

Synthesis of dimethyl carbonate from urea and methanol over solid base catalysts

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Abstract

The synthesis of dimethyl carbonate (DMC) from urea and methanol was found to take place over solid base catalysts. In the first step, the intermediate MC was produced with high yield by urea monomethanolysis and then MC further converted to DMC by reacting with methanol, which was the key step. Solid bases were found to be effective catalysts for the second step and their basic properties were measured by CO₂-TPD. The function of basic catalysts could be attributed to the activation of CH₃OH via the abstraction of H^{δ+} by base sites.

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1. Introduction

Dimethyl carbonate (DMC), as an environmentally benign building block, becomes more important in the chemical industry [1–4]. It is mainly used as methylation reagent for safely substituting extremely toxic dimethyl sulfate or methyl halides and as carbonylation reagent for replacing phosgene. In addition, it is an ideal additive for gasoline because of its high oxygen content (53%) and good blending octane ((R + M)/2 = 105) [5].

Currently, DMC is mainly prepared by the oxy-carbonylation of methanol (EniChem process and UBE process) and transesterification method [6–9]. However, both routes suffer from some drawbacks such as, using poisonous and/or corrosive gases of chlorine, nitrogen oxides and carbon monoxide and bearing a possibility of explosions. Recently, urea methanolysis method has been proposed to prepare DMC (see Scheme 1). Saleh et al. [10] patented that organotin catalysts had high activity for urea methanolysis, but the existence of several side reactions made DMC selectivity on poor level. Then, in order to avoid side reactions,

Ryu et al. [11] patented a novel process by using organotin catalysts and high boiling electron donor atom solvent such as triethylene glycol dimethyl ether, as co-catalyst, and partly increased DMC selectivity. However, the organotin using as homogeneous catalyst was very expensive, difficult to handle, and suffered from the problem of product separation. Besides, Cho et al. [12] revealed that simple homogeneous bases, like K₂CO₃, CH₃ONa and so on, could be used as another kind of catalyst for this route, but the DMC yield was under 5% (based on urea), which was far from satisfactory.

In this work, heterogeneous solid bases catalysts were first used to prepare DMC by urea methanolysis method. The relationship between the catalytic activity and their basic properties was characterized, and the function of solid base catalysts was discussed.

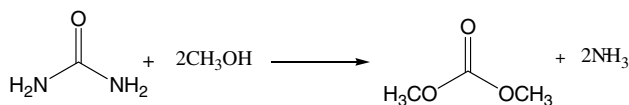
2. Experimental

2.1. Catalyst

CaO, MgO, ZrO₂ were prepared by thermal decomposition of calcium carbonate at 800 °C for 2 h, magnesium hydroxide at 600 °C for 3 h, zirconium hydroxide at 350 °C for 3 h in N₂, respectively. Zirconium hydroxide

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Scheme 1.

was made by precipitation of zirconium nitrate solution and ammonia solution at room temperature at a constant pH of 10, and then dried at 120 °C for 3 h after washed with deionized water. La_2O_3 was purchased and then pre-treated at 700 °C for 2 h in nitrogen atmosphere before used. Other chemicals and catalysts were used without further purification.

The surface area of catalysts was determined with the BET method using N_2 through Micromeritics ASAP-2000. Basic properties of the catalysts were measured by temperature programmed desorption of adsorbed CO_2 (CO_2 -TPD). The measurement was performed with 0.10 g sample at a heat rate of 10 °C/min under N_2 flow (50 mL/min) and CO_2 desorbed was detected by a Balzers Omnistar™ mass spectrometer.

2.2. Catalytic reaction

The catalytic reaction was carried out in an autoclave reactor with strong magnetic stirring and a reflux column by which ammonia, liberated from the reaction, could be partly removed. The reaction procedure as follow: 1.5 mol methanol and 1.0 g catalyst were charged into the autoclave, and then heated to desired temperature. After that a solution contained 2.5 mol methanol and 0.20 mol urea (methyl carbamate) was pumped into the autoclave within 10 min, and then the reaction was carried out for desired time. The stirring speed was 600 ± 50 rpm, and the temperature was controlled to a range of ± 2 °C. During the performance, ammonia was removed three times through a valve above reflux column. After shut down the reaction, the autoclave was cooled down to room temperature, and the product solution in autoclave was clarified and analyzed with a gas chromatograph (GC) equipped with TCD.

3. Results and discussion

3.1. Catalytic performance

It was found that methyl carbamate (MC) was prepared easily from methanol and urea even in the absence of catalyst. Fig. 1 illustrates the effects of reaction temperature and reaction time on the methyl carbamate yield of non-catalytic reaction. It could be seen that the MC yield reached 99% at 160 °C for 2 h. In addition, only a trace amount of DMC (lower than 1% based on urea) was found in products even at 190 °C for 10 h.

Table 1 gives some typical results of urea methanolysis over basic catalysts. CaO, a well known strong solid base

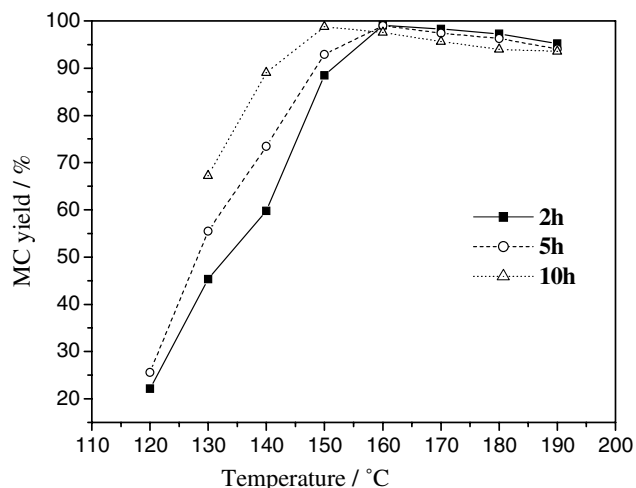


Fig. 1. Effect of reaction time and reaction temperature on MC yield without catalyst. (Reaction conditions: urea, 0.2 mol; methanol, 4 mol.)

[15,16], exhibited the highest activity towards DMC, giving 15.83% DMC and 55.70% MC in the selectivity after 11 h of reaction at 180 °C. At the same reaction conditions, La_2O_3 showed low activity. Compared with CaO and La_2O_3 , MgO and ZrO_2 were inert at 180 °C, but exhibited a little activity at 200 °C. The activity of solid catalysts followed this order: $\text{CaO} > \text{La}_2\text{O}_3 > \text{MgO} > \text{ZrO}_2$.

Those results indicated that the synthesis of DMC from urea and methanol could be divided into two steps (see Scheme 2): first, methyl carbamate (MC) was synthesized from urea and methanol and then MC further reacted with methanol to produce DMC, which was a key step for the synthesis of DMC from urea and methanol. Those results were consistent with the work of Ball et al. [13] and of Beinfest et al. [14] in which carbamates were synthesized from urea and alcohols.

The results in Table 2 indicated that using MC as the feed, the DMC yield was almost equal to that of using urea (in Table 1). Thus, it strongly suggested that solid catalysts here catalyzed the second step.

3.2. Catalyst characterization

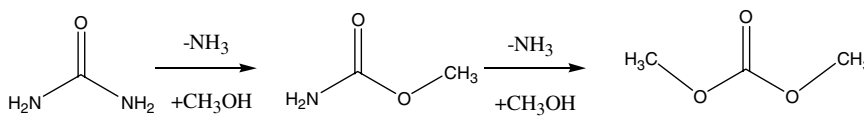
Fig. 2 depicts the TPD profiles of CO_2 adsorbed on ZrO_2 , MgO, La_2O_3 , and CaO. A peak around 110 °C was observed on ZrO_2 . Three broad desorption peaks were observed on MgO at 150, 250 and 330 °C, respectively. Only one peak was detected at 420 °C on La_2O_3 . For CaO, a sharp peak at 630 °C with a shoulder at 520 °C was observed. Thus, strong basic sites existed on CaO surface and weak basic sites on ZrO_2 . Based on CO_2 -TPD, the basic strength of solid bases followed this order: $\text{CaO} > \text{La}_2\text{O}_3 > \text{MgO} > \text{ZrO}_2$, which was in accordance with their activity order for the synthesis of DMC.

Table 3 shows the CO_2 uptake of solid basic catalysts. Obviously, the amount of basic sites per unit weight of catalysts ranked this order: $\text{CaO} > \text{MgO} > \text{La}_2\text{O}_3 > \text{ZrO}_2$, i.e.,

Table 1
Synthesis of DMC from urea and methanol over solid bases

Run	Catalyst	Reaction temperature (°C)	Urea conversion (%)	Selectivity (%)		Yield (mmol/g-cat./h)	
				MC	DMC	MC	DMC
1	CaO	180	100	55.70	15.83	10.13	2.88
2	CaO	200	100	23.64	10.95	4.30	1.99
3	La ₂ O ₃	180	100	78.37	6.12	14.25	1.30
4	La ₂ O ₃	200	100	34.00	10.98	6.18	2.80
5	MgO	180	100	85.15	2.43	15.48	0.54
6	MgO	200	100	40.32	16.89	7.33	3.07
7	ZrO ₂	180	100	84.42	2.40	15.35	0.44
8	ZrO ₂	200	100	49.42	9.77	8.98	1.78

Reaction conditions: catalyst, 1 g; urea, 0.2 mol; methanol, 4 mol; 11 h.



Scheme 2.

Table 2
Synthesis of DMC from MC and methanol over solid bases

Run	Catalyst	Reaction temperature (°C)	MC conversion (%)	DMC selectivity (%)	DMC yield (%)	DMC yield (mmol/g-cat./h)
1	CaO	180	39.40	37.81	14.90	2.98
2	CaO	200	70.03	14.73	10.31	2.06
3	La ₂ O ₃	180	13.90	48.24	6.70	1.34
4	La ₂ O ₃	200	68.03	16.86	14.34	2.87
5	MgO	180	14.20	19.48	2.77	0.55
6	MgO	200	44.27	39.48	17.48	3.50
7	ZrO ₂	180	10.75	26.33	2.83	0.57
8	ZrO ₂	200	27.87	28.39	7.91	1.58

Reaction conditions: catalyst, 1 g; MC, 0.2 mol; methanol, 4 mol; 10 h.

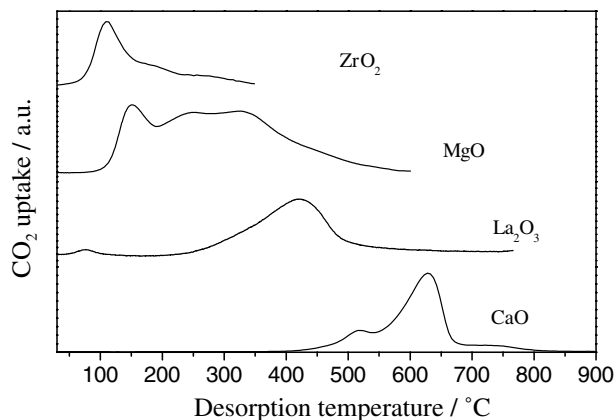


Fig. 2. CO₂-TPD profiles of solid catalysts.

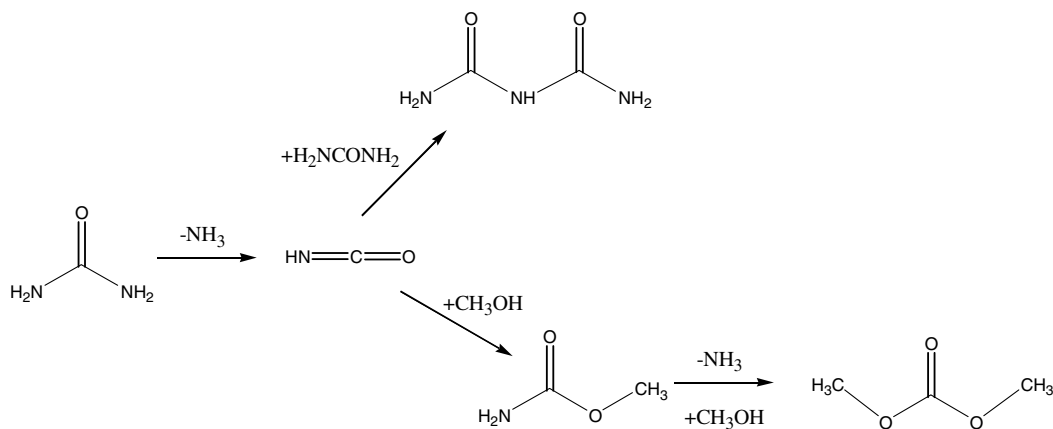
3.3. Reaction mechanism

The synthesis of DMC from urea and methanol over solid base catalysts could be divided into two steps (see Scheme 2), but the first step was easier far more than the second step. The first step involved the formation of isocyanic acid intermediate (see Scheme 3), in which urea decomposed into isocyanic acid very easily at high temperature, especially higher than its melting point (134 °C). Isocyanic acid was such an active intermediate compound that it hardly existed in nature. If it reacted with a urea molecular, the biuret was obtained [17], and if it reacted

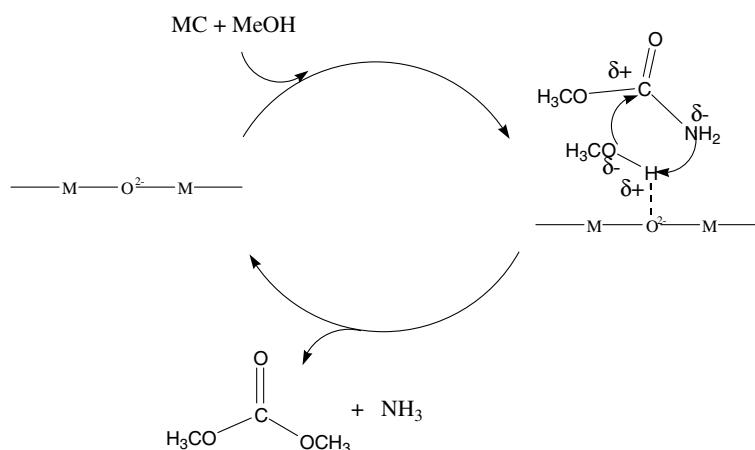
Table 3
BET surface area and CO₂ uptake of metal oxides

Catalyst	BET surface area (m ² /g)	CO ₂ uptake (mmol/g)
CaO	9.0	0.22
La ₂ O ₃	4.7	1.22E – 2
MgO	54.6	3.88E – 2
ZrO ₂	152	8.12E – 3

the CO₂ uptake amounts were 0.22, 1.2E – 2, 3.9E – 2, 8.1E – 3 mmol/g for CaO, La₂O₃, MgO, ZrO₂, respectively.



Scheme 3.



Scheme 4. Possible reaction mechanism over basic catalyst.

with a methanol molecular, the methyl carbamate was obtained. Here, due to in methanol solution the latter reaction was the major one. Thus, a high yield of MC could be achieved in the absence of catalyst.

Obviously, converting MC into DMC was hardly achieved via the isocyanic acid intermediate and the substitution mechanism catalyzed by base was proposed in Scheme 4. Generally, in a substitution reaction, strong nucleophilic group was prone to substituting a weak one. Due to NH_2^- was a stronger nucleophile than CH_3O^- , this reaction was thermodynamically unfavorable, and the liberation of ammonia was the driving force for this step [5].

As for solid bases, basicity (basic sites amount per unit weight of catalysts) and basic strength are two important factors for their catalytic properties. As shown in Table 1, La_2O_3 had higher activity than that of MgO , and it had less basic sites but higher basic strength based on CO_2 -TPD. It implied that basic strength was more important than basicity towards DMC synthesis. In the present reaction, the main function of solid base catalysts was to activate CH_3OH through the abstraction of $\text{H}^{\delta+}$ by base sites, and consequently the $\text{CH}_3\text{O}^{\delta-}$, which would react with MC to give DMC, was generated. Therefore, it was

possible that the higher base strength lead to the more negative charge of $\text{CH}_3\text{O}^{\delta-}$, and consequently the lower was the free energy of $\text{CH}_3\text{O}^{\delta-}$ with MC. Thus, the base sites with strong strength had high activity because they had a high ability to activate methanol [18].

4. Conclusion

The synthesis of DMC from urea and methanol was a two-step reaction. In the first step, the intermediate MC was produced with high yield by urea monomethanolysis and then MC further converted to DMC by reacting with methanol, which was the key step. Solid bases were found to be effective catalysts for the second step. The function of basic catalysts could be attributed to the activation of CH_3OH via the abstraction of $\text{H}^{\delta+}$ by base sites.

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