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A New Process for Synthesis of Dimethyl Carbonate from Ethylene Carbonate and Methanol without any Catalyst under Supercritical Conditions

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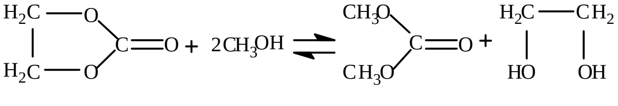
Abstract: Dimethyl carbonate was synthesized by transesterification reaction between ethylene carbonate and methanol under supercritical conditions without any catalyst. Experimental results showed that the residence time and the molar ratio of methanol to ethylene carbonate all can affect the conversion of ethylene carbonate. When the molar ratio of methanol to ethylene carbonate was 8:1, 81.2 % conversion can be achieved at 9.0 MPa and 250˚C after 8 h.

Keywords: Supercritical methanol, dimethyl carbonate, ethylene carbonate, transesterification.

Dimethyl carbonate (DMC) has extensive applications as an environmentally benign solvent, an octane booster in gasoline to meet oxygenate specifications and a precursor for polycarbonate resins[1,2]. Also, it can be used as a substitute reagent of poisonous phosgene and dimethyl sulphate for carbonylation and methylation in organic synthesis[3,4]. DMC is mainly synthesized by oxidative carbonylation of methanol (non-phosgene route) or phosgenation of methanol (phosgene route)[5]. Both routes involve the use of poisonous or corrosive phosgene or carbon monoxide. DMC was also synthesized by transesterification reaction between ethylene carbonate and methanol in the presence of a Lewis acid or base catalyst[5~11](**Scheme 1**). However, to our best knowledge, there is no report on the transesterification of ethylene carbonate and methanol for the synthesis of dimethyl carbonate in the absence of any catalyst under supercritical conditions. It is of great interest to study a practically possible process without any catalyst.

Scheme 1



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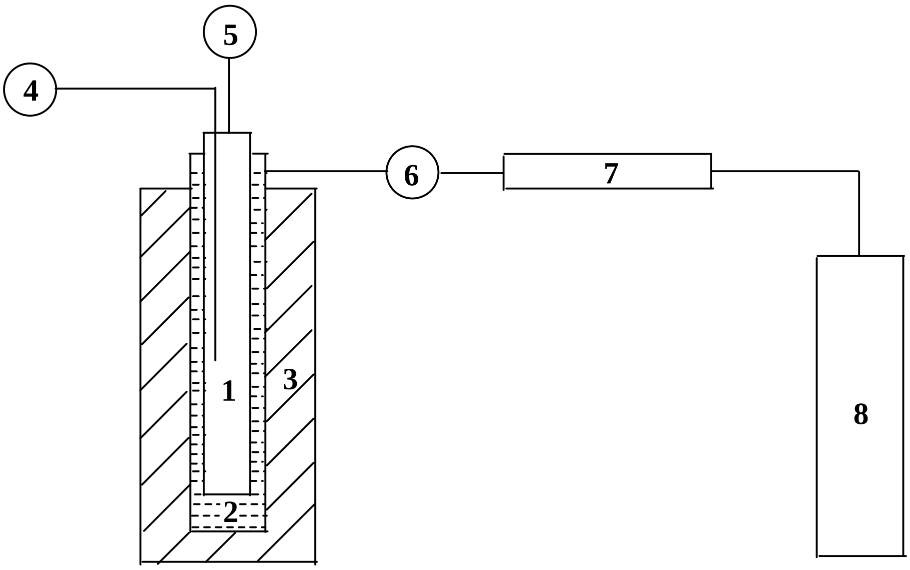
Recently, the use of supercritical fluids as substitute solvent has received much attention because of their tunable solvent properties by variation of pressure and temperature[12,13]. Furthermore, supercritical fluid may be a particularly advantageous reaction medium when it serves as both reactant and solvent. The improved rates for catalytic hydrogenation of carbon dioxide to formic acid in supercritical conditions provided support for this approach[14]. However, only limited reactions have been explored based on this idea[15]. Herein, we report an efficient synthesis of DMC from supercritical methanol/ethylene carbonate mixture without any catalyst. Supercritical methanol serves as both reactant and solvent.

Experimental

The reactions were carried out in a 15 mL stainless steel autoclave reactor which has inner diameter of 6 mm and length of 480 mm (**Figure 1**). In a typical procedure, methanol and ethylene carbonate mixture were put into the reactor. The reactor retained at a constant temperature and pressure. The effluent from the reactor was cooled and reduced to atmospheric pressure, then collected in a vessel. The conversion based on ethylene carbonate was analyzed by gas chromatography method (Agilent 6890, DB-FFAP30 m×0.25 mm, injection temp.=250˚C, column temp.=200˚C, detection temp.=250˚C, N_2 flow rate =30 mL/min).

Figure 1 Equipment used for the transesterification reaction



(1) reactor, (2) oil bath, (3) electrical furnace, (4) temperature control monitor, (5) pressure control monitor, (6) product exit valve, (7) condenser, (8) product collecting vessel.

Results and Discussion

In **Table 1** shown, the transesterification reaction between ethylene carbonate and methanol proceeded in a very fast rate and achieved 57.9 % conversion of ethylene carbonate within 5 minutes. The residence time of the reactants in the reactor has a positive effect on the conversion of ethylene carbonate. The conversion of ethylene carbonate increases with the enhancement of the residence time. For example, the residence time increases from 5 minutes to 30 minutes, the conversion of ethylene carbonate was enhanced from 57.9 % to 58.9 %.

It is well-known that transesterification of ethylene carbonates with methanol is an equilibrium reaction. The enhancement of the ratio of methanol to ethylene carbonate is beneficial for this reaction. The result was illustrated in **Figure 1.**

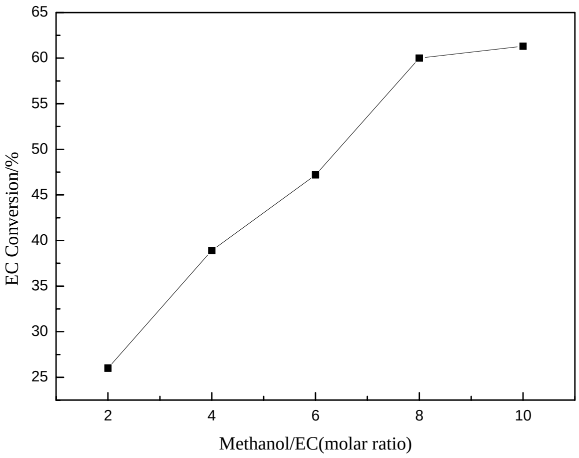
D. Kusdiana and S. Saka reported supercritical methanol as acid catalyst in the transesterification of rapeseed oil[16]. It supported our hypothesis of an acid self-catalyzed in the transesterification reaction between methanol and ethylene carbonate and we proposed a plausible mechanism in this transesterification reaction as follows.

Table1 Effect of residence time on the conversion of ethylene carbonate

Residence time(min)	480	360	240	120	60	30	15	10	5
EC Conversion/ %	81.2	76.4	70.9	64.4	60.0	58.9	58.0	58.0	57.9

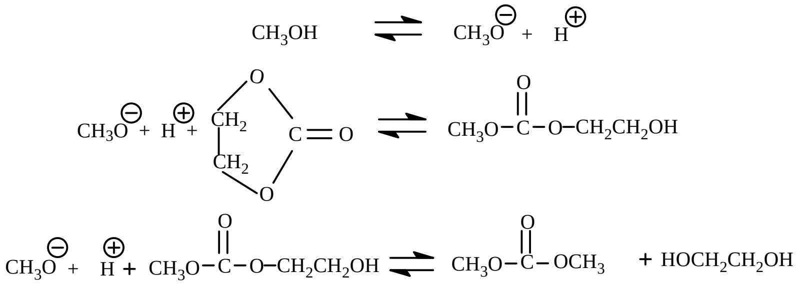
Conditions: temperature, 250˚C; pressure, 9.0 MPa; methanol/ethylene carbonate=8/1(molar ratio)

Figure 1 Effect of methanol/EC (molar ratio) on the conversion of ethylene carbonate



Conditions: temperature, 250˚C; pressure, 9.0 MPa; Reaction time, 60 min.

Scheme 2



In conclusion, we found that DMC could be rapidly, successively synthesized from supercritical methanol/ethylene carbonate mixture in the absence of any catalyst. In particular, the reaction perfectly eliminates any problem probably caused by the use of catalysts, and completely conforms to “environmentally benign concept”.

Acknowledgment

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