High-Yield Synthesis of Dimethyl Carbonate from Urea and Methanol Using a Catalytic Distillation Process

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Reaction equilibrium for the dimethyl carbonate (DMC) synthesis from urea and methanol was calculated based on the Benson method, and results showed that the reaction was thermodynamically unfavorable. In addition, urea methanolysis was conformed to be a consecutive reaction. Major side reactions in the DMC synthesis included the thermal decomposition of DMC and reaction between methyl carbamate (MC) and DMC, which reduced the DMC yield in the batch process. A catalytic distillation technique was proposed in this study to minimize the side reactions and unfavorable equilibrium for DMC synthesis. The DMC yield reached 60−70% in the catalytic distillation reactor over a Zn-based catalyst.

1. Introduction

As an environmentally benign building block in chemical syntheses, dimethyl carbonate (DMC) has drawn much attention in recent years.[1−4] DMC has versatile chemical properties and is used extensively in methylation and carbonylation as a safe substitute for dimethyl sulfate, methyl halides, and phosgene. In addition, DMC is an ideal additive for gasoline because of its higher oxygen content (53%) and good blending octane (($R + M$)/2 = 105).[5]

DMC was traditionally produced by phosgenation of methanol. This method has been phased out in recent years because of the use of extremely toxic phosgene. DMC is currently synthesized by the oxidative carbonylation of methanol (the so-called EniChem process and Ube process) through non-phosgene routes and a transesterification method.[6] A major shortcoming in the oxidative carbonylation involves poisonous or/and corrosive gases such as carbon monoxide, hydrogen chloride, and methyl nitrate and the explosion hazards of methanol and oxygen.[7−10] A drawback in the transesterification method is the limiting thermodynamic equilibrium, which leads to a low reaction conversion in synthesis and produces ethylene glycol as a byproduct along with DMC.[11−13] Recently, Bhanage et al.[14] synthesized ethylene carbonate by transesterification of urea and ethylene glycol with a high yield and selectivity, followed by DMC synthesis from ethylene carbonate by the transesterification method. However, both steps in this route need product separation by distillation, and distillation is energy intensive because ethylene glycol, ethylene carbonate, and DMC all have high boiling points. On the other hand, a direct synthesis has been proposed for carbonate production via urea alcoholysis.[15] In this case, DMC is produced by the reaction of urea with methanol via intermediate methyl carbamate (MC). In addition, ammonia released during reaction could be recycled for urea synthesis. No poisonous or corrosive gases were involved in this approach, and naturally abundant carbon dioxide was used

as one of the starting materials. Those features made the direct carbonate synthesis more attractive from the environmental perspective.

Catalysts in the direct synthesis method reported in the literature were bases,[16,17] organotin catalysts,[18−21] and metal oxides.[16,17,22−24] The corresponding DMC yields were usually low (below 40%) in the batch reactors. Ryu et al.[19] have patented a novel process, in which DMC was withdrawn during reaction via a reflux column above an autoclave reactor in the presence of organotin catalysts. A high DMC selectivity was obtained, but the organotin and cocatalyst were very complex, expensive, and difficult to handle. Sun[25] and his co-workers reported a new process using polyphosphoric acid as the catalyst as well as an ammonia captor. The DMC yield in the batch operation was improved. Ammonium polyphosphate was however precipitated in the reactor during reaction, which caused problems in operation and separation. In our previous work, ZnO exhibited high activity toward the DMC synthesis.[17] It was simple and nontoxic in comparison with the tin compounds. In this work, a new strategy was proposed for the DMC synthesis from urea and methanol based on the analysis of thermodynamic equilibrium and side reactions. The objective was to increase the DMC yield using catalytic distillation technique over a Zn-based catalyst.

2. Experimental Section

2.1. Materials and Catalyst Preparation. Chemicals used in this study include methanol (99.5% purity), urea (99.5%), CaCO₃ (99%), and La₂O₃ (99.5%) obtained from Tianjin University Chemical Factory (Tianjin, China). In addition, DMC (99%) was obtained from Fluka (packed in Switzerland). Methyl carbamate (99%) was purchased from Acros Organics (USA). Zn(NO₃)₂·6H₂O (99%) and zinc carbonate (99%) were provided by Shanghai Chemical Reagent (Shanghai, China). γ-Al₂O₃ (99%, 3 mm grain) was from China Research Institute of Daily Chemical Industry (Taiyuan, China).

Catalysts CaO and ZnO were prepared by heating calcium carbonate at 1073 K for 2 h and zinc carbonate at 773 K for 4 h in a muffle furnace in an N₂ atmosphere. ZnO−Al₂O₃ was prepared by the following procedure: γ-Al₂O₃ was impregnated by Zn(NO₃)₂·6H₂O followed by drying at 373 K for 12 h and calcination at 1073 K for 4 h in air. The exhaust gas during

calcination was washed by a 0.5 M NaOH solution. The ratio of ZnO/Al_2O_3 was 20/80 by weight. Commercially available γ-Al_2O_3, PbO, and La_2O_3 were used in this study.

2.2. Experimental Procedure. The batch reaction was conducted in an autoclave reactor, composed of a 250-mL stainless-steel autoclave with a reflux column, a liquid pump, and a magnetic stirrer.[17] A 1.5 mol sample of methanol and 2.0 g of catalyst were loaded into the autoclave and heated to the scheduled temperature (433−463 K). A urea solution containing 0.20 mol of urea in 2.5 mol of methanol was then pumped into the autoclave within 10 min. The solution was constantly stirred at 600 ± 50 rpm. The reaction was carried out at the scheduled temperature (±2 K) for the duration of time (2−22 h). Ammonia was released three times during the process through a valve above the reflux column. After the completion of reaction, the autoclave was shut and cooled to room temperature. The product solution was clarified and analyzed with a gas chromatograph (GC) equipped with a thermal conductivity detector.

Catalytic distillation experiments were carried out in a reactor as shown in Figure 1.[31] The reactor included a kettle bottom, a rectifying column, a reactive column, a stripping column, and a condenser. The volume of the kettle bottom was 1000 mL. The inside diameters for the rectifying, reactive, and stripping columns were 30 mm each and their heights were 500, 500, and 1000 mm, respectively. The rectifying and stripping columns were packed with Rashing rings, and the reactive column was filled with catalyst (50 g, 10−20 mesh). N_2 was introduced into the reactor and compressed to a desired pressure (close to 1.0−1.5 MPa at the reaction temperature) prior to reaction. The pressure was controlled by a back-pressure regulator at the vent. The reactants, urea solution (30 wt % in methanol) and methanol, were continuously fed into the reactive column from top and bottom, respectively. Products from both the tower top and bottom were taken out every 12 h for GC analysis.

3. Results and Discussion

3.1. Thermodynamic Analysis. The reaction formulas of DMC synthesis from urea and methanol via the intermediate MC are as follows:

(1)

(2)

(3)
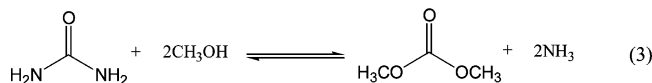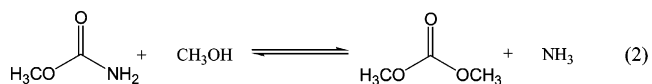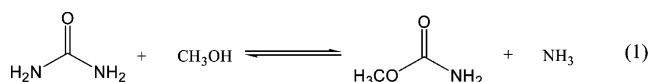
Our previous work[17,22,24] has conformed that reaction 1 and reaction 2 are the two elemental steps of reaction 3. Therefore, reactions 1 and 2 are important to reaction 3 in terms of reaction mechanism. Thermodynamic calculations[26] based on the data in Table 1 showed that the enthalpy change ($\Delta_r H$) of reactions 1 and 2 were −10.31 and 13.11 kJ·mol⁻¹, respectively, at 0.1013 MPa and 298.15 K. Reaction 1 was exothermic and reaction 2 was endothermic. The dependence of $\Delta_r G$ and equilibrium constant K on temperature estimated by the Benson method[27] are listed in Table 2. $\Delta_r G$ increased with increasing temperature for reaction 1 and decreased with increasing temperature for reaction 2. Therefore, reaction 1 was thermodynamically favorable and reaction 2 was unfavorable. The equilibrium constant K was not very high for reaction 1 and not very low for reaction
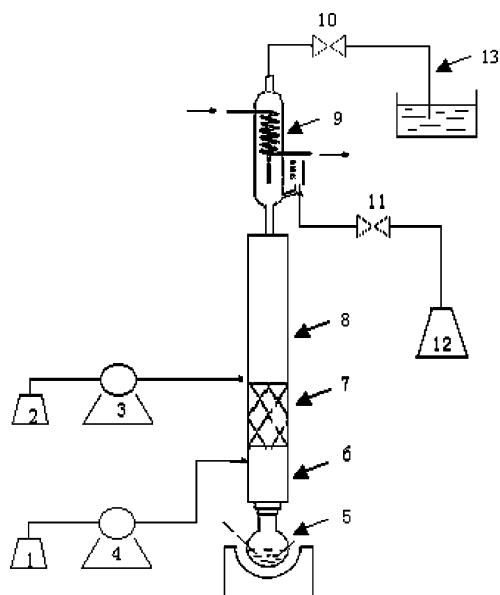
Figure 1. Schematic diagram of catalytic distillation reactor: 1, methanol; 2, urea solution; 3 and 4, pumps; 5, kettle bottom; 6, stripping column; 7, reactive column; 8, rectifying column; 9, condenser; 10 and 11, valves; 12, overhead liquid product; 13, vent.
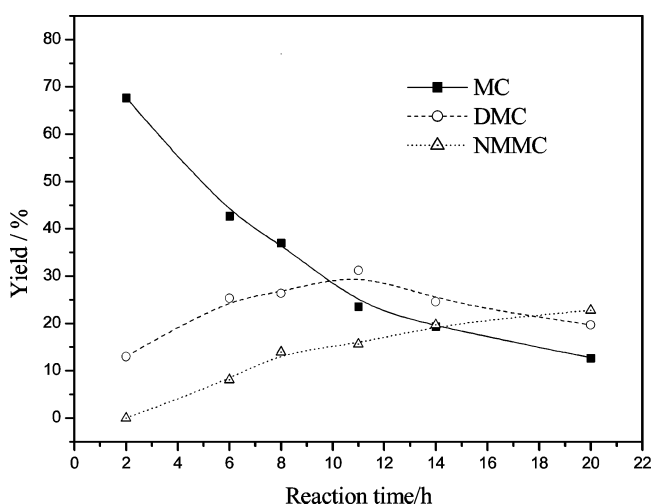
Figure 2. Effect of reaction time on DMC, MC, and NMMC yield in the batch reactor. Reaction conditions: 2 g of ZnO, 0.20 mol of urea, and 4 mol of methanol at 453 K.

Table 1. Standard Gibbs Free Energy and Enthalpy of the Compounds for DMC Synthesis (Ideal Gas at 298 K)

component	$\Delta_f G°$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)
NH_3[a]	−16.63	−46.19
CH_3OH[a]	−161.92	−201.25
CH_3OCONH_2[b]	−333.88	−427.47
NH_2CONH_2[b]	−175.35	−262.10
DMC[b]	−463.78	−569.42

[a] Obtained from the literature.[26]   [b] Calculated using Benson's bond addition method.[27]

2 in the range of 300−600 K. This means that kinetics can be used to shift the reaction equilibrium as well as to increase the rate.

3.2. DMC Synthesis in a Batch Reactor. Experimental results of DMC synthesis in the batch process are listed in Table 3. In noncatalytic reactions (runs 1 and 2) urea could completely convert to MC quickly, while MC hardly converted to DMC. This indicates that reaction 2 was the key step for DMC synthesis.

Table 2. Dependence of $\Delta_r G$ and the Equilibrium Constant K on Temperature for Reactions 1−3

	1		2		3	
T (K)	$\Delta_r G$ (kJ·mol^{-1})	K	$\Delta_r G$ (kJ·mol^{-1})	K	$\Delta_r G$ (kJ·mol^{-1})	K
300	−13.26	203.88	15.41	2.08×10^{-3}	2.14	0.42
350	−13.95	120.88	15.85	4.30×10^{-3}	1.89	0.52
400	−14.82	86.07	16.41	7.20×10^{-3}	1.59	0.62
450	−15.91	70.27	17.08	1.04×10^{-2}	1.15	0.74
500	−17.21	62.74	17.84	1.37×10^{-2}	0.63	0.86
550	−18.60	58.40	18.73	1.66×10^{-2}	0.10	0.98
600	−20.23	57.65	19.72	1.92×10^{-2}	−0.51	1.11

Table 3. Performance of Urea Methanolysis over Select Metal Oxides[a]

run	catalyst	urea conversion (%)	MC yield (%)	DMC yield (%)	NMMC yield (%)
1		100	97		
2		100	95	0.8	
3	CaO	100	72	16	1.0
4	La$_2$O$_3$	100	75	6.2	3.5
5	PbO	100	43	25	12
6	ZnO	100	40	26	14
7	ZnO−Al$_2$O$_3$	100	45	24	12

[a] Reaction conditions: 12 g of urea, 128 g of methanol, 2 g of catalyst at 453 K for 8 h (except for run 1, at 2 h).
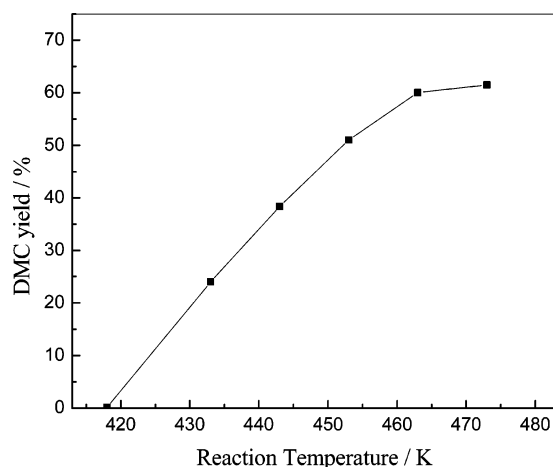

Figure 3. Effect of reaction temperature on DMC yield in the catalytic distillation reactor. Reaction conditions: 30 wt % urea solution (in methanol), urea solution LHSV 0.3 h^{-1}, methanol LHSV 0.6 h^{-1}, and 2:1 reflux ratio at 1.2 MPa.
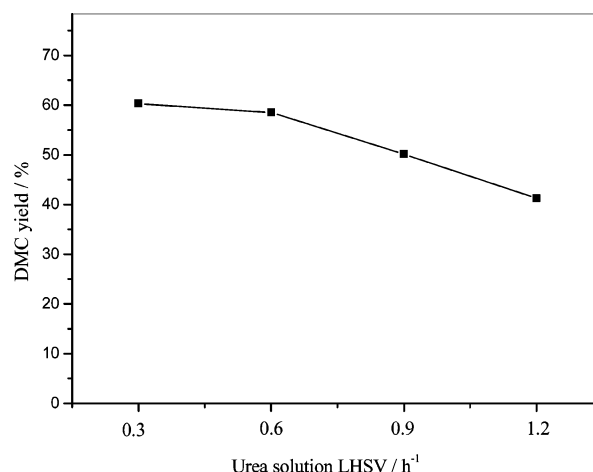

Figure 4. Effect of urea LHSV on DMC yield in the catalytic distillation reactor. Reaction conditions: urea concentration 30 wt %, methanol LHSV 0.6 h^{-1}, and reflux ratio 2:1 at 1.2 MPa and 458 K.

**Table 4. Physical Properties of the Reactants and Products in the DMC Synthesis**

compound	mp (K)	bp (K)
urea	407	
methanol	175	337
MC	327	450
ammonia	195	240
DMC	273.5	363
DMC−methanol azeotrope		336

Besides main reactions 1 and 2, there were many side reactions in urea methanolysis. In our investigation, *N*-methyl methyl carbamate (NMMC) was detected as the major byproduct in the product mixture (Table 3). It might be produced from the reaction of MC and DMC, because DMC is an excellent methylating agent for the amino group.[3] In addition, Fu et al. reported that DMC was prone to thermal decomposition over ZnO.[28] Ono et al. revealed further that DMC could decompose to dimethyl ether and CO$_2$ in the presence of metal oxides.[29] To the best of our knowledge, side reactions were similar no matter what catalyst systems were used.[17−19,21] The reaction pathway of urea methanolysis is illustrated in Scheme 1. It is worthwhile to note that the whole reaction was consecutive and DMC was not the final product. Therefore, side reactions in the batch process were inevitable.

The effect of reaction conditions such as reaction time on both main and side reactions was optimized in the batch process.[17] Figure 2 shows the effect of reaction time using ZnO as the model catalyst. Over extended reaction time, the MC yield decreased monotonically from 70% at 2 h to 10% at 22 h, the DMC yield increased gradually to the maximum of 35% at 11 h, and the NMMC yield increased monotonically. Side reactions consumed both MC and DMC, and reduced the DMC yield by passing the maximum. At the optimal conditions, the highest DMC yield is only 35% for the batch process.[17] This was consistent with the recent work by Lin, who obtained the highest DMC yield of 35−40% with 95% urea conversion over organotin catalysts.[21]

3.3. DMC Synthesis Using Catalytic Distillation over a Zinc-Based Catalyst. To overcome the problems in unfavorable equilibrium and complicated side reactions, a catalytic distillation technique was introduced into the DMC synthesis in our laboratory. Catalytic distillation carries out chemical reactions and separations in one apparatus, and has demonstrated potential for industrial application.[30] The catalytic distillation reactor used in this study is shown in Figure 1. It is mainly composed of the stripping, reactive, and rectifying sections. The zinc-based heterogeneous catalyst (ZnO−Al$_2$O$_3$) was packed in the reactive section of the column. During reaction, urea in methanol solution was fed above the reactive section, and methanol was fed below

Scheme 1. Reaction Pathway of Urea Methanolysis
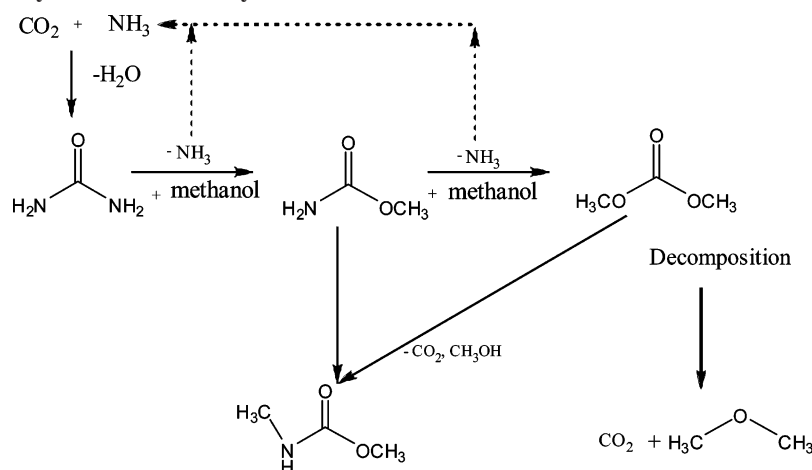
the reactive section. Because urea (or MC) has a high melting (or boiling) point (Table 4), it moved downward and through the reactive section. As reactions took place between urea, MC, and methanol, DMC and ammonia was produced; they were withdrawn from the reaction zone as soon as they were produced by distillation, because the boiling points of ammonia and DMC−methanol azeotrope are much lower than that of urea or MC. As a result, this process could enhance the DMC yield by (i) shifting the reaction equilibrium and (ii) minimizing the side reactions of DMC.

First, the effects of reaction conditions of reaction temperature and urea liquid hourly space velocity (LHSV) on the DMC yield were investigated using the catalytic distillation reactor in this study. Figure 3 shows that the DMC yield increases with increasing reaction temperature from 413 to 473 K. The maximal DMC yield reached about 60%−70%, which was almost 2-fold that in the batch process. Our previous work concluded that high temperature could greatly accelerate side reactions;[17] therefore, the optimal reaction temperature for the DMC synthesis in the catalytic distillation reactor was around 463 K. Figure 4 exhibits the effect of urea solution LHSV on the DMC yield. The DMC yield decreased slightly with increasing urea solution LHSV from 0.3 to 0.6 h^{-1}, and it dropped sharply while the urea solution LHSV increased from 0.6 to 1.2 h^{-1}. Higher LHSV of the urea solution meant more reactant was used. The

catalytic activity of the catalyst was constant, so decrease in the DMC yield indicated that low LHSV was beneficial to achieving high DMC yields.

Finally, direct synthesis of DMC in the catalytic distillation reactor was investigated at 0.3 h^{-1} urea solution LHSV and 458 K. Figure 5 illustrates a typical continuous performance of the DMC synthesis in this study. There was a 60 h induced period because the DMC yield was measured based on the overhead liquid product, and the DMC could not be removed completely from the beginning of operation until the DMC content reached an equilibrium in the reactor. After the induced period, the DMC yield was maintained around 50−60% for 500 h. The catalytic distillation process demonstrated a stable performance. It also substantially improved the DMC yield compared with the batch process. In addition, steady reactor performance also implied the high stability of the catalyst used in this study.

In summary, using the catalytic distillation technique for DMC synthesis has two major advantages: (i) using low toxic chemicals, inexpensive catalysts, and free-of-solvent reaction environment; (ii) running continuous experimental operation and easy product separation.

4. Conclusion

Calculations of thermodynamic equilibrium showed that the reaction of urea with methanol is thermodynamically unfavorable for DMC synthesis. The urea methanolysis reaction was found to be a consecutive reaction. Major side reactions included the thermal decomposition of DMC and reaction between MC and DMC, which reduced the DMC yield. The highest DMC yield was measured about 35% over a ZnO catalyst in the batch process. In comparison, catalytic distillation reactor effectively increased the DMC yield by stripping off DMC from the reaction zone, which also minimized the side reactions simultaneously. The highest DMC yield reached 60−70% over a Zn-based catalyst using catalytic distillation in this study. The catalytic distillation process demonstrated a stable performance and a substantial improvement in the DMC yield compared with the batch process.
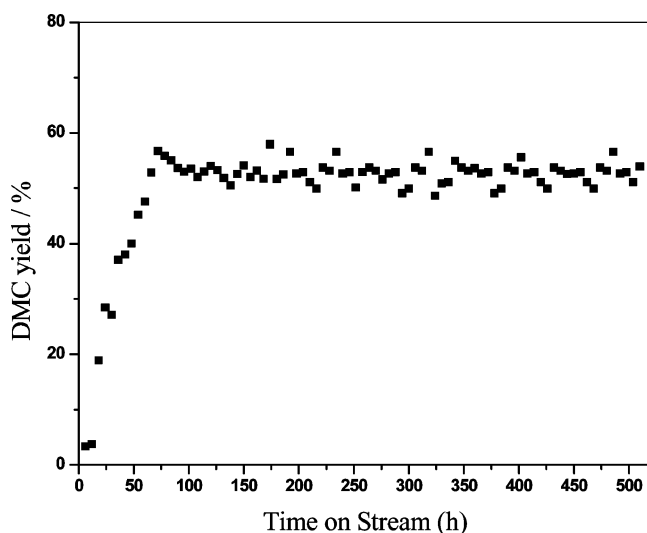
Figure 5. DMC yield over time using the catalytic distillation process. Reaction conditions: urea concentration 30 wt %, urea solution LHSV 0.3 h^{-1}, methanol LHSV 0.6 h^{-1}, and reflux ratio 2:1 at 1.2 MPa and 458 K.

Literature Cited

(1) Shaikh, A. G.; Sivaram, S. Organic Carbonates. *Chem. Rev.* **1996**, *96*, 951.

(2) Tundo, P. New developments in dimethyl carbonate chemistry. *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.: Gen.* **1997**, *155*, 133.

(4) Delledonne, D.; Rivetti, F.; Romano, U. Developments in the production and application of dimethylcarbonate. *Appl. Catal., A.: Gen.* **2001**, *221*, 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*, 2.

(6) Wei, T.; Wang, M.; Wei, W.; Sun, Y.; Zhong, B. Synthesis of dimethyl carbonate by transesterification over CaO/carbon composites. *Green Chem.* **2003**, *5*, 343.

(7) Romano, U.; Twsel, R.; Maurl, M. M.; Rebora, P. Synthesis of Dimethyl Carbonate from Methanol, Carbon Monoxide, and Oxygen Catalyzed by Copper compounds. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 396.

(8) Itoh, H.; Watanabe, Y.; Moric, K.; Umino, H. Synthesis of dimethyl carbonate by vapor phase oxidative carbonylation of methanol. *Green Chem.* **2003**, *5*, 558.

(9) Yamamoto, Y.; Matsuzaki, T.; Tanaka, S.; Nishihira, K.; Ohdan, K.; Nakamura, A.; Okamoto, Y. Catalysis and characterization of Pd/NaY for dimethyl carbonate synthesis from methyl nitrite and CO. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (20), 3721.

(10) Ruixia, J.; Shufang, W.; Xinqiang, Z.; Yanji, W.; Chengfang, Z. The effects of promoters on catalytic properties and deactivation-regeneration of the catalyst in the synthesis of dimethyl carbonate. *Appl. Catal., A.: Gen.* **2003**, *238*, 131.

(11) Wang, H.; Wang, M.; Zhao, N.; Wei, W.; Sun, Y. CaO−ZrO2 Solid solution: A highly stable catalyst for the synthesis of dimethyl carbonate from propylene carbonate and methanol. *Catal. Lett.* **2005**, *105* (3−4), 253.

(12) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Torii, K.; Arai, M. Synthesis of dimethyl carbonate and glycols from carbon dioxide, epoxides and methanol using heterogeneous Mg containing smectite catalysts effect of reaction variables on activity and selectivity performance. *Green Chem.* **2003**, *5*, 71.

(13) Wei, T.; Wang, M.; Wei, W.; Sun, Y.; Zhong, B. Effect of base strength and basicity on catalytic behavior of solid bases for synthesis of dimethyl carbonate from propylene carbonate and methanol. *Fuel Process. Technol.* **2003**, *83*, 175.

(14) 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*, 429.

(15) (a) Ball, P.; Füllmann, H.; Heitz, W. Carbonates and polycarbonates from urea and alcohol. *Angew. Chem., Int. Ed. Engl.* **1980**, *19* (9), 718. (b) Ball, P.; Füllmann, H.; Schwalm, R. Synthesis of carbonates and polycarbonates by reaction of urea with hydroxyl compounds. *C1 Mol. Chem.* **1984**, *1*, 95.

(16) Cho, T.; Tamura, T.; Cho, T.; Suzuki, K. Process for preparing dialkyl carbonates. U.S. Patent 5,534,649, July 9, 1996.

(17) Wang, M.; Zhao, N.; Wei, W.; Sun, Y. Synthesis of Dimethyl Carbonate from Urea and Methanol over ZnO. *Ind. Eng. Chem. Res.* **2005**, *44*, 7596.

(18) 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, Oct 15, 1996.

(19) Ryu, J. Y.; Gelbein, A. P. Process and catalyst for making dialkyl carbonates. U.S. Patent 6,392,078 B1, May 21, 2002.

(20) Suciu, E. N.; Kuhlmann, B.; Knudsen, G. A.; Michaelson, R. C. Investigation of dialkyltin compounds as catalysts for the synthesis of dialkyl carbonates from alkyl carbamates. *J. Organomet. Chem.* **1998**, *556*, 41.

(21) 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*, 21.

(22) Wang, M.; Zhao, N.; Wei, W.; Sun, Y. Synthesis of dimethyl carbonate from urea and methanol over metal oxides. *Stud. Surf. Sci. Catal.* **2004**, *153*, 197.

(23) 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*, 694.

(24) Wang, M.; Zhao, N.; Wei, W.; Sun, Y. Synthesis of dimethyl carbonate from urea and methanol over solid base catalysts. *Catal. Commun.* **2006**, *7*, 6.

(25) Sun, J.; Yang, B.; Wang, X.; Wang, D.; Lin, H. Synthesis of dimethyl carbonate from urea and methanol using polyphosphoric acid as catalyst. *J. Mol. Catal. A: Chem.* **2005**, *239*, 82.

(26) Yao, Y.; Xie, T.; Gao, Y. *Handbook of Physical Chemistry* (in Chinese); Shanghai Science and Technology Press: Shanghai, China, 1985.

(27) Benson, S. W. *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*; Wiley: New York, 1968

(28) Fu, Y.; Zhu, H.; Shen, J. Thermal decomposition of dimethoxymethane and dimethyl carbonate catalyzed by solid acids and bases. *Thermochim. Acta* **2005**, *434*, 88.

(29) Suzuke, E.; Akiyama M.; Ono, Y. Direct transformation of silica into alkoxysilanes by gas−solid reactions. *Chem. Commun.* **1992**, 136.

(30) Taylor, R.; Krishna, R. Modelling reactive distillation. *Chem. Eng. Sci.* **2000**, *55*, 5183.

(31) Sun, Y.; Wei, W.; Zhao, N.; Sun, B.; Zhang, B.; Chen, Y. Catalyst for the synthesis of dimethyl carbonate from urea and methanol, preparation and use thereof. CN1597096, 2005 (see also EP1629888, JP2006061905, US2006047136).