

Synthesis of dimethyl carbonate from urea and methanol over metal oxides

Mouhua Wang, Ning Zhao, Wei Wei, Yuhan Sun*

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry
Chinese Academy of Sciences, Taiyuan, 030001 PR China

A series of metal oxide were used as solid catalysts for synthesis of dimethyl carbonate from urea and methanol. Among them, ZnO was shown to be the highest active catalyst. It was also found that the activity of other oxides such as CaO, MgO, ZrO₂ was closely related to their basic strength.

1. INTRODUCTION

In recent years, much attention has been paid to dimethyl carbonate (DMC). As an environmentally benign building block^{1,2}, DMC shows versatile chemical property and is mainly used for methylation and methoxycarbonylation as a safe substitute for dimethyl sulfate or methyl halides, and it is also used as a solvent to replace halogenated solvents such as chlorobenzene^{3,4}. In addition, DMC is believed to be a good additive of gasoline in the future due to its higher oxygen content (53%) and good blending octane ((R+M)/2=105).

Dimethyl carbonate was usually produced from methanol and phosgene in a concentrated sodium hydroxide solution⁵. Because of the use of phosgene, DMC synthesis has been limited in industry. Thus, a non-phosgene process for preparing DMC by oxidative carbonylation of methanol in liquid phase or gas phase was put on stream in the EniChem-Ravenna factory using CuCl as the catalysts⁶⁻⁸. However, the shortcomings of this process were low production rate and high cost of the separation. Another non-phosgene process for the synthesis of DMC was the transesterification from methanol and propylene(ethylene) carbonate which was prepared from CO₂ and propylene(ethylene) oxide via cyclic addition. The reaction of cyclic carbonate with methanol was limited by equilibrium. Moreover, the reactant involved in the process (such as epoxides) was explosive and expensive.

Recently, urea methanolysis method has been used to prepare of dimethyl carbonate. Firstly, urea and methanol reacted to produce carbamate and ammonia, and then carbamate and methanol were further converted into DMC and ammonia. Ammonia could be recycled to produce urea with CO₂ (see Scheme 1). Obviously, this was an economically benign process.

*To whom all corresponding should be addressed, E-mail: yhsun@sxicc.ac.cn or weiwei@sxicc.ac.cn; Fax: +86-351-4041153; Tel: +86-351-4053801

However, the related study except several U.S. patents^{10,11,12} for this process has not been reported till now. Homogenous catalysts such as some complexes of organotin were used with high boiling electron donor compound as the solvent (such as bidentate ligands). However, the preparation of the catalyst and the solvent was very difficult and costly. In addition, the separation of the products and the catalyst was also complicated. Thus, homogeneous catalysts were not satisfactory for industrial use. Considering the reaction thermodynamic and the reaction mechanism over homogenous catalysts, solid catalysts (such as CaO and MgO and ZrO₂) were developed for synthesis of dimethyl carbonate from urea and methanol here.

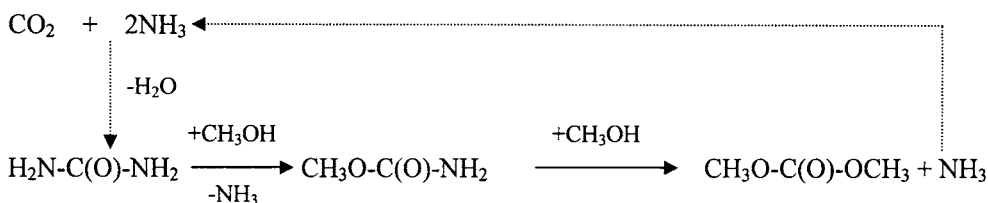


Fig. 1. Synthesis of DMC by urea methanolysis method

2. EXPERIMENTAL

The catalysts, such as ZnO, CaO, MgO, ZrO₂, were prepared by thermal decomposition of zinc carbonate at 500°C for 4 hours, calcium carbonate at 800°C for 2 hours, magnesium hydroxide at 600°C for 3 hours and zirconium hydroxide at 350°C in nitrogen atmosphere, respectively. All experiments were carried out in a stainless steel autoclave with an inner volume of 250 ml provided with a magnetic stirrer and an electric heater, a flux column connected with the autoclave which refluxed the methanol and removed ammonia from the reaction system. The products were analyzed by GC. CO₂-TPD measurement was performed at a heat rate of 10K min⁻¹ under nitrogen flow (50 mL min⁻¹), and CO₂ desorbed was detected by a BALZA Q-Mass spectrometer.

3. RESULTS AND DISCUSSION

3.1. Synthesis of MC from urea and methanol

Figure 2 shows the effect of temperature and reaction time on the yield of methyl carbamate (MC). It was found that methyl carbamate was easily prepared from methanol and urea even if no catalyst was added. Under the reaction condition of 160°C and 10 atm, the methyl carbamate yield was over 98% in 2 hours. Obviously, the reaction rate increased with temperature. The MC yields hardly changed at higher temperature than 160°C even though the reaction time was prolonged from 2 hours to 10 hours. Trace amount of DMC in products (lower than 1%, see table 1, entry 11) was also found when the reaction temperature was higher than 160°C. It was concluded that the first step in figure 1 performed quickly and completely even without catalyst while the second step was slow which might be due to the limitation of thermodynamic equilibrium. As a result, the main purpose in the present work

was the effect of metal oxide on the synthesis of DMC from MC and methanol.

3.2. Synthesis of DMC from MC and methanol

Table 1 lists the performance of solid catalysts for the synthesis of DMC from MC (or urea) and methanol. DMC could be effectively synthesized over the metal oxides. The yield of DMC was 40% or so for ZnO, which was much better than for the homogenous catalysts reported elsewhere^{10, 11, 12} (entry 10). The activity of CaO for DMC synthesis was lower than that of ZnO but higher than MgO and ZrO₂. The DMC yield for CaO was almost the same whether urea or MC as the feed (entry 3 and 4), suggesting that the rate determine step of synthesis of DMC from urea was the second step. However, urea as the feed led to the different DMC yield from MC as the feed with ZnO as the catalyst (entry 8 and 9), implying that the conversion of urea and MC into DMC followed different reaction mechanisms over ZnO. It is worth to note that N-methyl methyl carbamate (NMMC) was detected by GC-MS at high temperature, which could be produced by the further reaction of DMC with MC because DMC was a good methylating reagent². So, the side reaction of producing NMMC as well as decomposition of DMC led the phenomenon of high MC conversion but low DMC yield at high temperature, especially above 180°C.

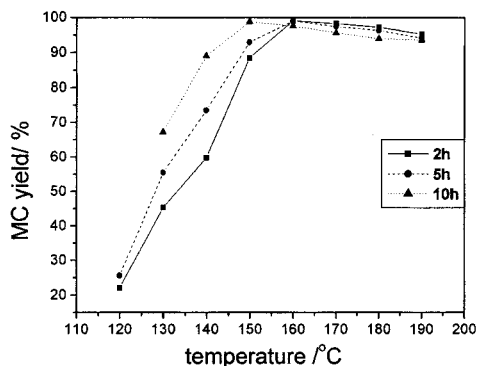


Fig. 2. Results of reactions without catalyst (0.2 mol urea and 4 mol methanol, MC yield based on urea)

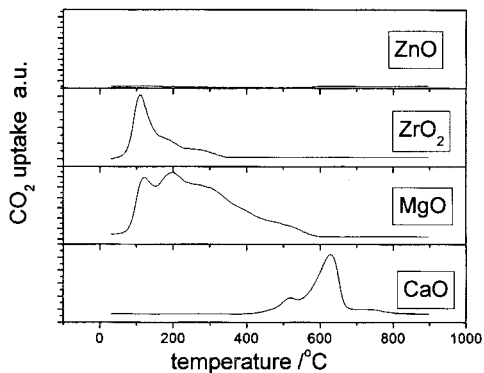


Fig. 3. CO₂-TPD profiles on oxide catalysts

Figure 3 depicts the TPD profiles of CO₂ adsorbed on ZnO, ZrO₂, MgO and CaO. Temperature programmed desorption (TPD) of CO₂ was usually used to measure the number and strength of basic sites, and high desorption temperature indicated high basic strength¹³. No CO₂ adsorption peak was observed on ZnO. For the others, the order of CO₂ uptake temperature was as follows: CaO > MgO > ZrO₂. This strongly suggested that the performance of catalysts was not closely related to their basicity, and the reaction mechanisms over those metal oxides might be different. ZnO had the highest activity although the activity of CaO, MgO and ZrO₂ was in accordance with their basic strength, indicating that the reaction over ZnO took place via a different route.

4. CONCLUSION

The synthesis of dimethyl carbonate from urea and methanol via two consecutive steps was elucidated through blank reaction. The second step, through which DMC was produced by reacting intermediate MC with methanol, could be carried out with metal oxides as the catalysts. Among those oxides, ZnO showed the highest activity for DMC synthesis. CO₂-TPD revealed that the activity of catalysts was not closely related to their basicity, and the reaction mechanisms over different metal oxides might be different.

Table 1. Results over metal oxides

No.	Catalyst	Weight, g	Temp. °C	Reaction time, h	MC conv.%	DMC yield%
1	CaO	1	160	10	22	8
2	CaO	1	180	10	39	15
3	CaO	1	200	10	70	10
4	CaO*	1	200	11	34	11
5	MgO	1	182	10	14	8
6	MgO	1	200	10	44	17
7	ZrO ₂	1.5	180	10	16	5
8	ZnO	1	180	10	9	6
9	ZnO*	1	180	10	42	37
10	SnO ₂ *	3	180	8	60	16
11	Void *	-	180	10	92	0.8

Reaction conditions: 0.2 mol MC, 4 mol methanol.

*Reactants here are urea and methanol. Values in column MC conversion here mean MC yields; DMC yield is based on urea or MC.

REFERENCES

1. P. Tundo, and M. Selva, *Chemtech*, 1995,25(5), 31-35.
2. Yoshio Ono. *Applied Catalysis A: General*, 1997, 155, 133-166.
3. A. G. Shaikh, *Chem. Rev.* 1996, 96, 951-976.
4. E. Suzuki, M. Akiyama and Y. Ono., *J. Chem. Soc., Chem. Commun.*,1992, 136-137.
5. H. Murdock, *J. Phys. Chem.*, 1919,23,508-516.
6. U. Romono, R. Tesei, et al, *Ind. Eng. Chem. Prod. Res. &Dev.*,1980, 19(3), 396-403.
7. J. Haggin, *C&EN*, 1987,65(44), 27-30.
8. S. K. King, *J. Catal.*, 1996,161(2),530-538.
9. J. Haggin, *C&EN*, 1992, 70(18), 25-26;
10. R.Y. Saleh, et al, US patent No.5565603 (1996).
11. J. Y. Ryu, et al, US patent No. 5902894 (1999).
12. J. Y. Ryu, et al, US patent 6392078 (2002).
13. H. Hattori, *Chem. Rev.*, 1995, 95, 537-558.