



High-yield synthesis of dimethyl carbonate from the direct alcoholysis of urea in supercritical methanol

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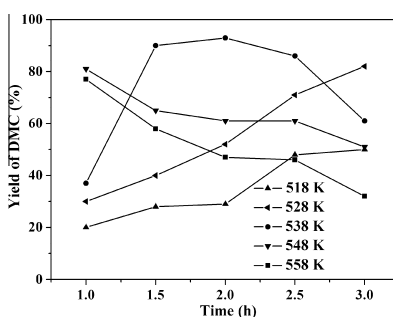
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HIGHLIGHTS

- A new strategy of urea in sub- and supercritical methanol method was proposed.
- The optimal reaction conditions were systematically investigated.
- The effects of treating reactor, pressure and water on DMC yield were investigated.
- The mechanism of urea in sub- and supercritical methanol system was proposed.

GRAPHICAL ABSTRACT

The effects of reaction temperatures and time on DMC yield at the molar ratio of methanol/urea of 25, the reactor loading of 285 μL , reaction pressure of 9.2 MPa, and the reactor treated using acetone.



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ABSTRACT

Herein the synthesis of dimethyl carbonate (DMC) from the direct alcoholysis of urea in supercritical methanol system was proposed. The effects of different reaction conditions, such as reaction temperature, reaction time, the molar ratio of methanol/urea, reaction pressure, the volume of reaction solution, the treating reactor and the amount of water on DMC yield were systematically investigated. The experimental results indicated that the optimal reaction conditions were reaction temperature of 538 K, time of 2 h, the molar ratio of methanol/urea of 14, and the reactor loading of 285 μL , respectively. And the DMC yield was 98% under the optimal reaction condition.

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1. Introduction

In recent years, increasing attentions were being paid to the preparation of dimethyl carbonate (DMC)—a very useful material widely used in medicine, pesticides and energy sources [1–4]. To date, methods used for the synthesis of DMC mainly included phosgenation of methanol [5,6], oxidative carbonylation of methanol, transesterification of ethylene carbonate with methanol [7,8], and the direct reaction between CO_2 and methanol with added cat-

alyst [9,10]. However, these methods showed many disadvantages such as usage of corrosive and poisonous gases [11], lower DMC yield, and lower DMC selectivity [6,12].

Recently, a new reaction route was proposed to prepare DMC by using the alcoholysis of urea in methanol in the presence of different catalysts [9,13–17]. Preparation of DMC from the alcoholysis of urea in methanol was promising from both ecological and economical points of view. Another advantage for this process was that ammonia—the co-product—can be used as a starting material for the urea production. This route was divided into two steps via a methyl carbonate (MC) intermediate. This process was an interesting route. The most active catalysts reported in the prior literature were metal oxides [5,8,9,13], polyphosphoric acid [14] and organotin

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derivatives [10,15]. Sun et al. [13] used ZnO to catalyze the alcoholysis of urea in methanol and studied the effects of reaction temperature and time on the yield of DMC. The results suggested that the highest DMC yield of 30 wt% was obtained at 443 K for 11 h. Compared to the single metal oxide catalyst, a mixed metal oxide catalyst of ZnO–CeO₂ could realize a higher DCM yield (40 wt%) under the optimal conditions (443 K, 4 h, and 20 bar) [9]. Yang et al. [14] tried to use polyphosphoric acid (PPA) as the catalyst to promote the reaction between urea and methanol. A desirable DMC yield of 67.4% was obtained at 413 K for 4 h with added 0.8 MPa CO₂. Wang et al. [15] used the Benson method to prepare DMC from urea and methanol by using a distillation reactor over a Zn-based catalyst. Under optimal conditions (473 K, urea solution LHSV 0.3 h⁻¹, methanol LHSV 0.6 h⁻¹, and 2:1 reflux ratio at 1.2 MPa N₂), the highest DMC yield of 70 wt% was achieved. These previous studies suggested that both catalyst and longer reaction time are two indispensable requirements in realizing higher DMC yield.

Material above its critical point, which usually defined as supercritical fluid, shows more merits than that of material below its critical point. The advantages of supercritical fluids mainly include the following points: (1) it was environment-friendly and free of catalyst; (2) shorter reaction time and higher conversion and product yield were always associated when conducting reactions in supercritical fluids compared to using traditional media; (3) no severe requirement for the quality of materials [18]. Of those supercritical fluids, supercritical methanol is one of the most promising one due to its milder reaction condition ($T_c = 513$ K), such as higher solubility and high ionic product, which was commonly used in methanolysis and preparing biodiesel fuels. Kamitanaka et al. [19] investigated the non-catalytic alcoholysis of benzonitrile in supercritical methanol. A 95% yield of methyl benzoate was obtained at 623 K for 12 h. This study indicated that supercritical alcohols had high reactivities toward unsaturated bonds. Song et al. [20] investigated the reaction behavior of refined, bleached and deodorized palm oil in supercritical methanol. Around 93% yield of fatty acid methyl esters was the highest at 623 K and 5 min. The results suggested that supercritical methanolysis is free of catalysts and significantly reduced the reaction time compared to the conventional method. Furthermore, supercritical process was also simpler and easier in product separation than that alkali catalyst method in biodiesel production. To the best of the authors' knowledge, however, the literature provides no reports on the preparation of DMC for the direct alcoholysis of urea in supercritical methanol. This article provides such report.

In the present work, high-yield of DMC was achieved from the alcoholysis of urea in supercritical methanol. Effects of reaction temperature (518–558 K), time (1–3 h), methanol/urea ratio (12–31), the reactor loading (265–315 μ L), pressure and amount of water were determined to find how these parameters affects the DMC yield. The final purpose of this study is to establish a highly-efficient method for the production of DMC.

2. Material and methods

2.1. Material

Urea (A.R.), methanol (A.R.), acetone (A.R.), dodecane (A.R.) and DMC (A.R.) were purchased with high purity ($\geq 99.9\%$) from Sinopharm Chemical Reagent Co. Ltd. and used as received.

Stainless-steel reactors assembled from a nominal 1/4-in Swagelok port connector and caps served as the batch reactors in all experiments. They provide a volume of 0.59 mL. Prior to their use in experiments, the metal reactors were loaded with water and conditioned for 8 h at 573 K to remove any lubricants/oils that remained from the manufacture of the Swagelok parts. These reactors were then cleaned with acetone and dried prior to use.

2.2. Experimental procedure and the reaction product collection

Stock solutions of reactant were prepared by completely dissolving urea in methanol at the desired room-temperature concentrations. A carefully measured amount of the desired reactant solution was added to the reactor by using a microliter syringe.

After being loaded, the reactors were sealed. Reactions were carried out by placing the reactors in a molten-salts bath (consists of NaNO₂, NaNO₃ and KNO₃ at a mass ratio of 40:7:53) pretreated to the desired temperature, and the temperature was controlled by an Omega temperature controller (HYA-7411) with a precision of ± 2 °C. When the desired reaction duration had been reached, the reactors were removed from the molten-salts bath. The stainless steel reactors were quenched by immersing them in an ice-water bath for about 5 min. The cooled reactors were opened and the liquid-phase contents withdrawn using a syringe. The reactor was then rinsed at least five times with acetone to ensure complete recovery of all material. Finally, acetone was added to the volumetric flask up to 5 mL. The experiments were conducted under supercritical methanol conditions.

2.3. Analysis and identification

Analytical GC–MS was performed on a Varian Saturn 3900/2100 system (Palo Alto, CA, USA) using a VF-5MS non-polar capillary column (30 m length, 0.25 mm i.d., 0.25 μ m film thickness). A volume of 1 μ L was injected in splitless mode, and the inlet temperature split ratio was 523 K. A two-minute solvent delay was set to protect the filament. The column was initially held at 333 K for 3 min. The temperature was ramped to 523 at 15 K/min and held isothermally for 10 min, giving a total runtime of about 25.67 min. Helium flowing at 1 mL/min served as the carrier gas. A Wiley mass spectral library was used for compound identification.

An SHIMADZU GC-2014 equipped with a FID detector was used to quantify the products. RT-10223 capillary column (30 m length i.d. 0.25 mm, film thickness 0.25 μ m) separated the constituents. All the samples were added into a known amount of dodecane as an internal standard. A volume of 2 μ L was injected in splitless mode, and the inlet temperature was 523 K. The column was initially held at 333 K. The temperature was ramped to 523 at 15 K/min, giving a total runtime of about 12.67 min. Helium flowing at 3 mL/min served as the carrier gas.

¹H NMR spectra of major by-product was recorded on a 300-MHz NMR spectrometer (Inova 300, Varian) at 298 K. The by-product was dissolved in deuteriochloroform (CDCl₃). About 256 scans were accumulated for the ¹H spectrum using a 45° pulse width together with broad band proton decoupling. Tubes of 5 mm diameter were used.

3. Results and discussion

3.1. Product identification

Products from the alcoholysis of urea in supercritical methanol were identified by GC–MS. DMC dominated the product profile. The DMC structure was proved by principal fragment ion peaks of 15, 29, 31, 45 and 59 in the mass spectra. In addition to DMC, fragment ion peaks of $m/z = 38, 42, 58, 83, 98, 113, 139$ and molecular peak of $M = 154.8$ were also observed. However, it was difficult to directly identify the structure of by product from the GC–MS due to the low computer matching degree to the standard compound stored in the GC–MS library. Therefore, we separated and purified the major by product which was identified by ¹H NMR. The detailed information of ¹H NMR analysis are listed as follows:

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