



Transesterification of urea and ethylene glycol to ethylene carbonate as an important step for urea based dimethyl carbonate synthesis

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Received 16th April 2003

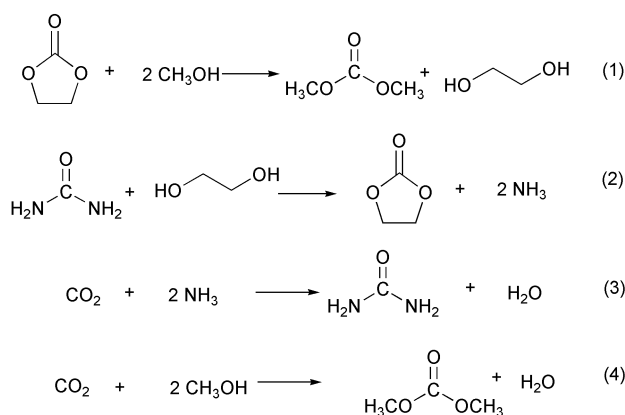
First published as an Advance Article on the web 9th June 2003

Two-step synthesis of dimethyl carbonate (DMC) from urea has been investigated with various solid catalysts. The first step involves reaction of urea with ethylene glycol (EG) to form ethylene carbonate (EC) and the second step transesterification of EC formed with methanol to give DMC and EG. It has been found that ZnO is highly active and selective for the two steps, of which the former should be conducted under reduced pressure. At around ambient pressure, 2-oxazolidone and ethyleneurea are formed in the first step. Similar to EG, other glycols such as 1,2- and 1,3-propanediols can also be transformed to corresponding cyclic carbonates.

Introduction

Dimethyl carbonate (DMC) is an important chemical, which finds extensive applications such as a solvent, an octane booster in gasoline to meet oxygenate specifications, and as a starting material for organic synthesis *via* carbonylation and methylation replacing the use of poisonous phosgene and dimethyl sulfate.¹ It is also used as a precursor for polycarbonate resins, for which phosgene is used.¹ DMC is synthesized by oxidative carbonylation of methanol (non-phosgene route, ENICHEM process) or by phosgenation of methanol. Both of these routes involve the use of poisonous and/or corrosive gases such as chlorine, phosgene, and carbon monoxide, and there is also a possibility of explosion hazards in the case of methanol carbonylation. Many researchers attempted direct synthesis of DMC from carbon dioxide and methanol in the presence of organometallic complexes, inorganic bases or zirconium oxide.² However, most of these systems suffer from several drawbacks such as low yields, high cost of the starting materials and problems associated with catalyst–product separation due to the homogeneous nature of the catalysts. The urea alcoholysis route has also been reported by many researchers and, in this case, urea and methanol are reacted together to form DMC and ammonia.³ Formation of several side products, which results in poor selectivity, is one of the major drawbacks of using this reaction. Use of homogeneous catalysts also poses catalyst product separation and deactivation problems in some cases.^{1e,3}

DMC can be synthesized *via* the transesterification of ethylene carbonate (EC) and methanol (reaction 1 of Scheme 1). There are several reports concerning this reaction.⁴ The present authors have also reported that basic metal oxide^{4e} and smectite catalysts^{4f,g} are active and selective for this reaction. Although DMC can be obtained at high yield *via* this reaction, ethylene glycol (EG) produced along with DMC could be a disadvantage of the reaction,^{1f} since the demands for these two products are usually different from each other. Note, however, that EG can be converted to EC *via* transesterification with urea, in which ammonia is co-produced (reaction 2). Ammonia formed can be



Scheme 1 Dimethyl carbonate (DMC) synthesis from carbon dioxide and methanol (reaction 4) involving three reactions such as (1) transesterification of ethylene carbonate and methanol producing DMC and ethylene glycol following (2) production of ethylene carbonate from urea and ethylene glycol, and (3) production of urea by recycling of ammonia.

Green Context

The importance of dimethylcarbonate in many application areas, its simple structure and the traditional use of toxic phosgene in its manufacture have combined to attract a lot of research directed at new, efficient and environmentally friendly synthetic processes. The new Enichem commercial route avoids phosgene but still employs a toxic chemical. Here we see good progress made in what is probably the ideal green chemistry route to this important chemical – the reaction of CO₂ with methanol. This is effectively achieved in a two-step process by first forming ethylene carbonate from urea and then carrying out a transesterification. The simple and inexpensive catalyst ZnO is highly active and selective for the two steps.

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easily converted to urea, since the urea synthesis from ammonia and carbon dioxide has been established (reaction 3). Thus, DMC synthesis from CO₂ and methanol (reaction 4) can be achieved by combining these three reactions. This has merit in that EG and ammonia are recyclable for reactions 2 and 3, respectively. The transesterification of urea with EG is first revealed in a patent of Mitsubishi Gas Chemicals.⁵ However, there is no available study on this reaction in the open literature. Since reaction 1 has been well studied as described above, the major aim of the present work is to establish suitable catalysts and reaction conditions for reaction 2, in which high EG conversion and high EC selectivity are important issues for achieving the urea based DMC synthesis (Scheme 1).

Results and discussion

When the transesterification of EG and urea was carried out at 150 °C for 4 h at a reduced pressure of 3 kPa (by dynamic evacuation), the main product was EC. Table 1 lists the reaction

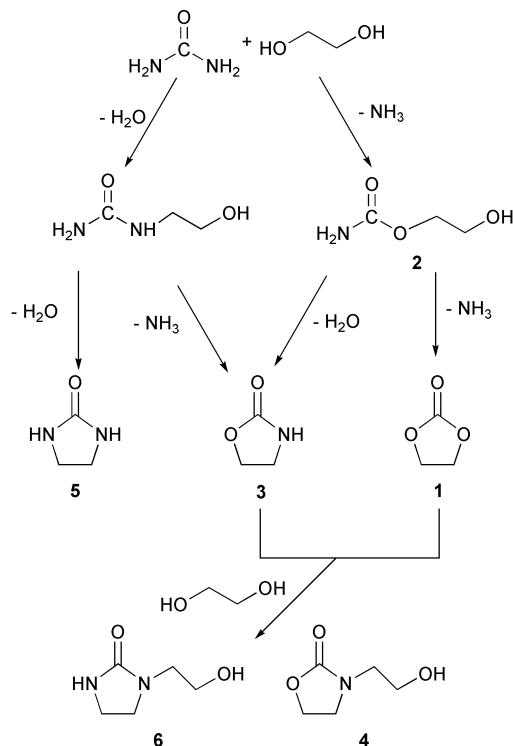
Table 1 Results of reaction (2) of urea and EG under reduced pressure

Entry	Catalyst	BET area/ m ² g ⁻¹	Urea conversion (%)	Selectivity (%) ^a		
				1	2	3
1	ZnO(1)	17	97	98	1.3	0.5
2	ZnO(2)	40	100	98	1.7	0.5
3	MgO	14	67	80	5.2	15
4	CeO ₂	40	47	45	47	6.6
5	La ₂ O ₃	5	55	71	12	16
6	CaO	173	16	trace	0	53 ^b
7	ZrO ₂	49	26	54	42	1.8
8	Zn(AcO) ₂	—	84	88	11	0.7
9	Hydrozincite	—	54	83	3.0	14

Urea, 200 mmol; EG, 270 mmol; catalyst, 1.2 g; pressure, 3 kPa; temperature, 150 °C; time, 3 h.^a Selectivity = moles of 1, 2 or 3 formed/mole of urea reacted. For 1, 2 and 3, see Scheme 2. ^b 2-Hydroxyethyl oxazolidone and ethylene urea were also formed with selectivities of 44 and 3%, respectively.

results obtained with various catalysts. ZnO(1) and ZnO(2) give high conversions of urea and selectivities for EC 1. By-products formed with these catalysts are 2-hydroxyethyl carbamate 2 and 2-oxazolidone 3. The other catalysts show lower urea conversions and EC selectivities as compared with the ZnO catalysts. With CaO, *N*-(2-hydroxyethyl)-2-oxazolidone 4 and ethyleneurea 5 were also formed in selectivities of 44 and 3.4%, respectively. These products were also formed in small quantities with La₂O₃. The lower urea conversions obtained with MgO, CeO₂, La₂O₃, CaO and ZrO₂, compared with ZnO(1) and ZnO(2), cannot be explained by their BET surface areas. Previously, the present authors measured the basic properties of the present oxide catalysts by temperature programmed desorption (TPD) of adsorbed carbon dioxide.^{4e} It was shown that ZnO and MgO have weakly and moderately basic sites, while the other oxide catalysts have strongly basic sites. Furthermore, it was also found that the strength of the moderately basic sites of ZnO is weaker than that of MgO. On the basis of these results, it was concluded that the high activity and selectivity of ZnO for reaction 2 result from its basic properties.

The reaction of EG and urea was carried out with ZnO(1) and ZnO(2) for various reaction times. When the reaction time was 30 min, the urea conversions were 29 and 49% for ZnO(1) and ZnO(2), respectively. There was also a difference in the selectivity for EC, being 63% with ZnO(1) and 70% with ZnO(2). Fig. 1 plots the selectivities for EC and 2 against the total urea conversion. It is seen that the EC selectivity depends



Scheme 2 Possible reaction pathways for the reaction (2) of urea and ethylene glycol.

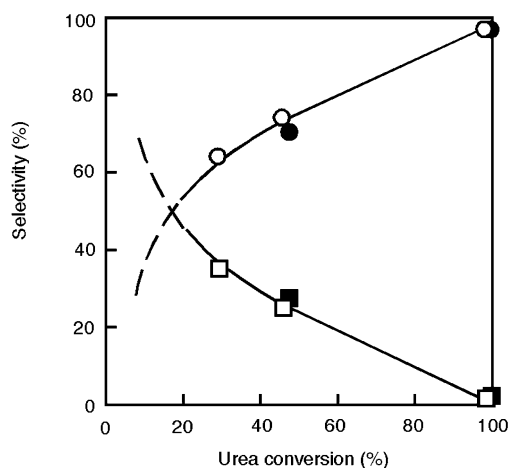


Fig. 1 Selectivities for EC (○, ●) and 2-hydroxyethyl carbamate (□, ■) versus urea conversion in reaction (2). Open and closed symbols represent the data obtained with ZnO(1) and ZnO(2), respectively. Reaction conditions: urea, 200 mmol; glycol, 270 mmol; catalyst, 1.2 g; pressure, 3 kPa; temperature, 150 °C.

on the conversion but not on the catalysts used when compared at the same conversion levels. Hence, the difference in the BET surface area between the catalysts (Table 1) would be responsible for the difference in the conversion observed, resulting in the different EC selectivities. Fig. 1 also shows that, at higher conversion levels, the selectivity for EC increases, while that for 2 decreases. These results lead us to the conclusion that 2 is the intermediate for the EC production from urea.

The effect of reaction pressure is shown in Fig. 2. The minimum urea conversion appears at around 100 kPa. The EC selectivity rapidly decreases with increasing the pressure. The selectivities for 3 and 4 show maxima at around 100 kPa and those for 5 and *N*-(2-hydroxyethyl)-2-imidazolidone 6 increase in a higher pressure region. Most plausible reaction pathways for the formation of all those products are illustrated in Scheme

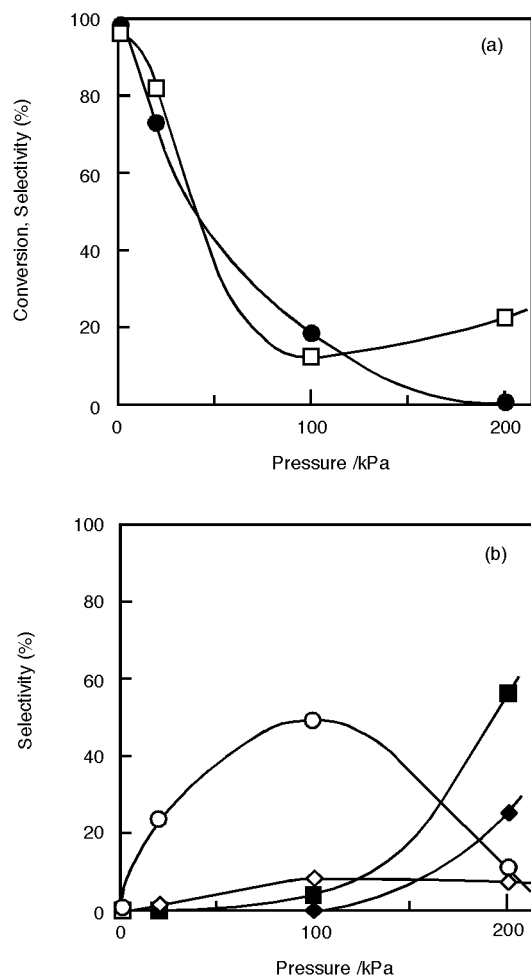


Fig. 2 Influence of reaction pressure on reaction (2), the transesterification of EG and urea. (a) Urea conversion (□) and selectivity for EC (●). (b) Selectivities for 2-oxazolidone (○), ethyleneurea (■), *N*-(2-hydroxyethyl)-2-oxazolidone (◇) and *N*-(2-hydroxyethyl)-2-imidazolidone (◆). Reaction conditions: urea, 200 mmol; glycol, 270 mmol; catalyst, 1.2 g; temperature, 150 °C; time 3 h.

2. EG and urea are condensed to **2** by releasing ammonia. Compound **2** is converted to EC or **3** via intramolecular deammonization or dehydration, respectively. In a similar manner, if the intermolecular dehydration reaction of EG and urea occurs, *N*-(2-hydroxyethyl)urea is formed as an intermediate and then converted to **5**. This intermediate can be also transformed to **3** by deammonization. Thus, only deammonization is required for the selective formation of EC and, on the other hand, only dehydration is required for the selective formation of **5**. The formation of **3** is possible by both reactions, dehydration and deammonization. Hence, the results of Fig. 2 mean that the deammonization is dominating over the dehydration at reduced pressures.

The formation of **4** and **6** is complicated. In separate runs, it was found that **4** and **6** were not produced from a mixture of EG and **3** nor from that of EG and **5** at 150 °C for 4 h in the autoclave in the presence of CaO catalyst. When a mixture of EG, EC and **3** was used, both **4** and **6** were formed, while a mixture of EG, EC and **5** gave no product under the same conditions. Thus, the presence of the three compounds EG, EC and **3** is required for the formation of **4** and **6**, although the reaction mechanisms are not clear at present.

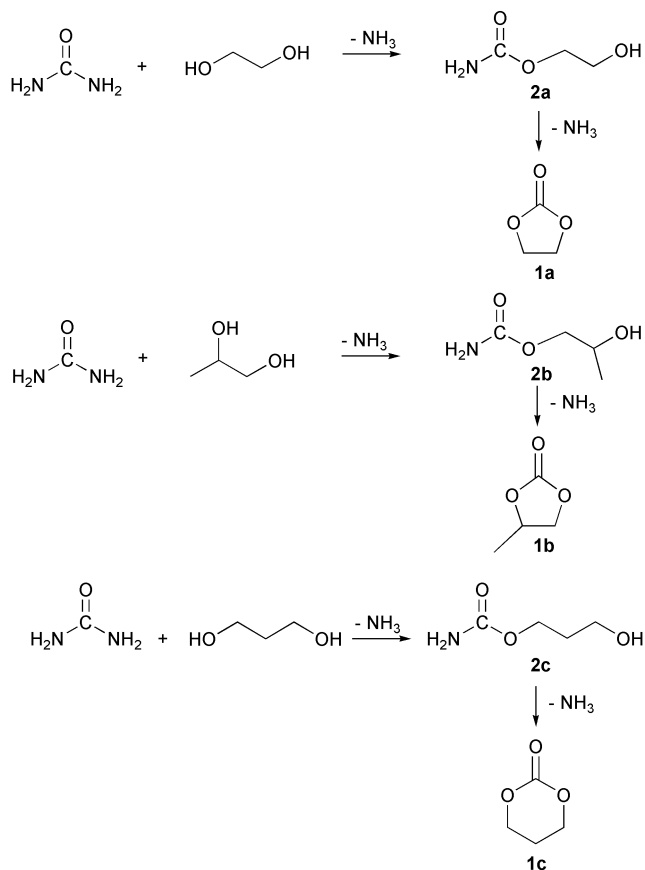
The ability to recycle the catalyst is important for mass production. Therefore, attempts were made to reuse the ZnO(1) catalyst 3 times by filtration, washing with ethanol and water, and drying after each run. The results obtained are given in Table 2, indicating that the catalyst can retain its activity and selectivity performance during the recycles.

Table 2 Results of catalyst recycling of ZnO(1) for reaction (2)

Run	Urea conversion (%)	Selectivity for EC (%)
1	97	98
2	97	96
3	100	97
4	99	97

Urea, 200 mmol; EG, 270 mmol; ZnO(1), 1.2 g; pressure, 3 kPa; temperature, 150 °C; time, 3 h.

The influence of the structure of glycol on the reaction was also investigated. 1,2-Propanediol and 1,3-propanediol were used for the transesterification with urea (Scheme 3). The



Scheme 3 Formation of cyclic carbonates via reaction (2) of urea and different glycols.

results are presented in Table 3. 1,2-Propanediol gives 77% conversion with 91% selectivity towards propylene carbonate **1b**. A very small quantity of a by-product of 1-methyl-1-hydroxyethyl carbamate **2b** was also formed. On the basis of

Table 3 Influence of the structure of glycols for reaction (2)

Entry	Glycol	Urea conversion (%)	Selectivity (%)	
			1	2
1	Ethylene glycol	97	98	1.3
2	1,2-Propanediol	77	91	9.0
3	1,3-Propanediol	59	72	27

Urea, 200 mmol; glycol, 270 mmol; ZnO(1), 1.2 g; pressure, 3 kPa; temperature, 150 °C; time, 3 h.

Scheme 2, this compound should be the intermediate for the production of **1b**. The conversion is lower than that obtained with EG. This may be attributed to the steric hindrance caused

by the bulky methyl group present in 1,2-propanediol as compared with EG. The reaction of 1,3-propanediol and urea produces 1,3-dioxan-2-one **1c** and 3-hydroxypropyl carbamate **2c**. The urea conversion and the cyclic carbonate selectivity decrease further by changing the glycol from EG to 1,3-propanediol. Probably, the 6-membered ring formation from this substrate should be more difficult than the other two glycols.

The transesterification of EC and methanol to form DMC and EG, reaction (1) of Scheme 1, was also investigated. After the reaction of EG and urea was carried out with ZnO(1), the reaction mixture was further subjected to the reaction with methanol at 150 °C for 4 h. EC was converted to DMC and EG with a conversion of 60%. The molar ratio of DMC/EG formed was 0.92, which was slightly lower than the expected value of unity from reaction 1, probably due to the decomposition of EC with water to EG and carbon dioxide and/or the decomposition of DMC with water to methanol and carbon dioxide.^{4e,6} As shown previously,^{4g} the reaction of EC and methanol to form DMC and EG is a reversible reaction and higher EC conversions can be obtained with higher initial ratios of methanol/EC. Hence, more DMC can be produced using an increased amount of methanol.

Conclusion

In conclusion, DMC can be synthesized with very high atom efficiency from urea as a starting material by using a ZnO catalyst. In the first step (reaction 2 of Scheme 1), the urea reacts with EG to form EC. This reaction needs to be conducted under reduced pressure to obtain high selectivity for EC. The catalyst is very stable and recyclable without any loss of the activity and selectivity performance. Besides EG, other glycols such as 1,2- and 1,3-propanediols can also be transformed to the corresponding cyclic carbonates but with smaller selectivities. In the second step (reaction 1), EC is transesterified with methanol to give DMC and EG in the presence of the same catalyst at high yield and selectivity. Thus, urea based two-step DMC synthesis will be one of the possible alternatives in the quest for an environmentally benign route to DMC synthesis.

Experimental

Catalysts

Two types of ZnO (ZnO(1), ZnO(2)), MgO, CeO₂, La₂O₃, CaO, ZrO₂, zinc acetate and hydroxy zinc carbonate (hydrozincite) were used. ZnO(2), CeO₂ and ZrO₂ were prepared by decomposition of hydroxy zinc carbonate at 350 °C for 4 h, cerium carbonate octahydrate at 500 °C for 3 h, and zirconium oxynitrate at 500 °C for 3 h, respectively. The other catalysts were commercially available reagents. BET surface areas of those catalysts are given in Table 1.

Reaction (2) of urea and ethylene glycol (EG)

The reactions were performed in a 100 cm³ glass reactor with a mechanical agitator attached and water-cooled condenser with a water aspirator attached above the condenser for creating suitable reduced pressure for removal of ammonia. After urea (200 mmol) and EG (270 mmol) along with 1.2 g of the catalyst were charged into the reactor, the reactor was agitated under a reduced pressure of about 3 kPa. Then the reactor was heated to 150 °C and kept at this temperature for 3 h. After the reaction, the reactor was cooled to room temperature. The reaction mixture was diluted with ethanol to 100 cm³ and then analyzed on a gas chromatograph equipped with a flame ionization

detector. The quantities of EG consumed and products formed were determined from the results obtained from authentic standards. The structures of the compounds were confirmed by mass spectrometry. A few runs were conducted in a 100 cm³ autoclave under auto-generated pressure.

Reaction of (1) of ethylene carbonate (EC) and methanol

After the reaction (2) of urea and EG, the reaction mixture including the catalyst was transferred to a 100 cm³ autoclave and 50 cm³ of methanol was added. Then, the reactor was purged with carbon dioxide, heated to 150 °C and kept at the same temperature for 4 h. After the reaction, the reaction mixture was analyzed using similar procedures as described above.

Reaction of EG, EC and 2-oxazolidone

EG (270 mmol), EC (25 mmol) and 2-oxazolidone (25 mmol) along with 1.2 g of CaO were charged into a 100 cm³ autoclave. Then, the reactor was heated to 170 °C and kept at the same temperature for 3 h. After the reaction, the reaction mixture was analyzed using similar procedures as described above.

Acknowledgements

The authors wish to express their thanks for financial support obtained from Japan Science and Technology (JST) under CREST program.

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