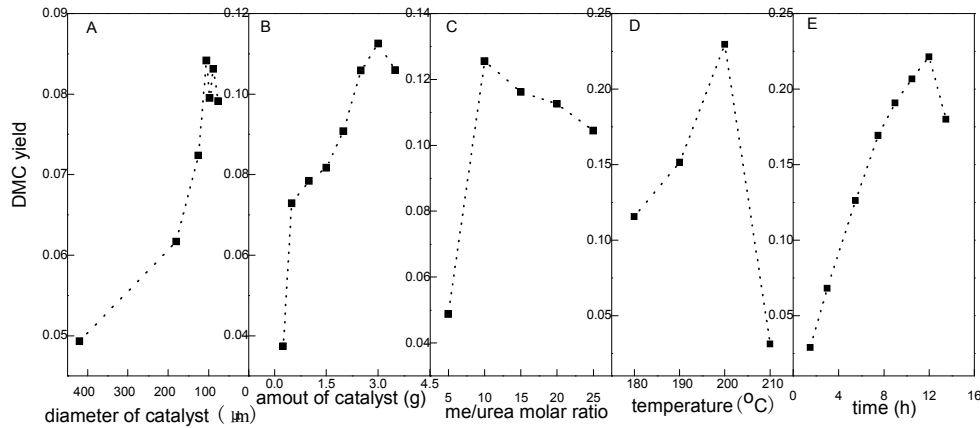

Figure 5 Effect of reaction condition on DMC yield. A, particulate size of catalyst; B, amount of catalyst; C, me/urea molar ratio; D, reaction temperature; E, reaction time.

In the presence of Zn-containing catalyst, just the reactions kinetics of MC to DMC was taken into account, since it was the rate-control step. The amount of solvent methanol was large in reaction, thus it can be considered as a constant. MC cannot evaporate for the high autogenous pressure in reaction vessel. It was a liquid-solid catalytic reaction for the synthesis of DMC and the volume of reaction solution did not change with the reaction process. Most part of the small molecular byproduct ammonia and carbon dioxide were considered to be separated from liquid for the distillation effect of reflux column. Thus, the reverse reactions in the synthesis of DMC could be neglected. Taking pseudo-homogeneous kinetics model, the reaction equations could be described as follows:

$$r1 = m_c \cdot K_{01} \cdot \exp(\frac{-Ea1}{RT}) \cdot C_{mc}^a \tag{5}$$

$$r2 = m_c \cdot K_{02} \cdot \exp(\frac{-Ea2}{RT}) \cdot C_{mc}^b \cdot C_{dmc}^c ; \tag{6}$$

$$\frac{dC_{dmc}}{dt} = r1 - r2 \tag{7};$$

$$\frac{dC_{mc}}{dt} = -r1 - r2 \tag{8};$$

$$\frac{dC_{nmmc}}{dt} = r2 \tag{9};$$

In these function, r is reactant rate; m_c is the amount of catalyst; K is preexponential factor; Ea is activation energy (KJ/mol); R is universal gas constant; T is reaction temperature (K); a, b, c is power exponents.

Defining

$$F = \sum_{1}^{M} \sum_{1}^{N} \left[(\frac{C_{dmc.exp} - C_{dmc.cal}}{C_{dmc.exp}})^2 + (\frac{C_{mc.exp} - C_{mc.cal}}{C_{mc.exp}})^2 + (\frac{C_{nmmc.exp} - C_{nmmc.cal}}{C_{nmmc.exp}})^2 \right] \tag{10}$$

as the objective function, where M is the number of experimental run, with concentrations measured at N reaction times. The fourth-order Runge-Kutta method was used to solve equation (7), (8) and (9). By minimizing the objective function (10) with Matlab Optimization Toolbox, the parameters of kinetic model were obtained as shown in Table 3.

The model-predicted reactants concentrations profile and the experimental data are plotted in Figure 6. The high prediction accuracy indicated that this model can be used for the DMC synthesis reactor analysis and design.

Table 3 Kinetic parameter for the synthesis of DMC on Zn-containing catalyst

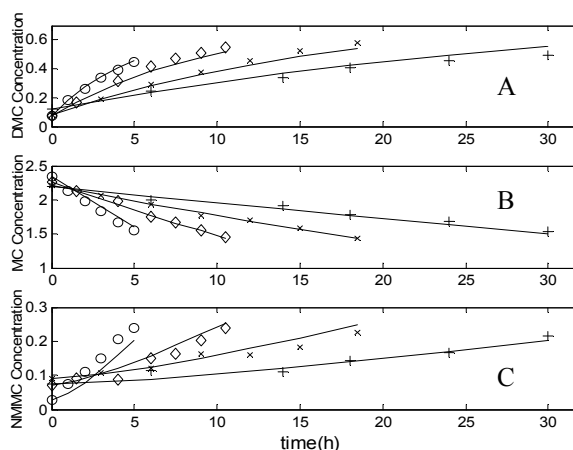| Parameter	K_{01} (s^{-1})	Ea1(KJ/mol)	a	K_{02} ($L{\cdot}mol^{-1}{\cdot}s^{-1}$)	Ea2(KJ/mol)	b	c
value	2.35 E+6	104	1.09	6.17 E+9	135	1.11	1.50

Figure 6 Experiment and predicted DMC (A), MC (B) and NMMC (C) concentration profiles at different temperatures. o 483 K; ◊ 473 K; × 463 K; 453 K

Conclusion

The kinetics investigations of the synthesis of DMC from urea and methanol without catalyst and with Zn-containing catalyst are individually carried out in a stainless steel batch. Without catalyst, the activation energies for the reaction of urea to MC and MC to DMC are 84.7 KJ/mol and 75.3 KJ/mol, respectively. On Zn-containing catalyst, the experimental results are properly described with a pseudo-homogenous model. The activation energies for the DMC synthesis and its consecutive reaction are 104 KJ/mol and 135 KJ/mol, respectively.

Acknowledgment

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