

Synthesis of Dimethyl Carbonate from Methyl Carbamate and Methanol with Zinc Compounds as Catalysts

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Various zinc compounds were used as the catalysts for the synthesis of dimethyl carbonate (DMC) from methyl carbamate (MC) and methanol in a batch reactor. Among them, ZnCl₂ showed the highest catalytic activity and led to the DMC yield of 33.6% under the optimal conditions. In addition, a possible reaction mechanism was proposed based on Fourier transform infrared (FTIR) and X-ray diffraction (XRD) characterization results.

1. Introduction

Dimethyl carbonate (DMC) as an environmentally benign building block has attracted much attention in recent years.^{1–5} It can replace phosgene, dimethyl sulfate, chloromethane, and methyl chloroformate as carbonylation, methylation, esterification or, ester interchange reagent, and it can also be used as additive for gasoline, flavoring agent of foodstuff, electronic chemical, etc. Thus, the effective synthesis of DMC becomes more and more important. The current processes reported mainly include phosgenation of methanol, oxidative carbonylation of methanol, ester exchange, and esterification of carbon dioxide with methanol, which all suffer from the corresponding shortcomings such as being poisonous, being easily explosive, having a complex reaction course, and having extremely low conversion.

Recently, a new route of the DMC synthesis from urea and methanol has been developed for low-cost and facile separation of production.⁶ In this synthesis approach, the intermediate methyl carbamate (MC) is produced first and further converted to DMC by reaction with methanol. The first step of the reaction is fast and highly selective even without catalysts, because urea can decompose easily to ammonia and isocyanic acid. The latter, as an active intermediate, can further react with solvent methanol to produce MC. However, the second step of the reaction, MC to DMC, is more difficult than the first step.^{7–9} The ammonia accumulated in the first step will restrict the shift of the reaction equilibrium to DMC, since it is also the byproduct of the second step. Consequently, dividing this reaction into two isolated steps will be a more promising approach toward the synthesis of DMC.

The key to the two-step technics is to effectively promote the second reaction, which is the rate-control step for the reaction of urea methanolysis, with proper catalyst. A lot of catalysts such as bases, organic tin, metal oxide, and zinc compounds have been tested in a batch reactor toward the direct reaction of urea and methanol or its analogues.^{10–18} However, as to the isolated second reaction, only a few studies have been reported about the exploitation of catalyst up to now. In this regard, organic tin compound was considered as a favorable catalyst for this reaction in previous literature, but it was not promising

from the viewpoint of the environment because of its strong toxicity.¹⁹ Our group found that CaO was the best one among solid base catalysts tested since it activated methanol effectively with its strongest basicity, but the DMC yield on it was still far from satisfactory.⁷ In this work, the synthesis of DMC from MC and methanol was investigated over many zinc compound catalysts in a batch reactor. Furthermore, the reaction conditions were explored in detail with ZnCl₂ as the model catalyst for its excellent catalytic performance.

2. Experimental Section

2.1. Preparation of Catalyst. Zn(CH₃COO)₂ and Zn(NO₃)₂ were obtained by evacuating Zn(CH₃COO)₂·2H₂O at 110 °C for 20 h and Zn(NO₃)₂·6H₂O at 115 °C for 24 h, respectively. Other chemicals and catalysts were commercial analytic reagents without further purification.

2.2. Catalytic Reaction. The reaction was conducted in a 350 mL stainless steel autoclave reactor equipped with electric heating, a reflux column, and a magnetic stirrer under the assigned conditions. In a typical process, 0.1 mol of MC, 2.0 mol of methanol, and 7.4 mmol of catalyst were put into autoclave first and then were rapidly heated to the desired temperature and kept for a certain time with magnetic stirring. The stirring speed was 600 ± 50 rpm, and the temperature error was < 1 °C. After the reaction, the autoclave was cooled to room temperature, and the product mixture in the autoclave was weighed, clarified, and determined by gas chromatography.

2.3. Analysis of Products. The product analysis was made on a GC-920 chromatography configured with the GDX-203 column and a thermal conductivity detector (TCD) using isobutyl alcohol as the internal standard. The byproduct dimethyl ether could not be detected by gas chromatography because it was easy to volatilize when the autoclave was opened.

2.4. Characterization. FTIR spectra were recorded on a Nicolet Magna 550 Fourier transform infrared spectrometer in the region 4000–800 cm⁻¹. Sixty-four scans with a resolution of 4 cm⁻¹ were collected. The reaction product of MC and ZnCl₂ (molar ratio = 6/1) at various temperatures for 4 h was dissolved with solvent methanol at room temperature and then dropped on the NaCl salt pellet. The FTIR spectra of MC interacted with ZnCl₂ were obtained after the methanol had volatilized completely. The experimental procedure for getting FTIR spectra of methanol interacted with ZnCl₂ was the same

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Table 1. Catalytic Performance of Catalysts^a

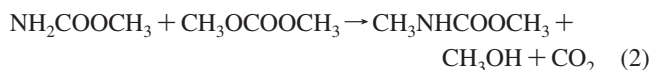
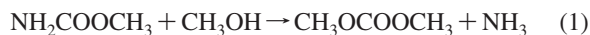
entry	catalyst	MC conversion (%)	DMC yield (%)	NMMC yield (%)
1	none	4.1	2.6	0
2	ZnO	5.6	4.2	0
3	Zn(OH) ₂	7.5	3.8	0
4	ZnSO ₄	10.2	3.7	0
5	Zn(NO ₃) ₂	23.2	11.9	0
6	Zn(CH ₃ COO) ₂	36.1	17.8	0
7	ZnCl ₂	50.9	33.6	9.1
8	ZnBr ₂	51.1	28.7	7.8
9	NaCl	4.1	3.4	0
10	KCl	4.1	3.7	0
11	Zn(NH ₃) ₂ Cl ₂	45.7	29.5	7.0

^a Reaction conditions: catalyst, 7.4 mmol; MC, 7.5 g; methanol, 64 g; temperature, 190 °C; time, 10 h. The DMC yields are based on MC.

to that of MC, excepting the product was dropped directly on NaCl salt pellet and covered by another one to prevent the volatilization of methanol. X-ray diffraction (XRD) of the precipitation obtained after reaction was measured by a Rigaku D/max-A X-ray diffractometer with $\lambda = 0.1541$ nm and Cu K α radiation in the 2θ range of 10–90° with the step of 0.02° at room temperature.

3. Results and Discussion

The reaction system of MC and methanol could be described approximately by expressions 1–3 no matter what catalysts were used.^{15,20–22}



At first, the amino of MC was substituted by the methoxy group in methanol to give DMC. The byproduct ammonia should be removed in time in order to shift the reaction equilibrium, which was thermodynamically unfavorable, because the nucleophilicity of NH_2^- was stronger than that of CH_3O^- . The product DMC, which was a favorable methylating agent for the amino group, could further react with MC to yield *N*-methyl methyl carbamate (NMMC). As a result, the byproduct NMMC increased correspondingly with the increase of the DMC concentration. Furthermore, at a relatively high temperature, DMC was also found to be easily thermally decomposed into dimethyl ether and carbon dioxide in the presence of solid basic and acidic oxides as well as residual Brønsted sites of copper zeolite.^{22,23} Besides, the formation of a trace of byproduct isocyanic acid, cyanamide, and cyanuric acid was mentioned elsewhere.⁶

3.1. Zinc Catalysts. As shown in Table 1, the yield of DMC was about 2.6% in the absence of catalysts (entry 1). ZnO, which was one of the best catalysts in the direct synthesis of alkyl carbonates from urea and alcohol,¹⁵ was almost inactive (entry 2). This was the same for Zn(OH)₂ and ZnSO₄ (entries 3 and 4). However, Zn(NO₃)₂ and Zn(CH₃COO)₂ exhibited high activity toward DMC synthesis, yielding 11.9% and 17.8% of DMC, respectively (entries 5 and 6). Especially, the MC conversion was 50.9% with the DMC yield of 33.6% when ZnCl₂ was used as the catalyst, although a part of DMC was further converted to NMMC (entry 7). On the basis of these results, it was likely that the Zn^{2+} ion appeared to catalyze the reaction of MC and methanol and the activities of zinc compounds were greatly influenced by their anions. Notably, only ZnCl₂, which was superior to other catalysts, could be

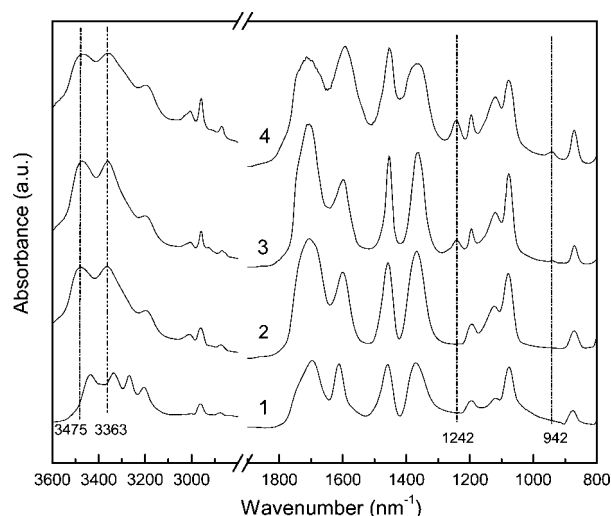


Figure 1. FTIR spectra of MC interacted with ZnCl₂: 1, MC; 2, 80 °C; 3, 130 °C; 4, 170 °C.

completely dissolved in methanol at room temperature among those active zinc compounds. This implied that the catalytic performances of zinc compounds were closely related to their solubility in methanol.

The role of Zn^{2+} ion was further confirmed by comparing the catalytic performance of zinc-containing compound with chlorine-containing compound. For catalyst ZnBr₂, which was also dissolved completely in methanol, its catalytic activity was the same high as that of ZnCl₂ (entry 8). Simultaneously, as that observed in ZnCl₂ catalytic system, the color of the solution changed from colorless and pellucid before reaction to yellow after reaction, which implied that the two systems had a similar catalytic mechanism. Oppositely, NaCl could also be completely dissolved in the reactive solution, but it was hardly shown to be active, which was the same for KCl (entries 9 and 10). All these phenomena revealed that Cl^- ion did not have any activity; the catalytic activity of ZnCl₂ only originated from Zn^{2+} ion in solution.

3.2. Interaction of MC and Methanol with ZnCl₂. ZnCl₂ had no absorption in the range of 4000–800 cm^{-1} , but MC gave the absorptions at 3434 and 3335 cm^{-1} assigned to the N–H antisymmetry and symmetry stretching vibrations, respectively (see Figure 1(1)),²⁴ which showed a red shift to 3269 and 3206 cm^{-1} for MC dimer associated via hydrogen bonds.²⁵ The bands at 1696 and 1612 cm^{-1} were due to the C=O stretching vibration (amide I band) and NH₂ bending vibration (amide II band), respectively. After the addition of ZnCl₂ (see Figure 1(2–4)), the N–H antisymmetry and symmetry stretching vibrations had a blue shift toward 3475 and 3363 cm^{-1} , respectively, while the N–H stretching vibration of the MC dimer decreased greatly. These suggested the weakening of intermolecular hydrogen bonds. Moreover, with the rise of temperature, the amide I band showed a blue shift gradually from 1696 to 1713 cm^{-1} , accompanying the red shift of the amide II band from 1612 to 1592 cm^{-1} . This implied the coordination of Zn^{2+} to the nitrogen atom of MC. If an amide group coordinated with metal ion through the nitrogen atom, the amide I band would shift to higher frequency and the amide II would shift to lower frequency. On the other hand, if the amide oxygen atom coordinated, the amide I and II bands should shift in the opposite direction.²⁶ In addition, two bands appeared distinctly at 1242 and 942 cm^{-1} at temperatures over 130 °C, which could be attributed to the blue shift of the previous OC–O and O–CH₃ stretching vibrations of MC at 1200 and 872 cm^{-1} ,

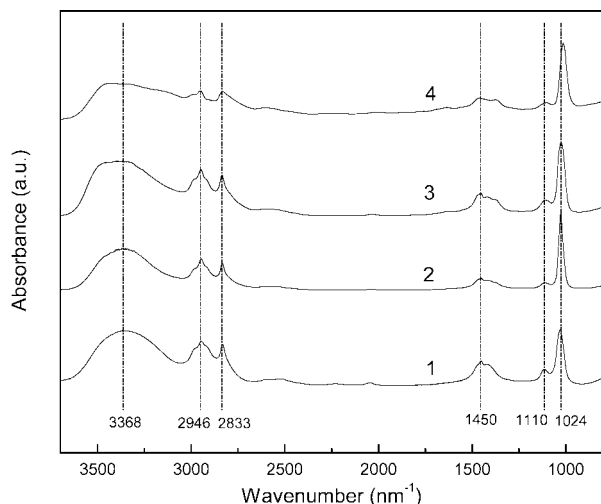


Figure 2. FTIR spectra of methanol interacted with ZnCl_2 1, methanol; 2, 80 °C; 3, 130 °C; 4, 170 °C.

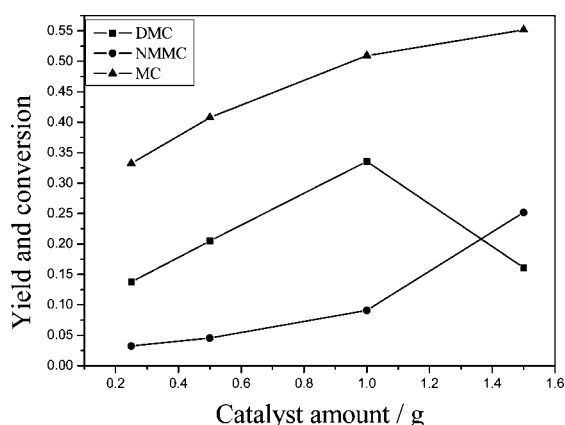


Figure 3. Effect of catalyst amount on DMC and NMMC yield and MC conversion: reaction temperature, 190 °C; reaction time, 10 h; MC, 7.5 g; methanol, 64 g.

respectively. This might be caused by the electron-attracting effect of Zn^{2+} ion after coordinating with nitrogen atom.

Methanol did not appear to interact with ZnCl_2 at various temperatures (see Figure 2). The C–H stretching vibration at 2946 and 2833 nm^{-1} , the CH_3 deformation vibrations at 1450 and 1110 nm^{-1} , and the C–O stretching vibration at 1024 nm^{-1} were all consistent with the standard infrared spectra of methanol (Aldrich Solvents FT-IR Spectral Library). No bands, which were related to the methoxyl species, were observed at 1055, 1097, or 2800 nm^{-1} .²⁷

3.3. Reaction Condition. Over catalyst ZnCl_2 , the experimental factors such as catalyst amount, reaction temperature, and reaction time were further optimized for their effects on MC conversion together with DMC and NMMC yields. Figure 3 illustrates the influence of catalyst amount. The conversion of MC always monotonically rose with the increase of catalyst amount, but the DMC yield reached the maximum of 33.6% at 1.00 g and then decreased. This might be due to the fact that the yield of further reaction product NMMC increased sharply if the catalyst amount was >1.00 g.

The effect of reaction temperature is illustrated by Figure 4. The conversion of MC was consistently enhanced with the increase of temperature, but the DMC yield reached its peak at 190 °C and then decreased. In theory, the high temperature was appropriate for synthesis of DMC, since this reaction was an endothermic reaction.²⁰ However, higher temperature also

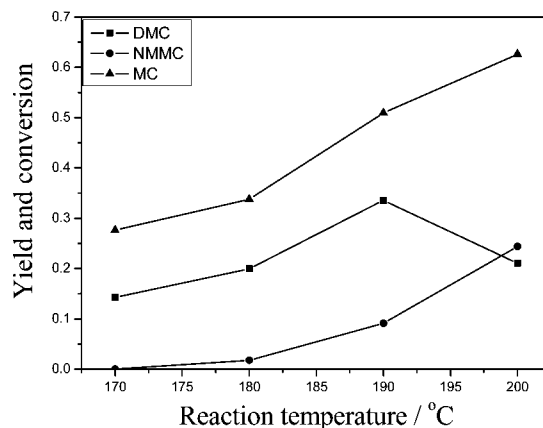


Figure 4. Effect of reaction temperature on DMC and NMMC yield and MC conversion: reaction time, 10 h; amount of catalyst, 1.00 g; MC, 7.5 g; methanol, 64 g.

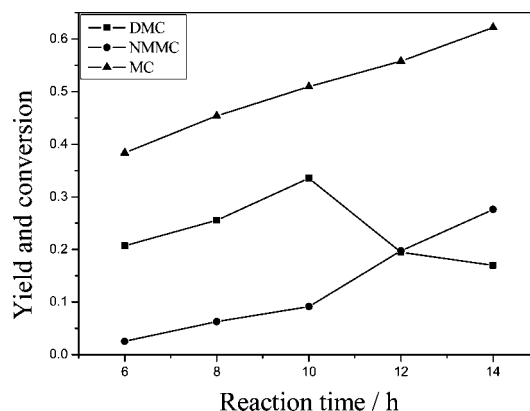


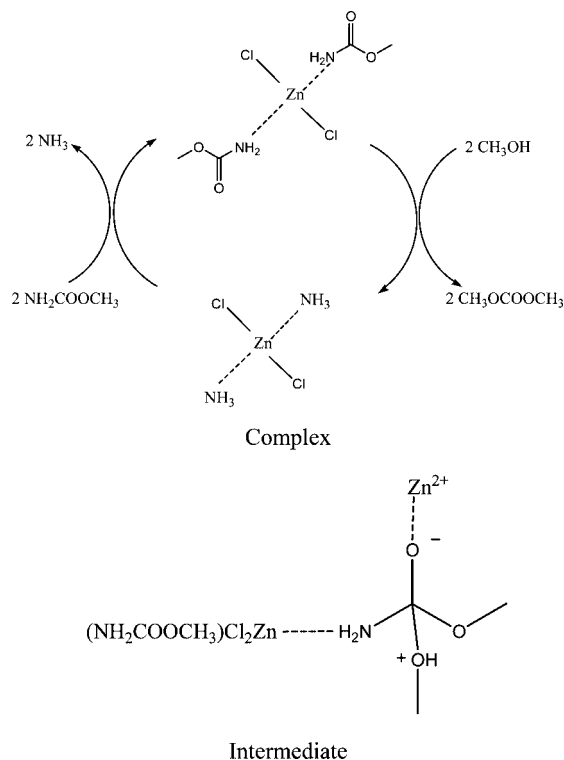
Figure 5. Effect of reaction time on DMC and NMMC yield and MC conversion: reaction temperature, 190 °C; amount of catalyst, 1.00 g; MC, 7.5 g; methanol, 64 g.

shortened the time needed to reach the maximum DMC concentration and accelerated the rate of further reaction. Accordingly, although byproduct NMMC could not be detected at 170 °C, as the temperature increased, its yield increased significantly at the cost of DMC consumption. Simultaneously, the thermal decomposition of DMC may aggravate gradually. Therefore, the suitable reaction temperature should be controlled below 190 °C.

Figure 5 demonstrates the effect of reaction time. The DMC yield increased at the first 10 h and reached its maximum of 33.6%, and then the consumption of DMC in the further reaction surpassed gradually the formation of DMC from MC. Thus, 10 h was the optimal reaction time for the reaction of MC with methanol. The detailed reaction kinetics for these three experimental factors still awaits further exploration.

3.4. Possible Mechanism. As a transition metal element, divalent Zn^{2+} ion with d^{10} electrons could coordinate with nitrogen, oxygen, and sulfur or phosphorus atom to reach the stable construction of 18 electrons.^{28–30} Thus, the nitrogen atom of amino and the two oxygen atoms of carbonyl and methoxy in the MC molecule all had a chance to coordinate with Zn^{2+} ion. Their electron densities computed by Hyperchem7.5 based on AM1 semiempirical method were -0.416 , -0.404 , and -0.286 of negative charge, respectively. This meant that the nitrogen atom was more possible than the oxygen atom to coordinate with Zn^{2+} ion. Furthermore, the hybridized orbital of nitrogen atom would change from sp^2 to sp^3 once it coordinated with Zn^{2+} ion, and correspondingly, the π -delo-

Scheme 1. Reaction Mechanism



calized bond of amide disappeared. Considering the FTIR spectra results, a possible mechanism for catalyst ZnCl_2 was proposed as shown in Scheme 1. At first, by the coordination of 2 equiv of MC through the nitrogen atom of amide, 1 equiv of Zn^{2+} ion reached the stable construction of 18 electrons (the two chloride atoms would provide one pair of electrons each). In the $\text{Zn}(\text{NH}_2\text{COOCH}_3)_2\text{Cl}_2$ complex, the amino bond of ligand MC was weakened, which facilitated the nucleophilic attack of methanol. Then, a lone pair of electrons of oxygen in methanol could form a bond to the electrophilic carbonyl carbon, and at the same time, the relatively weak π -bond of the carbonyl group broke; consequently, both electrons moved to the oxygen and provided the third lone pair of electrons and a negative charge. It was noteworthy that the oxygen in methanol gained a positive charge, since it had effectively lost an electron by sharing its lone pair with carbon in the new bond. Such a zwitterion intermediate might be stabilized by another Zn^{2+} ion. Then, the proton of O—H moved to nitrogen, and the lone pair of electrons on oxygen returned to reform the carbonyl π -bond. As a result, the C—N bond broke with both electrons moving onto the nitrogen to produce the corresponding complex $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ and DMC. Because of the strong nucleophilic ability of MC and the liberation of NH_3 , the NH_3 in the complex was substituted by MC to finish the catalytic circle.

Notably, a white crystal, which was proved to be $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ by XRD (see Figure 6), was precipitated after the reaction solution was cooled to 0°C in our experiment. It showed the same catalytic activity as ZnCl_2 (entry 11), which powerfully supported the above reaction mechanism. In addition, it was obvious that the higher ZnCl_2 amount, the higher reaction temperature and the longer reaction time, would give rise to the higher yield of complex $\text{Zn}(\text{NH}_2\text{COOCH}_3)_2\text{Cl}_2$. Thus, the MC conversion was observed to increase monotonically along with those variables. However, the yield of DMC did not always increase as described in the reaction mechanism because of the side-reactions of DMC.

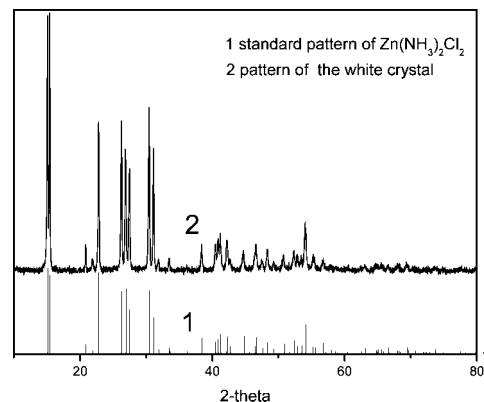


Figure 6. XRD pattern of the white crystal.

4. Conclusions

Among the zinc compound catalysts for the synthesis of DMC from MC and methanol, ZnCl_2 and ZnBr_2 showed the highest activity, probably due to their favorable solubility in methanol. Their high catalytic performance only originated from Zn^{2+} ion. FTIR spectra and XRD characterization indicated that MC was activated by Zn^{2+} through the coordination of the nitrogen atom. In addition, the reaction time, reaction temperature, and catalyst amount had a strong effect on the performance of model catalyst ZnCl_2 . The MC conversion and DMC yield under the optimal conditions reached 50.9% and 33.6%, respectively.

Acknowledgment

The authors acknowledge the financial support from State Key Program for Development and Research of China (No. 2006BAC02A08).

Literature Cited

- (1) Shaikh, A. A.; Sivaram, S. Organic Carbonates. *Chem. Rev.* **1996**, 96 (3), 951.
- (2) Tundo, P. New Developments in Dimethyl Carbonate Chemistry. *Pure Appl. Chem.* **2001**, 73 (7), 1117.
- (3) Ono, Y. Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign building block. *Appl. Catal., A* **1997**, 155 (2), 133.
- (4) Delledonne, D.; Rivetti, F.; Romano, U. Developments in the production and application of dimethylcarbonate. *Appl. Catal., A* **2001**, 221 (1–2), 241.
- (5) Pacheco, M. A.; Marshall, C. L. Review of Dimethyl Carbonate (DMC) Manufacture and Its Characteristics as a Fuel Additive. *Energy Fuels* **1997**, 11 (1), 2.
- (6) Ball, P.; Fuellmann, H.; Heitz, W. Carbonates and Polycarbonates from Urea and Alcohol. *Angew. Chem., Int. Ed. Engl.* **1980**, 19 (9), 718.
- (7) Wang, M.; Wang, H.; Zhao, N.; Wei, W.; Sun, Y. Synthesis of dimethyl carbonate from urea and methanol over solid base catalysts. *Catal. Commun.* **2006**, 7 (1), 6.
- (8) Sun, J. J.; Yang, B. L.; Lin, H. Y. A semicontinuous process for the synthesis of methyl carbamate from urea and methanol. *Chem. Eng. Technol.* **2004**, 27 (4), 435.
- (9) Kaminskaia, N. V.; Kostic, N. M. Alcoholysis of Urea Catalyzed by Palladium(II) Complexes. *Inorg. Chem.* **1998**, 37 (17), 4302.
- (10) Cho, T.; Tamura, T.; Cho, T.; Suzuki, K. Process for preparing dialkyl carbonates. U.S. Patent 5,534,649, 1996.
- (11) Lin, H.; Yang, B.; Sun, J.; Wang, X.; Wang, D. Kinetics studies for the synthesis of dimethyl carbonate from urea and methanol. *Chem. Eng. J.* **2004**, 103 (1–3), 21.
- (12) Saleh, R. Y.; Michaelson, R. C.; Suciu, E. N.; Kuhlmann, B. Process for manufacturing dialkyl carbonate from urea and alcohol. U.S. Patent 5,565,603, 1996.
- (13) Ryu, J. Y.; Gelbein, A. P. Process and catalyst for making dialkyl carbonates. U.S. Patent 6,392,078, 2002.

- (14) Wu, C.; Zhao, X.; Wang, Y. Effect of reduction treatment on catalytic performance of Zn-based catalyst for the alcoholysis of urea to dimethyl carbonate. *Catal. Commun.* **2005**, 6 (10), 694.
- (15) Wang, M.; Zhao, N.; Wei, W.; Sun, Y. Synthesis of Dimethyl Carbonate from Urea and Methanol over ZnO. *Ind. Eng. Chem. Res.* **2005**, 44 (19), 7596.
- (16) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M. Transesterification of urea and ethylene glycol to ethylene carbonate as an important step for urea based dimethyl carbonate synthesis. *Green Chem.* **2003**, 5 (4), 429.
- (17) Li, Q. B.; Zhang, W. Y.; Zhao, N.; Wei, W.; Sun, Y. H. Synthesis of cyclic carbonates from urea and diols over metal oxides. *Catal. Today* **2006**, 115 (1–4), 111.
- (18) Zhao, X. Q.; Zhang, Y.; Wang, Y. J. Synthesis of propylene carbonate from urea and 1,2-propylene glycol over a zinc acetate catalyst. *Ind. Eng. Chem. Res.* **2004**, 43 (15), 4038.
- (19) Suciu, E. N.; Kuhlmann, B.; A.; Knudsen, G.; Michaelson, R. C. Investigation of dialkyltin compounds as catalysts for the synthesis of dialkyl carbonates from alkyl carbamates. *J. Organomet. Chem.* **1998**, 556 (1–2), 41.
- (20) Wang, M.; Wang, H.; Zhao, N.; Wei, W.; Sun, Y. High-Yield Synthesis of Dimethyl Carbonate from Urea and Methanol Using a Catalytic Distillation Process. *Ind. Eng. Chem. Res.* **2007**, 46 (9), 2683.
- (21) Yang, B.; Wang, D.; Lin, H.; Sun, J.; Wang, X. Synthesis of dimethyl carbonate from urea and methanol catalyzed by the metallic compounds at atmospheric pressure. *Catal. Commun.* **2006**, 7 (7), 472.
- (22) Fu, Y.; Zhu, H.; Shen, J. Thermal decomposition of dimethoxymethane and dimethyl carbonate catalyzed by solid acids and bases. *Thermochim. Acta* **2005**, 434 (1–2), 88.
- (23) Anderson, S. A.; Manthata, S.; Root, T. W. The decomposition of dimethyl carbonate over copper zeolite catalysts. *Appl. Catal., A* **2005**, 280 (2), 117.
- (24) Carter, J. C.; Devia, J. E. Vibrational analysis of methylcarbamate and *N,N*-dichloromethylcarbamate. *Spectrochim. Acta, Part A* **1973**, 29 (4), 623.
- (25) Furer, V. L. Hydrogen bonding in ethyl carbamate studied by IR spectroscopy. *J. Mol. Struct.* **1998**, 449 (1), 53.
- (26) Sahni, S. K. Novel five- and six-coordinate zinc(II), cadmium(II) and mercury(II) complexes of macrocyclic ligands. *Transition Met. Chem.* **1979**, 4 (2), 73.
- (27) Zhang, W.; Wang, H.; Wei, W.; Sun, Y. Solid base and their performance in synthesis of propylene glycol methyl ether. *J. Mol. Catal., A* **2005**, 231 (1–2), 83.
- (28) Niu, W. J.; Wong, E. H.; Weisman, G. R.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L. Copper(II) and zinc(II) complexes of amide pendant-armed cross-bridged tetraamine ligands. *Polyhedron* **2004**, 23 (6), 1019.
- (29) Mohamadou, A.; Gerard, C. Synthesis and characterisation of zinc(II) complexes of tripodal N-7 ligands involving pyridine and amine or amide nitrogen donors. Crystal structure of a zinc(II) complex. *J. Chem. Soc., Dalton Trans.* **2001**, (22), 3320.
- (30) Kimura, E.; Gotoh, T.; Aoki, S.; Shiro, M. Study of pH-dependent zinc(II)–carboxamide interactions by zinc(II)–carboxamide-appended cyclen complexes (cyclen=1,4,7,10-tetraazacyclododecane). *Inorg. Chem.* **2002**, 41 (12), 3239.

Received for review March 6, 2008

Revised manuscript received May 8, 2008

Accepted May 12, 2008

IE8003732