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Synthesis of Dimethyl Carbonate from Urea and Methanol over ZnO

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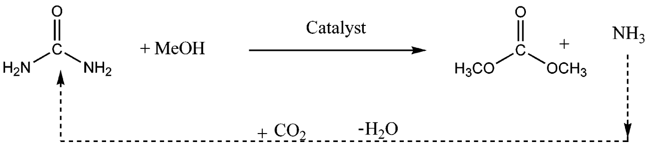
The synthesis of dimethyl carbonate (DMC) from urea and methanol was investigated, to explore the catalysts and reaction conditions. Among the catalysts, ZnO showed the highest catalytic activity toward DMC synthesis. Based on the experimental investigation, the reaction conditions over ZnO for a batch process were optimized, and the highest DMC yield attained (based on urea) was ∼30%, because of the presence of side reactions. In addition, the reusability test indicated that ZnO had high stability.

1. Introduction

Recently, much attention has been given to dimethyl carbonate (DMC).[1] As an environmentally benign building block,[2−4] DMC shows versatile chemical properties. It is mainly used in methylation and carbonylation reactions as a safe substitute for dimethyl sulfate, methyl halides, and phosgene. It is also believed to be an ideal additive for gasoline, because of its higher oxygen content (53%) and good blending octane ($(R + M)/2 = 105$).[5] In addition, DMC can be used as an electrolytic solution in a secondary lithium battery.[6]

DMC was conventionally prepared via the phosgenation of methanol. Because of the use of extra toxic phosgene, this method had been limited in industry. Currently, DMC is synthesized by nonphosgene routes via the oxidative carbonylation of methanol (the EniChem process and the Ube process) and the transesterification method.[7] The major shortcomings of the former method involve (i) poisonous or/and corrosive gases (such as carbon monoxide, hydrogen chloride, and methyl nitrate) and (ii) bearing the explosion hazards of methanol and oxygen.[8−11] The drawbacks of the latter are the limit in thermodynamic equilibrium conversion, which leads to low production of DMC, along with the production of ethylene glycol.[12,13] Hence, the synthesis of DMC by urea methanolysis is an attractive alternative. In this case, DMC and ammonia are produced by reacting urea with methanol (see Scheme 1), and ammonia that is liberated during the reaction can be, in principle, recycled for urea synthesis; thus, it is possible to synthesize DMC from carbon dioxide (CO_2) by combining the reactions of urea synthesis and urea methanolysis. However, relative research in the open literature has been few. Cho et al.[14] revealed that simple homogeneous bases, such as K_2CO_3 and CH_3ONa, could be used as catalysts for this process, but the DMC yield based on urea was <5%. Saleh, Ryu, and co-workers[15−17] disclosed that organotin derivatives, such as $Bu_2Sn(OMe)_2$ and $SnOBu_2$, were active catalysts with high selectivity, but the homogeneous nature of the organotin posed separation and deactivation problems.

Scheme 1. DMC Synthesis from Urea and Methanol



Recently, zinc, lead, magnesium, and calcium, and their compounds, have been used as catalysts in the synthesis of alkylene carbonate from urea and corresponding glycol,[18,19] and some of them also showed activity in the urea alcoholysis reaction.[20,21] In this work, the synthesis of DMC from urea and methanol over those catalysts was investigated, and the reaction conditions were explored using ZnO as the model heterogeneous catalyst for the synthesis of DMC with higher yield than those reported.

2. Experimental Section

2.1. Preparation of Catalysts. CaO, MgO, and ZrO_2 were prepared via the thermal decomposition of calcium carbonate at 800 °C for 2 h, magnesium hydroxide at 600 °C for 3 h, and zirconium hydroxide at 350 °C for 3 h in N_2, respectively. Zirconium hydroxide was made via the precipitation of zirconium nitrate solution and ammonia solution at room temperature at a constant pH of 10, and then drying at 120 °C for 3 h, after washing with deioned water. Other chemicals were used as purchased.

2.2. Experimental Setup and Procedure. The reaction was conducted in an autoclave reactor, which was composed of a liquid pump, a 250-mL stainless-steel autoclave with a reflux column, and a magnetic stirrer (revolving at a rate of 600 ± 50 rpm). After 48 g of methanol and the desired amount of catalyst were charged into the autoclave and heated to the desired reaction temperature, the feed (80 g of methanol and 12 g urea (dissolved)) was pumped into the autoclave within 10 min (128 g methanol and 12 g urea in total, i.e., $n_{\mathrm{urea}}:n_{\mathrm{methanol}} = 1:20$) for the reaction. During the performance, ammonia was removed three times through a valve above the flux column. After the reaction, the autoclave was cooled to room temperature, and the product mixture in the autoclave was clarified and analyzed by gas chromatography.

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Scheme 2. Intermediates Formation during DMC Synthesis

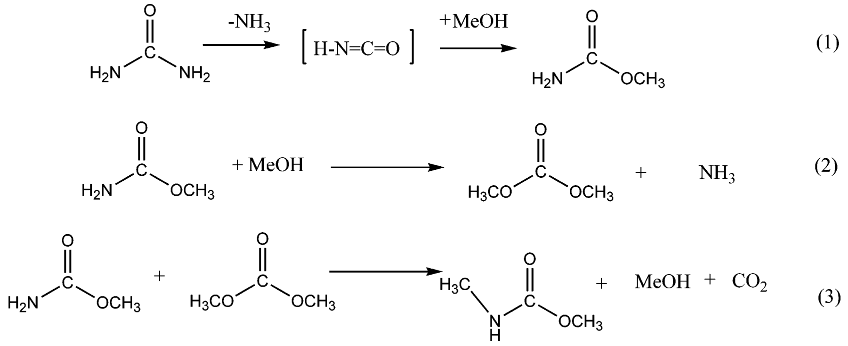

Table 1. Effect of the Catalyst on Methyl Carbamate (MC) and Dimethyl Carbonate (DMC)[a]

run	catalyst	urea conversion (%)	Yield (%)[b] MC	Yield (%)[b] DMC
1		100	94	0.8
2	ZnO(a)	100	48	29
3	$Zn(NO_3)_2{\cdot}6H_2O$	100	64	18
4	$ZnCl_2$	100	79	8
5	$Zn(CH_3COO)_2{\cdot}2H_2O$	100	79	10
6	$Zn(OH)_2$	100	88	1.2
7	$ZnCO_3$	100	84	1.4
8	PbO	100	58	22
9	$Pb(CH_3COO)_2{\cdot}3H_2O$	100	64	8
10	$Pb(NO_3)_2$	100	50	24
11	CaO	100	73	8
12	MgO	100	89	1
13	ZrO_2	100	87	1
14[c]	$SnOBu_2$	100	73	12

[a] Reaction conditions: urea, 12 g; methanol, 128 g; catalyst, 1 g; temperature, 170 °C; time, 8 h. [b] The MC and DMC yields are based on urea. [c] Three grams of catalyst were used in this run.

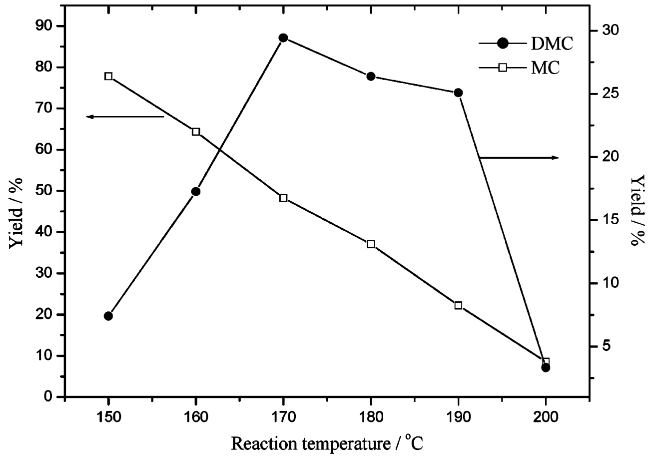

Figure 1. Effect of reaction temperature on dimethyl carbonate (DMC) and methyl carbamate (MC) yield.

3. Results and Discussion

3.1. Screening for Catalysts. As shown in Table 1, the noncatalytic performance (run 1) yielded 94% methyl carbamate (MC) and 0.8% DMC (based on urea). The MC was an intermediate for DMC synthesis (see Scheme 2, eq 1). This indicated that MC was easily prepared, even in the absence of a catalyst, but it hardly converted to DMC. The synthesis of MC is known to involve active isocyanic acid (HNCO), which could be obtained easily by urea thermal decomposition, especially when the temperature was higher than the melting point of urea (134 °C). Isocyanic acid was such an active intermediate that it could react with active polar compounds immediately.[22] Here, methanol acted as the polar compound and reacted with isocyanic acid quickly and completely, so a high yield of MC could be achieved in the absence of catalyst. However, converting MC to DMC was hardly achieved via the isocyanic acid intermediate (see Scheme 2, eq 2). Therefore, this step is a speed-limited reaction for the synthesis of DMC from urea and methanol, and catalysts must be introduced.

Among the catalysts screened in Table 1, ZnO showed the highest activity, producing 29% DMC and 48% MC after 8 h of reaction at 170 °C (run 2). Other zinc salts such as $Zn(NO_3)_2{\cdot}6H_2O$, $ZnCl_2$, and $Zn(CH_3COO)_2{\cdot}2H_2O$ were also active, yielding 18%, 8%, and 10% DMC, respectively (runs 3−5). However, not all zinc compounds were active toward DMC synthesis; for instance, $Zn(OH)_2$ and $ZnCO_3$ were almost inert (runs 6 and 7). Lead-based catalysts also exhibited high activity, especially for $Pb(NO_3)_2$ and PbO (runs 8 and 10). CaO, MgO, and ZrO_2, which are well-known solid basic catalysts, were also used here, but only CaO exhibited low activity for DMC synthesis (run 11). MgO and ZrO_2 were not active toward the reaction. $SnOBu_2$, which was used as the typical catalyst in the literature,[17] had low activity for DMC synthesis, yielding 12% DMC and 73% MC with 3 g of catalyst at 170 °C for 8 h of reaction (run 14).

Obviously, ZnO was superior to other catalysts for the synthesis of DMC from urea and methanol, and the activity of ZnO was considered to be related to its acidic and basic properties, as revealed in the research of Bhanage et al.[18] Because ZnO was nontoxic, in comparison to lead or tin compounds, and unlike other active zinc salts (it was insoluble in methanol and could be easily separated from the product mixture by filtration), ZnO was considered to be the model heterogeneous catalyst for the synthesis of DMC from urea and methanol.

3.2. Effect of Reaction Conditions. Figure 1 indicates that the DMC yield was only 7% after 8 h of reaction at 150 °C. As the reaction temperature increased, the DMC yield increased sharply and reached the maximal value at 170 °C; i.e., the DMC yield was ~30%, based on urea, then decreased slightly from 170 °C to 190 °C, but then significantly at 200 °C. This demonstrated that the DMC synthesis was sensitive to the reaction temperature.

The effect of the reaction time on the DMC yield is shown in Figure 2. The reaction yielded 12% DMC and 68% MC after 2 h. As the reaction proceeded, the DMC yield reached a maximum of 30% at 11 h and then decreased. This suggested that the DMC participated in side reactions.

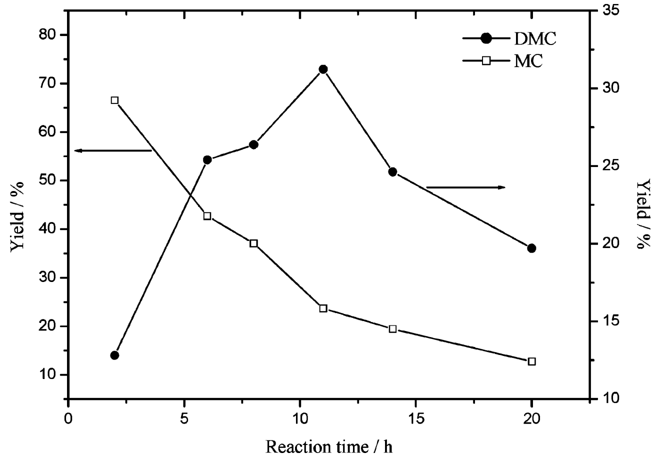

Figure 2. Effect of reaction time on DMC and MC yield.

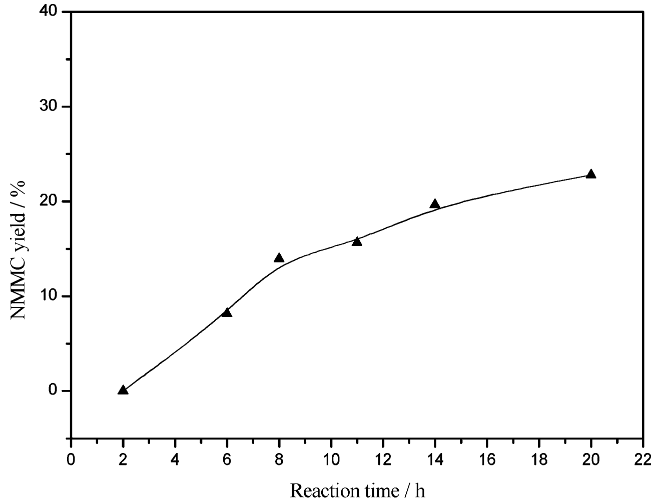

Figure 3. Effect of reaction time on N-methyl methyl carbamate (NMMC) yield.

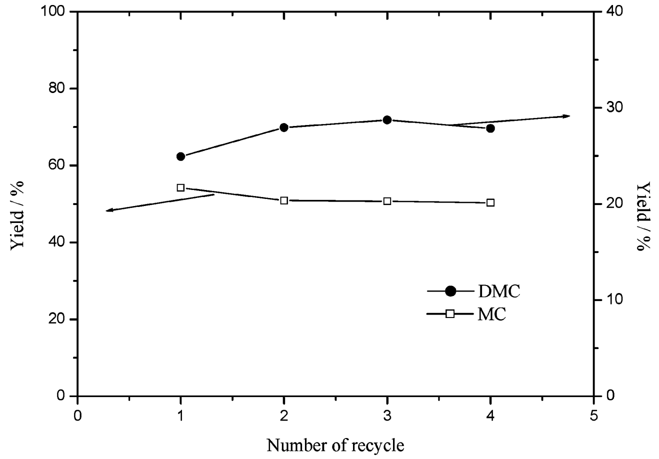

Figure 4. Recycle use of ZnO for the reaction of urea and methanol.

According to gas chromatography−mass spectroscopy (GC−MS) analysis of the product mixture, N-methyl methyl carbamate (NMMC) was detected as a major byproduct, which might be produced by the reaction of MC with DMC (see Scheme 2, eq 3), because of the fact that DMC was a N-methylating agent, such as that observed for aniline.[3] This was confirmed by the results that NMMC yield increased with the reaction time (see Figure 3). The product of NMMC consumed both MC and DMC, so it was impossible to obtain a very high yield of DMC in a batch process. Even so, for the viewpoint of application, the suitable reaction temperature for DMC synthesis should be between the range of 170−190 °C, and a reaction time of 6−12 h was believed to be feasible for DMC synthesis for a batch process.

3.3. Reusability of ZnO Catalyst. To investigate the reusability of ZnO, the performance was first performed at 170 °C for 8 h with 2 g of ZnO. After each reaction, ZnO was separated by filtration and washed with 20 mL of methanol three times, and then used for the next run. As shown in Figure 4, the ZnO catalyst could be used four times without deactivation. This indicated that ZnO had high stability for the performance.

4. Conclusions

Among the catalysts for the synthesis of dimethyl carbonate (DMC) from urea and methanol, ZnO showed the highest performance. The optimal reaction conditions for batch processing over ZnO were as follows: reaction time of 6−12 h, and reaction temperature of 170−190 °C. The highest DMC yield was ~30% in batch processing, because of the presence of side reactions. Furthermore, ZnO was shown to have high stability, in regard to the reusability test.

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