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Synthesis of cyclic carbonates from urea and diols over metal oxides

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Abstract

Several metal oxides were used for synthesis of ethylene carbonate from urea and ethylene glycol. ZnO showed high activity towards the reaction. TPD, FTIR and reaction test indicated that the catalysts with appropriate acid and base properties were favorable to the synthesis of cyclic carbonate. Furthermore, the reaction of urea with various diols revealed that the selectivity of five-membered cyclic carbonates was higher than that of six-membered cyclic carbonates.

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Keywords: Cyclic carbonates; Urea; ZnO; TPD; FTIR; Acid–base properties

1. Introduction

Cyclic carbonates with low toxicity, biodegradability and high boiling point are useful solvents and chemical intermediate. They have many applications as inert solvents, processing agents for the production of polyacrylonitrile fibers, diluents for polyurethanes and epoxy resins, accelerant in dyeing and printing, additive in fuel, lube and hydraulic fluids, separation of carbon dioxide and hydrogen sulfide, component of electrolytes in lithium-ion rechargeable batteries, metal extraction, etc. [1,2]. As chemical intermediates, they are used as monomers for the preparation of polycarbonates and other polymeric materials in the field of engineering plastics, precursors for biomedical applications, protecting groups in carbohydrate chemistry, and as feed for synthesis of dimethyl carbonate (DMC) via transesterification with methanol [3,4].

Cyclic carbonates could be synthesized from diols with phosgene, or with alkyl trichloroacetate [5,6], direct oxidation of olefins with carbon dioxide [7,8], and transesterification of alkylene glycol with alkyl carbonate [9,10]. However, these reactions are not eco-friendly or lack economical viability due to risks associated with the use of the poisonous compounds such as phosgene or the low conversion and yield. Recently, a novel route for synthesis of propylene carbonate from propylene glycol and carbon dioxide was reported [11]. Nevertheless, the yield of propylene carbonate was very low and also limited by the equilibrium. One of valuable approaches for the synthesis of cyclic carbonates is the coupling of carbon dioxide and epoxide cycloaddition reaction [12], and a large number of catalyst systems have been developed for this process, including alkali metal salts, ammonium salts, ionic liquids, metal oxides, transition metal and main group complexes [13–21]. However, these catalysts currently suffered from drawbacks such as low catalyst reactivity or selectivity, the need for co-solvent, or the requirement for high pressure and/or high temperature. Moreover, homogeneous catalysts were disadvantageous in terms of catalyst separation. The exploration of highly efficient heterogeneous catalysts under low temperature and low carbon dioxide pressure still remains a challenging subject.

Urea can be considered as a potential feed for indirect carbon dioxide utilization. Compared with these traditional routes for synthesis of cyclic carbonates, the route from urea and diols has many advantages, such as cheap and easily available raw material without explosiveness and poisons, mild reaction conditions, safe operations and higher yield of product. Especially for the synthesis of dimethyl carbonate (DMC) via transesterification of ethylene carbonate or propylene carbonate with methanol, this approach increases the efficiency of utilization of the raw material and greatly lowers the cost for the production of DMC. As shown in Scheme 1, the by-product ethylene glycol or propylene glycol reacts with urea to produce

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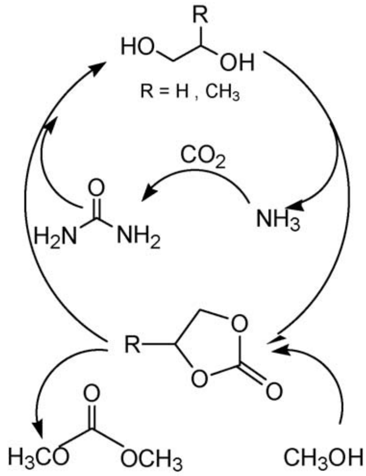


Scheme 1. The cycle routes for synthesis of cyclic carbonates by urea alcoholysis.

ethylene carbonate or propylene carbonate, which is the raw material for the synthesis of DMC. The released ammonia can be recycled to produce urea by reaction with CO_2. So the overall process forms a green chemical cycle.

The reaction of urea with alkylene glycol was first reported by Su and Speranza [22]. However, the decomposition of urea was severe. Doya et al. [23] increased the yield of products by using zinc, magnesium and lead, or their compounds as catalysts under vacuum. Ball et al. [24] investigated the reaction of primary and secondary alcohols with urea to form carbonate and found that the reaction proceeded in two steps. Moreover, the combination of a weak Lewis acid and a Lewis base improved the carbonate formation. Thus, the major aim of the present work was to elucidate the influence of the acid and base properties of the catalysts on cyclic carbonate synthesis.

2. Experimental

2.1. Catalysts preparation

CaO, La_2O_3, MgO, ZnO, ZrO_2, and Al_2O_3 were used as catalysts. CaO was prepared by decomposition of calcium carbonate at 1123 K for 3 h, La_2O_3, MgO, and ZnO were the commercially available reagents. Al_2O_3 was prepared by decomposition of aluminium hydroxide at 923 K for 3 h, and ZrO_2 was prepared by decomposition of zirconium hydroxide at 773 K for 3 h.

2.2. Characterization of catalysts

BET surface areas of the samples were measured at 77 K by nitrogen adsorption using a Micromeritics ASAP-2000 apparatus.

Ammonia gas and carbon dioxide were used as the probe molecule to determine the acid property and base property of the catalysts. About 100 mg of the samples was placed in the quartz reactor bed, and was pretreated by TPD procedure in flowing argon at assigned temperature for 60 min, and then the sample was cooled to room temperature. The molecular probe was pulsed to the reactor by using six-way valve until reaching saturation. Once the physically absorbed molecular probe was purged off, TPD experiment was started with heating rate of 10 K/min under argon flow (50 ml/min), and the effluent was monitored by a Balzers Omnistar^{TM} Mass spectrometer through the whole process.

FTIR spectra were recorded on a Nicolet Magna 550II Fourier-transform infrared spectrometer in the region of 4000–400 cm^{-1}, and were scanned with a resolution of 4 cm^{-1}. The sample was prepared by mixing catalyst and urea with equal mole ratio at 423 K for 30 min under nitrogen gas, then 1 mg mixture samples with 200 mg KBr was grinded completely and pressed into thin disks for scanning.

2.3. Catalytic test for synthesis of cyclic carbonates

The reaction was performed in a 250 ml three-necked-flask equipped with a mechanical agitator and cycle reflux condenser equipped with gas–liquid separators along with thermocouple thermometer. After 0.75 mol diols, 0.5 mol urea and 0.9 g catalysts were charged into the reactor, the reactor was heated to the desired temperature for desired time under vacuum. After reaction, the reactor was cooled to room temperature and solid catalyst was separated from liquid by centrifuge. The products were analyzed by gas chromatography (GC-920) equipped with a HP-5 capillary column and a FID detector. The products were identified by HP-6890 mass spectrometer equipped with a HP-5MS capillary column and HP-5973 mass selective detector.

3. Results and discussion

3.1. Acid and base properties of catalysts

In order to elucidate the difference between the catalysts, acid and base properties of these metal oxide catalysts were examined by TPD of adsorbed NH_3 and CO_2, respectively. The results of catalysts characterizations were listed in Table 1. For NH_3–TPD (see Fig. 1), the amount of acidity for CaO, La_2O_3, MgO and ZnO were less than that of ZrO_2 and Al_2O_3. All the acid sites were located at over 473 K except for La_2O_3 at 427 K. The acid sites for CaO were located at 667 K, for MgO at 483 and 614 K, respectively, and a broad peak at 524 K and a sharp peak at 770 K for ZnO. ZrO_2 showed a broad desorption peaks at 475 and 583 K with a considerable amount of acidity, and Al_2O_3 also had a broad desorption peak at 476 K. For CO_2–TPD (see Fig. 2), CaO showed desorption peaks at 803 K, accompanied by the shoulder peaks at 769, 847 and 919 K. Based on the results of Table 1, this demonstrated that CaO possessed of the strong base sites and base density. The base site of La_2O_3 presented 723 K, and MgO had three desorption peaks at 427, 475 and 557 K. This indicated that La_2O_3 had strong base site and MgO had weak and moderate strength base site. The basic quantity of ZnO was very little and two base sites located at 641 and 687 K. Though there was much basicity on the surface of ZrO_2 and Al_2O_3, the base sites were weak, located at 437 and 439 K, respectively. It can be concluded in

Table 1
The results of catalyst characterization

Entry	Catalyst	S_{BET} ($m^2\ g^{-1}$)	Acidity		Basicity		A/B[a]
			$\mu molNH_3\ g^{-1}$	Peak temperature (K)	$\mu molCO_2\ g^{-1}$	Peak temperature (K)	
1	CaO	9.5	2.30	667	63.66	769, 803, 847	0.036
2	La_2O_3	21	0.54	427	1.69	723	0.32
3	MgO	7.4	3.93	483, 614	17.82	427, 475, 557	0.22
4	ZnO	6.7	1.08	524, 770	0.88	641, 687	1.22
5	ZrO_2	33.4	29.10	475, 583	3.22	437	9.04
6	Al_2O_3	136.5	20.90	476	6.93	439	3.02

[a] Acidity/basicity ratio.

Table 1 that CaO, La_2O_3 and MgO exhibited much more base property than acid property. ZrO_2 and Al_2O_3 were in the opposite way. The acid property was nearly close to base property for ZnO.

3.2. Catalytic activation of urea

Fig. 3 showed the FTIR spectra of urea interacted with various catalysts. Three adsorption bands were observed at 3440, 3350 and 3210 cm^{-1}, which could be assigned to the N–H symmetry stretching vibration and antisymmetry stretching vibration of urea. Two bands at 1670 and 1620 cm^{-1} were corresponded to the C=O stretching vibration and N–H bending vibration of urea, respectively, and the band at 1470 cm^{-1} was attributed to the C–N stretching vibration of urea [25,26]. The band around 2210 cm^{-1} was observed over CaO, La_2O_3, MgO and ZnO, which was assigned to N=C=O asymmetric stretching vibration [27,28], whereas no obvious band at 2210 cm^{-1} appeared over ZrO_2, Al_2O_3 and no catalyst. The peak area at 2210 cm^{-1} in Fig. 3 was listed in Table 2, and the peak area followed such order: ZnO > CaO > MgO > La_2O_3 > Al_2O_3 > ZrO_2. Combined with the acidity of catalysts in Table 1, it was considered that the formation of isocyanic species was promoted by the catalysts with appropriate acid density and acid sites.

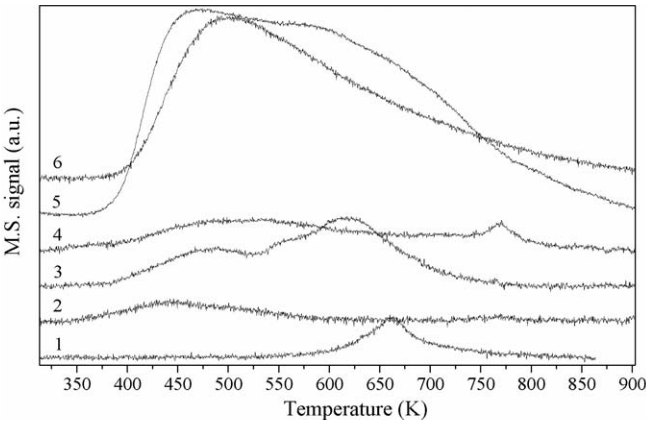


Fig. 1. NH_3–TPD of metal oxides: (1) CaO; (2) La_2O_3; (3) MgO; (4) ZnO; (5) ZrO_2; (6) Al_2O_3.

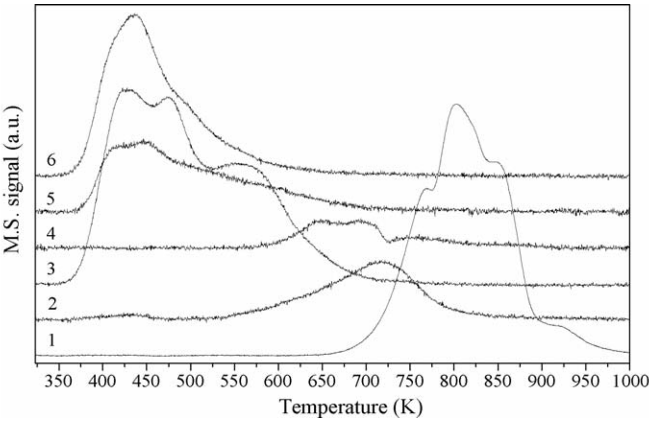


Fig. 2. CO_2–TPD of metal oxides: (1) CaO; (2) La_2O_3; (3) MgO; (4) ZnO; (5) ZrO_2; (6) Al_2O_3.

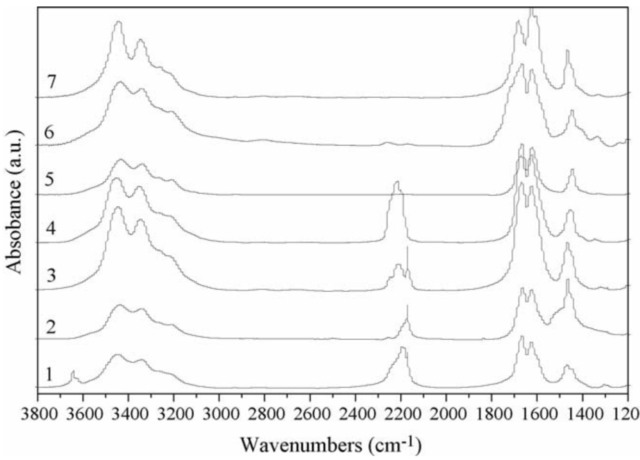
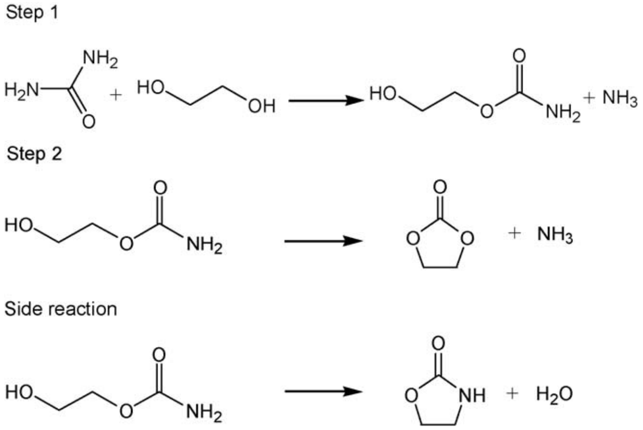


Fig. 3. FTIR spectra of urea interacted with metal oxides: (1) CaO; (2) La_2O_3; (3) MgO; (4) ZnO; (5) ZrO_2; (6) Al_2O_3; (7) no catalyst.

Table 2
The peak area around 2210 cm^{-1} in Fig. 3

Entry	Catalysts	Peak area at 2210 cm^{-1}
1	CaO	77.5
2	La_2O_3	24.1
3	MgO	43.3
4	ZnO	82.1
5	ZrO_2	0.8
6	Al_2O_3	4.1
7	Non-catalyst	0.5



Scheme 2. Synthesis of ethylene carbonate from urea and ethylene glycol.

3.3. Catalytic performance of synthesis cyclic carbonates

The catalytic performance was tested for the synthesis of ethylene carbonate from urea and ethylene glycol. According to the GC–MS analysis of the reaction product mixture, the major components were ethylene glycol, ethylene carbonate, 2-hydroxyethyl carbamate, and 2-oxazolidone. Obviously, the synthesis of ethylene carbonate from urea and ethylene glycol was a multiple reaction system, and the reaction procedure was proposed in Scheme 2.

The reaction for the synthesis of ethylene carbonate proceeded in two steps, 2-hydroxyethyl carbamate was formed at the first step, and then the ethylene carbonate was produced by loss of ammonia from 2-hydroxyethyl carbamate. The side reaction was occurred by dehydration reaction of 2-hydroxyethyl carbamate to form 2-oxazolidone.

The results of catalytic performance were listed in Table 3. In the absence of catalyst, the yield of ethylene carbonate was only 32.3%, and the yield of 2-hydroxyethyl carbamate was 36.8%. For ZrO_2 and Al_2O_3, the yields of ethylene carbonate were 31.1% and 28.7%, respectively. It could be considered that the acid property catalyst restrained the reaction at some extent. For CaO, La_2O_3 and MgO, the yield of ethylene carbonate were 65.7%, 72.0% and 84.5%, and the yield of 2-oxazolidone were 13.2%, 8.1% and 5.2%, respectively. It showed that the catalysts with stronger base were disadvantaged to increase the yield of ethylene carbonate. Moreover, the strong base catalyst was inclined to promote the by-product (2-oxazolidone) formation. ZnO showed high activity for the formation of ethylene carbonate, and the yield was 93.1%. Compared with the catalytic activation for synthesis of ethylene carbonate, the results of catalytic activation for urea in Table 2 exhibited the similar regularity except for CaO (probably because of much 2-oxazolidone formed). Only when the urea was activated, could the synthesis of ethylene carbonate have high yields. It indicted that the catalytic activation of urea had an important function for the synthesis of ethylene carbonate. Summing-up all these catalytic performances, it could be concluded that the catalysts with appropriate acid and base properties were favorable to the synthesis of ethylene carbonate.

The synthesis of cyclic carbonates from urea and various diols were performed over ZnO (see Table 4.). It was found that the high selectivity of five-membered cyclic carbonates could be obtained from diols and urea. However, the selectivity of

Table 3
Catalytic performance of metal oxides for synthesis of ethylene carbonate

Catalysts	Glycol conversion (%)	Urea conversion (%)	Yield (%)		
			2-Hydroxyethyl carbamate	Ethylene carbonate	2-Oxazolidone
None	21.5	69.1	36.8	32.3	0
CaO	43.7	79.9	1	65.7	13.2
La_2O_3	48.3	87.4	7.5	72	8.1
MgO	56.0	94.1	4.4	84.5	5.2
ZnO	62.6	97.8	3.9	93.1	0.6
ZrO_2	20.6	70.8	39.6	31.1	0
Al_2O_3	19.0	71.2	42.5	28.7	0

Reaction conditions: temperature 423 K, pressure 11 kPa, time 180 min. Note: the yields of the products were based on the urea conversion.

Table 4
Synthesis of cyclic carbonates from urea and various diols

Diols	Cyclic carbonates	Cyclic carbonates selectivity (%)	Urea conversion (%)
1,2-Ethanediol	1,2-Ethylene carbonate	97.1	97.9
1,2-Propanediol	1,2-Propylene carbonate	99.8	99.8
1,2-Butanediol	1,2-Butylene carbonate	99.8	99.8
2,3-Butanediol	2,3-Butylene carbonate	94.1	98.2
1,2-Cyclohexanediol	1,2-Cyclohexylene carbonate	95.3	94.9
1,3-Propanediol	1,3-Propylene carbonate	83.3	87.6
1,3-Butanediol	1,3-Butylene carbonate	83.1	89.4

Reaction conditions: temperature 423 K, pressure 11 kPa, time 240 min.

Table 5
Influence of reaction time for synthesis of ethylene carbonate

Time (min)	Urea conversion (%)	Selectivity (%)	
		2-Hydroxyethyl carbamate	Ethylene carbonate
30	69.9	43.8	56.2
60	85.3	12.2	87.2
120	95.0	4.8	94.5
180	97.8	4.0	95.3
240	99.7	3.3	96.1
300	99.2	3.2	96.2

Reaction conditions: temperature 423 K, pressure 11 kPa.

Table 6
Effect of reaction temperature for synthesis of ethylene carbonate

Temperature (K)	Pressure (kPa)	Urea conversion (%)	Selectivity (%)		
			2-Hydroxyethyl carbamate	Ethylene carbonate	2-Oxazolidone
413	8	80.1	11.1	88.2	0.7
423	11	97.8	4.1	95.3	0.6
433	18	95.4	1.8	96.8	1.4
443	26	89.2	1.0	94.2	4.8

Reaction conditions: time 180 min. Note: the relation of temperature and pressure was affected by Antoine equation of ethylene glycol.

six-membered cyclic carbonates was lower than that of five-membered cyclic carbonates. It was reported that the different vicinal glycols reacted with urea to synthesize corresponding cyclic carbonates [22]. The selectivity of cyclic carbonate was affected by the polarity of vicinal glycols, and the greater polarity of the vicinal glycol had an adverse effect on the selectivity of cyclic carbonate. Herein we thought the reaction was influenced by the difference of dimensional structure between 1,2-diols and 1,3-diols.

3.4. Influence of reaction conditions

The influence of reaction time for the synthesis of ethylene carbonate over ZnO was showed in Table 5. The conversion of urea increased with the prolonged reaction time, and the selectivity of 2-hydroxyethyl carbamate decreased from 43.8% to 3.2%. Especially the transformation was very obvious within 120 min, after which the selectivity of ethylene carbonate increased gradually. It was demonstrated that 2-hydroxyethyl carbamate was the reaction intermediate. The formation of 2-hydroxyethyl carbamate was a fast reaction in the first step, and the formation of ethylene carbonate by 2-hydroxyethyl carbamate loss of ammonia was a rate controlling step.

The effect of reaction temperature for the synthesis of ethylene carbonate over ZnO was showed in Table 6. When the temperature was raised, the conversion of urea increased at first, and then decreased; moreover, the selectivity of ethylene carbonate had the similar rule. Although the transformation of 2-hydroxyethyl carbamate was promoted by the raised temperature, the selectivity of 2-oxazolidone was enhanced. So it was very important to have a proper temperature for the synthesis of ethylene carbonate.

4. Conclusions

The acid and base properties were measured by TPD, CaO, La_2O_3 and MgO exhibited much more base property than acid property. ZrO_2 and Al_2O_3 were in the opposite way. The acid property was nearly close to base property for ZnO. Catalytic activation of urea indicated that the formation of isocyanic species was promoted by the catalysts with appropriate acid density and acid sites, moreover, only when the urea was activated, could the synthesis of ethylene carbonate have high yields. The catalysts with stronger base were inclined to promote the by-product formation. So the catalysts with appropriate acid and base properties were favorable to the synthesis of ethylene carbonate, furthermore for the synthesis of other five-membered cyclic carbonates also had high selectivity by urea alcoholysis.

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