

Synthesis of dimethyl carbonate from urea and methanol catalyzed by iron-chloride ionic liquid

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The direct synthesis of dimethyl carbonate (DMC) from methanol and urea using iron-chloride ionic liquid as catalyst was investigated with a batch operation. The results showed that the ionic liquid $\text{Et}_3\text{NHCl-FeCl}_3$ is an effective catalyst; the raised yield (about 27%) and high selectivity (ca.100%) of DMC at 180°C were achieved without any specially designed equipment. The effect of the reaction conditions, such as reaction temperature, the molar ratio of urea to methanol, the amount and composition of catalysts, on the reaction was also discussed. The suggested reaction mechanism was proposed, which is very different from the reported ones in literatures.

Keywords: dimethyl carbonate; urea; methanol; ionic liquids; carbonylation

INTRODUCTION

Dimethyl carbonate (DMC) has been attracting much attention as an important chemical feedstock. It can be effectively used as an environmentally benign substitute for highly toxic phosgene and dimethyl sulfate in carbonylation and methylation [1], as monomer for several types of polymers and an intermediate in the synthesis of pharmaceutical and agricultural chemicals. Furthermore, DMC has been considered as an option for meeting the oxygenate specifications for transportation fuels [2]. The conventionally synthesis method of DMC is the oxidative carbonylation of methanol by carbon monoxide and transesterification of ethylene (or propylene) carbonate with methanol [3, 4]. It is expensive in using CO, epoxide as raw materials and accompanied by a potential explosion and poison hazard. Recently, utilization of carbon dioxide, a readily available, inexpensive and environmentally acceptable starting material, as raw material of DMC synthesis has widely been investigated [5-7]. But, the direct synthesis of DMC from methanol and carbon dioxide is still far from satisfactory due to the difficulty in activation of carbon dioxide, deactivation of the catalysts and the thermodynamic limitation. As an indirect method of utilizing CO_2 for DMC

synthesis, the synthesis of DMC from urea and methanol has been developed recently due to some advantages, such as abundant resource and low cost of urea and methanol, ternary azeotrope of methanol-water-DMC not to be formed because of no water produced and easiness of the product separation. Thus, this new route is considered to have alluring foreground in industry application. Although many research works on the new route have been reported yet [8-10], there are also several shortcomings, such as low conversion of the reactant or selectivity to DMC, higher reaction temperature and specially designed equipment to be used *etc.*

Recently, our group has disclosed the homogeneous and heterogeneous synthesis of DMC from urea and methanol catalyzed by zinc-chloride ionic liquid [11] and over $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ [12]. As our continuous research work, here we wish report the direct synthesis of DMC from urea and methanol catalyzed by the ionic liquid $\text{Et}_3\text{NHCl-FeCl}_3$. The raised yield and high selectivity to DMC were achieved. The effect of various reaction conditions, such as reaction temperature, time and amount of the catalyst was also discussed in this paper.

EXPERIMENTAL SECTION

The catalyst $\text{Et}_3\text{NHCl-FeCl}_3$ was synthesized according to literature method [11, 13]. All

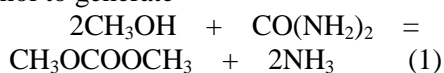
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experiments were carried out in a stainless steel reactor with inner volume of 500 mL fixed with a mechanical stirrer and an electric heater. In a typical procedure, 67 mL (1.83 mol) of anhydrate methanol, 1 g (0.017 mol) of urea and 6.5 mmol of catalyst were added to the reactor. After being purged three times with N₂ gas, the reactor was heated to 180°C with stirring and the reaction was carried out for 6 h. At the end of the reaction, the reaction mixture was distilled to separate the catalyst from the mixture. The distillate was cooled, sampled and analyzed by GC and GC-MS. The yield was calculated on the basis of urea.

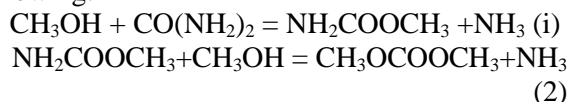
RESULTS AND DISCUSSION

Ionic liquid, Et₃NHCl-FeCl₃, exhibited a good catalytic activity for synthesis of DMC from methanol and urea (Fig. 1). The yield of DMC increased with amount of catalyst, it reached maximum 26.8% with 6.5 mmol of Et₃NHCl-FeCl₃ used. Then it declined as the amount of the catalyst was continuously increased. The fall of the yield was ascribed to the reduction of the selectivity to DMC since excess catalyst can also catalyze further conversion of the products into some by-products such as N-methyl urea, N-methyl methyl carbamate etc, which were detected by GC-MS in the reaction mixture.

According to the report [14], the synthesis reaction (1) from methanol and urea includes two steps: at first, urea reacts with one molecule of methanol to generate



carbamate (i); and then the carbamate continuously reacts with another one molecule of methanol to produce DMC (ii), as shown in following:



It was found that methyl carbamate (MC) was easily prepared from urea and methanol even in the absence of catalyst. It means the step (i) is a fast one and the second step (ii) is rate-determining step. In the case that the amount of the catalyst dose not exceeds 6.5 mmol, MC has been not detected in the samples, implying that the rate of the step (ii) was so fast that the intermediate rapidly reacted with urea once it was generated. In other words, the catalyst catalyzing the step (ii) is very effective and the selectivity is very high, nearly 100%.

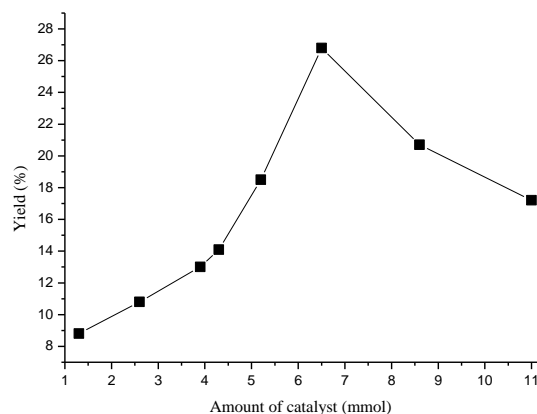


Fig. 1. Effect of catalyst amount on the reaction Conditions: T=180°C; CH₃OH/Urea ratio = 107.6/1; t = 6 h; FeCl₃/Et₃NHCl = 2:1.

The effect of the reaction time on the yield of DMC was investigated (the data not list here). It is known from the data that the yield reached to about 27% at the reaction time of 6 h. With the time continuously prolonged, the yield basically kept on constant. This finding suggested that the equilibrium state of the reaction was almost achieved under this condition. In addition, we can also calculate the ratio of initial urea concentration C₀ to its surplus concentration C in the reacting mixture from the data, then the ratio was taken logarithm, and the plot of ln(C₀/C) vs t (reaction time) is drawn in Fig. 2. It is evident that the relation curve is almost straight line, which indicated that the synthesis reaction is one order reaction for urea concentration in this system. Rate constant obtained from the figure is k_{Fe} = 0.0584 h⁻¹. As compared with zinc-chloride ionic liquid system (k_{Zn} = 0.0412 h⁻¹), Et₃NHCl-FeCl₃ system possesses higher reaction rate.

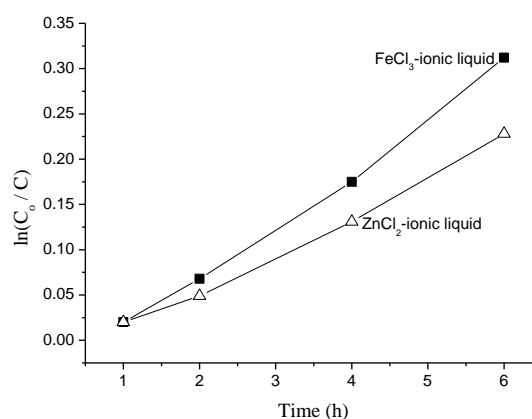


Fig. 2. Plot of ln(C₀/C) vs time. The lines fit the kinetic equation of first-order reaction.

As the raise of temperature, the yield increased rapidly to about 27% at 180 °C, and then fell to very low at 200 °C (Fig. 3). The changing rule of the yield is maybe attributed to the thermodynamic character of the reaction and reactant urea at higher temperatures. It

was reported that the heat of the synthesis reaction is $\Delta H^\ominus = 47.11$ KJ/mol [15], which shows that it is an endothermic reaction. Thus, in view of the thermodynamics, the increase of the reaction temperature is of a great advantage to the generation of DMC. On the other hand, from a view point of kinetics, raise of the reaction temperature can accelerate the reaction and shorten the time approaching to the equilibrium. Therefore, the yield increased with the temperature rising in the range from 130°C to 180 °C. On the other hand, it was recorded that the melting point of urea is 133-135 °C and it begins to decompose into HNCO and NH₃ [16] when the temperature increased more than its melting point. The increase of the temperature can promote the decomposition leading to

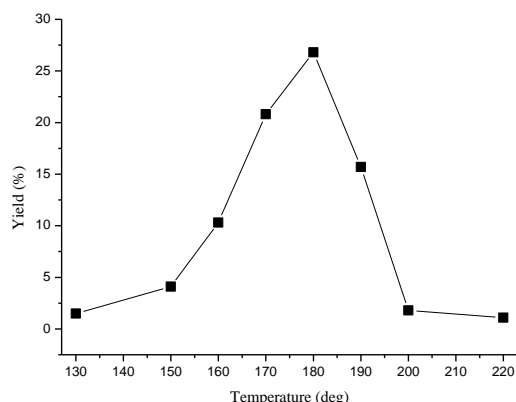


Fig. 3. Effect of reaction temperature on the reaction. Conditions: catalyst 6.5 mmol; CH₃OH/urea ratio = 107.6/1; t = 6 h; FeCl₃/Et₃NHCl = 2:1.

the increase of the HNCO concentration. The excess active particles HNCO caused some side reactions happened, resulting in the fall of the selectivity and the reduction of the yield.

Molar ratio of FeCl₃ to Et₃NHCl in the ionic liquid can greatly affect the synthesis reaction; the results were shown in Fig. 4. It is evident that a maximum of DMC yield was achieved when the ratio was 2:1; and when only the salt FeCl₃ was used as catalyst, the yield of DMC was merely 10.9%. This result implied that the ionic liquid formed by FeCl₃ and Et₃NHCl is very important for catalyzing DMC synthesis reaction. The better performance of the ionic liquid is most likely due to its enhancement to polarity and electrostatic field of the reaction medium, which may stabilize the charged intermediate [17]. In addition, the catalytic activity of metal-chloride ionic liquids is ascribed to their stronger acidity, which can absorb the released NH₃ to shift the reaction equilibrium to the direction producing DMC [11,

12]. Contrarily, too strong acidity of the ionic liquid is disadvantageous to the reaction according to our previous reports, which may cause strong

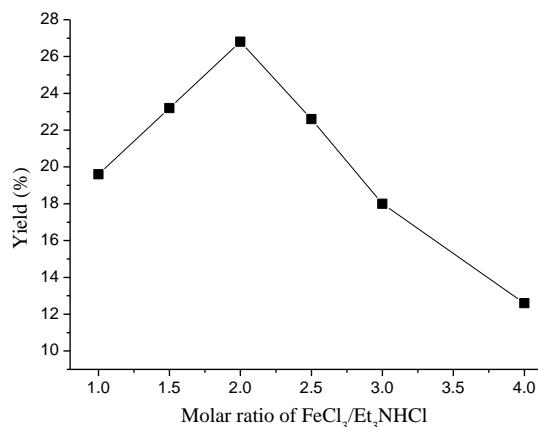
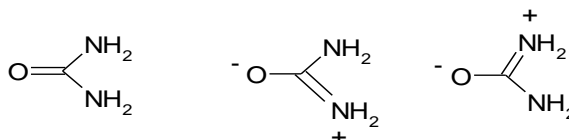


Fig. 4 Effect of molar ratio of FeCl₃ or ZnCl₂ to Et₃NHCl on the reaction. Conditions: catalyst 6.5 mmol; CH₃OH/urea ratio = 107.6/1; t = 6 h; T=180°C.

interaction with NH₂ in urea molecule to restrain its further reaction. Therefore, the catalyst with medium acidity could effectively activate urea and methanol and interact with release NH₃ gas produced in the reaction to promote shift of the reaction equilibrium to the direction producing DMC.

Suggested reaction mechanism

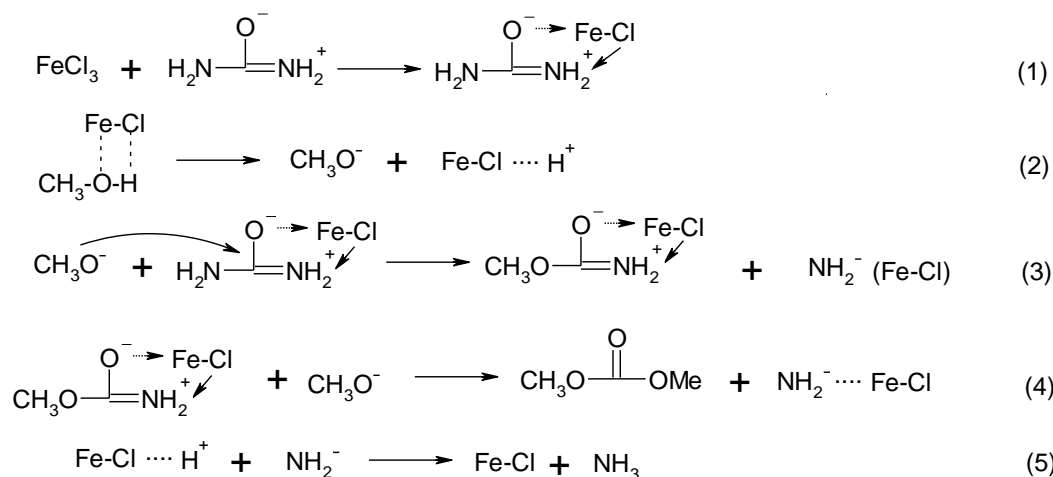
It was reported that the molecular structure of urea involves resonance between the three structures (following molecular structure of urea), the observed values of the interatomic distance indicating 30% double bond character for the carbon-to-nitrogen bonds leaving 40% for carbon-to-oxygen bond [18].



The molecular structure of urea

Therefore, the complexes were easily formed by urea molecules coordinating with metal ions through the oxygen as well as the nitrogen atoms. For example, six urea molecules coordinate with iron chloride to generate a complex, Fe[OC(NH₂)₂]₆Cl₃. The complex was formed by urea molecules coordinating with iron (III) ion through the oxygen atom [19]. On the basis of the above facts, the reaction mechanism of DMC synthesis from urea and methanol involved mutual activation of methanol and urea by the catalyst was proposed, as shown in Scheme 1.

This network involves the activation of urea and methanol by means of interaction of them with



Scheme 1. Suggested reaction mechanism.

catalysts to form two activated intermediates, complex of urea coordinated with (1) and methoxide anion CH_3O^- (2). Then, methoxide anion CH_3O^- attacks the carbon charged positively in the molecule of activated urea to generate methyl carbamate(3), which is also in the form of complex coordinated to FeCl_3 . The produced NH_2^- was stabilized by the ionic liquid $\text{Et}_3\text{NHCl}-\text{FeCl}_3$ due to its higher polarity and the stronger electrostatic interaction between the cations and anions, which is very advantageous to the step shifting to the right hand side. Finally, the activated methyl carbamate reacts with another CH_3O^- to produce the target product DMC (4), and the step (5) realize the catalytic cycle. As seen from the mechanism, it was the existence of the three activated particles, such as methoxide anion, complexes of urea and methyl carbamate coordinated with the transition metals Fe (III) in the catalyst, which results in high efficiency of the synthesis reaction via greatly accelerating the step (3) and (4). This is also the reason that no byproduct, methyl carbamate, was detected in the samples.

CONCLUSIONS

When the synthesis reaction of DMC was carried out in a batch operation and without any specially designed equipment, the ionic liquid $\text{Et}_3\text{NHCl}-\text{FeCl}_3$ is an effective catalyst for the direct synthesis of dimethyl carbonate (DMC) from methanol and urea by one step reaction; the raised yield (27%) and high selectivity (100%) to DMC under temperature of 180°C were achieved. Besides, the results were basically explained by the thermodynamics and kinetics of the reaction. The reaction mechanism that is different from that reported was proposed

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СИНТЕЗА НА ДИМЕТИЛ-КАРБОНАТ ОТ КАРБАМИД И МЕТАНОЛ, КАТАЛИЗИРАНА ОТ ЙОННА ТЕЧНОСТ И ЖЕЛЕЗЕН ТРИХЛОРИД)

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(Резюме)

Изследвана е синтезата на диметил-карбонат (DMC) от карбамид и метанол при периодични условия при използването на железен три хлорид като катализатор и йонна течност. Резултатите показват че йонната течност Et₃NHCl-FeCl₃ е ефективен катализатор с повишен добив (около 27%), като се постига висока селективност (близо до 100%) спрямо DMC at 180°C в проста апаратура. Обсъдени са ефекта на условията на реакцията (температура, моларното отношение на карбамида към метанола, количеството и състава на катализатора). Предложен е нов механизъм на реакцията, различен от известните досега.