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Review

Catalytic performance of metal oxides for the synthesis of propylene carbonate from urea and 1,2-propanediol

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Abstract

The influences of acid–base properties of metal oxides on the catalytic performance for synthesis of propylene carbonate from urea and 1,2-propanediol was investigated, and the reaction was stepwise. The amphoteric ZnO showed the best activity, and the yield of propylene carbonate reached 98.9%. The urea decomposition over oxides was characterized by using FTIR. ZnO, CaO, MgO and La_2O_3 were favorable to promote urea decomposition to form the isocyanate species, and the formation of isocyanate species was the key to urea alcoholysis. The catalytic activity of urea decomposition was consistency to the catalytic performance for synthesis of propylene carbonate. Based on these, the probable reaction mechanism was proposed.
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Keywords: Propylene carbonate; Urea; Metal oxides; Acid–base properties

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1. Introduction

Propylene carbonates have been found numerous applications as both inert solvents and reactive intermediates. As an excellent solvent with low toxicity, biodegradability and high boiling point, propylene carbonates favors many applications, such as processing agent for the production of polyacrylonitrile fibers, additives in fuel, lube and hydraulic fluids; separation of carbon dioxide and hydrogen sulfide, component of electrolytes in lithium-ion rechargeable batteries, etc. As reactive intermediates, propylene carbonates is used for pharmaceutical and polymer synthesis [1,2], and for the production of dimethyl carbonate (DMC) via transesterification with methanol [3,4].

Propylene carbonates could be synthesized from 1,2-propanediol with phosgene, transesterification of 1,2-propanediol with alkyl carbonate [5,6], direct oxidation of olefins with carbon dioxide [7,8]. However, these reactions are not eco-friendly or lack economical viability due to risks associated with the use of the poisonous compounds or the low conversion and yield. Now propylene carbonates are mainly produced industrially by the cycloaddition of carbon dioxide with propylene oxide [9], which causes serious safety problems because propylene oxide is a dangerous chemical substance. Furthermore, these homogeneous catalysts [10–20], including alkali metal salts, ammonium salts, ionic liquids, transition metal and main group complexes, 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, and catalyst separation as well.

Compared with those traditional routes for synthesis of propylene carbonates, the route from urea and 1,2-propanediol shows advantages, such as cheap and easily available feedstock, mild reaction condition and safe operation. The synthesis of alkylene carbonates from urea and alkylene glycol was first revealed by Su and Speranza [21] over a toxic organictin catalyst or without any catalysts, and the yield of propylene carbonates reached 84%. Doya et al. [22] improved the yield of propylene carbonates up to 97% by using a catalyst of zinc, magnesium, lead, and calcium or their compounds under vacuum, which was the innovative work. However, only the results of propylene carbonate at different reactive conditions was given as reaction examples in the patent. Zhao et al. [23] reported the catalysts performance of homogeneous and supported zinc acetate, and the yield of propylene carbonates reached 94% and 78%, respectively. Ball et al. [24] considered that the urea alcoholysis reaction for synthesis of organic carbonates proceeded in two steps. The carbamate was formed very quickly in the first step, and the rate of the subsequent reaction to carbonates was very low. The stepwise process for synthesis of propylene carbonate from urea and 1,2-propanediol over oxides was not identified yet. The present work was aimed to confirm the reaction process and elucidate the influences of acid–base properties of metal oxides on the catalytic performance for synthesis of propylene carbonate, and then focused on the understanding of the reaction mechanism of urea alcoholysis.

2. Experimental

2.1. Preparation of catalysts

CaO, La_2O_3, MgO, ZnO, ZnS, ZrO_2 and Al_2O_3 were used as catalysts. CaO was prepared by decomposition of calcium carbonate at 850 °C for 3 h, La_2O_3, MgO, ZnO and ZnS were the commercially available reagents. ZrO_2 was prepared by decomposition of zirconium hydroxide at 500 °C for 3 h, and Al_2O_3 was prepared by decomposition of aluminum hydroxide at 650 °C for 3 h.

2.2. Characterization of catalysts

2.2.1. BET measurement

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

2.2.2. Temperature programmed desorption-mass spectrometry experiments

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

2.2.3. FTIR spectrometry of catalytic activation of urea

The sample was prepared by mixing catalyst and urea with equal mol ratio at 150 °C for 30min under nitrogen gas, then 1 mg mixture samples and 200 mg KBr were ground completely and pressed into thin disks for scanning. 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}.

2.3. Catalytic test

The reaction was performed in a 250 mL three-necked-flask, which was equipped with a mechanical agitator, cycle reflux condenser along with gas–liquid separators and thermocouple thermometer. After 0.75 mol 1,2-propanediol, 0.5 mol urea and 0.6 g catalysts were charged into the reactor, the reactor was heated to 170 °C for 2 h at a pressure of 280 mmHg. After reaction, the reactor was cooled to room temperature and solid catalyst was separated from liquid by centrifuge.

The products were identified by HP-6890 equipped with a HP-5MS capillary column and HP-5973 mass selective detector, and analyzed by gas chromatography (GC-920) equipped with a HP-5 capillary column and a FID detector.

Table 1
BET surface area and acid–base properties of metal oxides

Entry	Catalyst	S_{BET} (m^2/g)	Acidity (μmol/g)	Basicity (μmol/g)	A/B[a]
1	CaO	9.5	2.30	63.66	0.04
2	La_2O_3	21.0	0.54	1.69	0.32
3	MgO	7.4	3.93	17.82	0.22
4	ZnO	6.7	1.02	0.98	1.04
5	ZnS	35.2	31.31	0.54	57.64
6	ZrO_2	33.4	29.10	3.22	9.04
7	Al_2O_3	136.5	20.90	6.93	3.02

[a] Acidity/basicity ratio.

3. Results

3.1. Acid and base properties

In order to illustrate the difference of acid–base properties of catalysts, CaO, La_2O_3, MgO, ZnO, ZrO_2, Al_2O_3 along with ZnS (as the comparison with ZnO) were measured by CO_2-TPD and NH_3-TPD, respectively. The data in Table 1 indicated that the dominant character of CaO, La_2O_3 and MgO were basic (A/B < 1), ZnS, ZrO_2 and Al_2O_3 showed acidic (A/B > 1), but ZnO almost had equal acid–base properties (A/B ≈ 1).

Fig. 1 shows CO_2-TPD profile of metal oxides (basicity). CaO gave desorption at 530 °C with shoulder peaks at 495 and 575 °C, La_2O_3 at 450 °C, and MgO at 154, 201 and 280 °C, respectively. ZnO showed a little desorption at 351 and 395 °C. For acidic oxides, ZnS almost had no adsorption, ZrO_2 and Al_2O_3 gave desorption at 161 and 165 °C, respectively. These results suggested that besides strong basic oxides CaO and La_2O_3, MgO showed both moderate and weak basic sites, ZnO between La_2O_3 and MgO, while ZrO_2 and Al_2O_3 were weak.

Fig. 2 shows NH_3-TPD spectra (acidity). Those oxides all had a certain adsorption towards ammonia. CaO gave desorption at 394 °C, La_2O_3 around 154 °C, and MgO at 210 and 345 °C, respectively, ZnO showed desorption at 251 and 497 °C. The acidity was very little for amphoteric ZnO and basic oxides, but their acidic site led to the following order: ZnO > CaO > MgO > La_2O_3. For acidic oxides, ZnS gave desorption at 357 °C, Al_2O_3 at 206 °C, and ZrO_2 at 202 and 311 °C, respectively, and a wide range of their acidic sites from 100 to 500 °C was remarkable. Their acidity was much higher than that of CaO, La_2O_3, MgO and ZnO (see Table 1). However, the acidity was hardly related with BET surface area. It might be determined by their cationic properties, i.e. the electrophilicity of metal cations. For instance, the larger amount of acidity over ZnS than ZnO might be due to that the electronegativity of sulfur atom is lower than that of oxygen atom, which further influenced the electrophilicity of zinc cation. Thus, ZnS, ZrO_2 and Al_2O_3 had high acidity compared with the others.

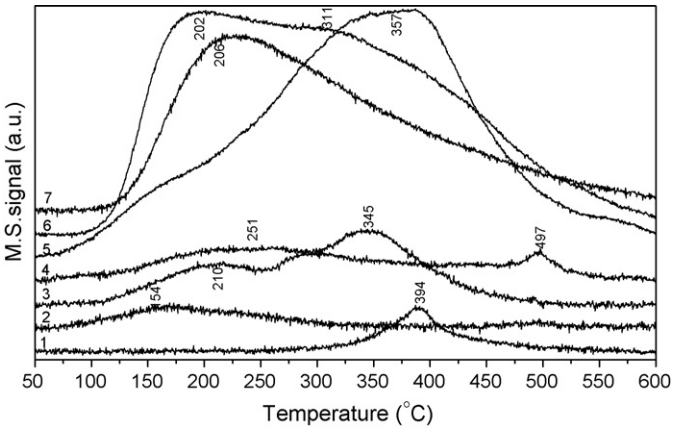


Fig. 2. NH_3-TPD of catalysts (1, CaO; 2, La_2O_3; 3, MgO; 4, ZnO; 5, ZnS; 6, ZrO_2; 7, Al_2O_3).

3.2. Urea activation

Fig. 3 shows the FTIR spectra of urea interacted with various metal oxides. The absorbance at 3440, 3350 and 3210 cm^{-1} were assigned to the N–H symmetry stretching vibration and antisymmetry stretching vibration of urea, respectively. The bands at 1670 and 1620 cm^{-1} were attributed to the C=O stretching vibration and N–H bending vibration of urea, respectively, and the band at 1470 cm^{-1} was due to the C–N stretching

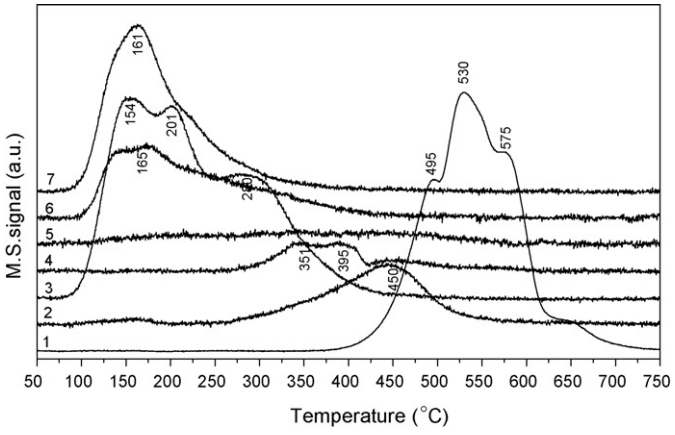


Fig. 1. CO_2-TPD of catalysts (1, CaO; 2, La_2O_3; 3, MgO; 4, ZnO; 5, ZnS; 6, ZrO_2; 7, Al_2O_3).

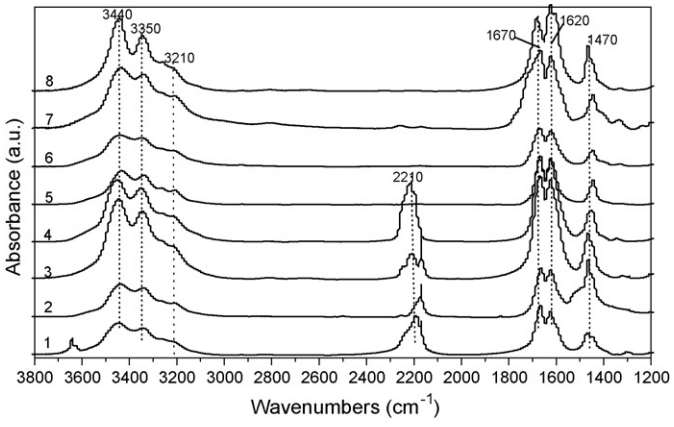


Fig. 3. FTIR spectra of urea interacted with catalysts (1, CaO; 2, La_2O_3; 3, MgO; 4, ZnO; 5, ZnS; 6, ZrO_2; 7, Al_2O_3; 8, blank).

vibration of urea [25,26]. Those absorbance resulted from urea itself. However, it was worth noting that the band around 2210 cm^{-1}, which could be assigned to N=C=O asymmetric stretching vibration of isocyanate species [27,28], was clearly observed over CaO, La_2O_3, MgO and ZnO, but no obvious absorbance at 2210 cm^{-1} appeared over ZnS, ZrO_2 and Al_2O_3. The appearance of isocyanate species could be considered to be indicative of the activation ability of oxide towards urea decomposition. Thus, acidic oxides hardly showed any catalytic activation. Toward amphoteric and basic oxides, their activation ability appeared to be in accordance with the order of their acidic site: ZnO > CaO > MgO > La_2O_3. The higher acidic site was, the stronger electrophilicity of metal cation was. This indicated that the metal cations of amphoteric ZnO and basic oxides with strong electrophilicity were favorable to the formation of isocyanate species by urea decomposition.

3.3. Catalytic performance

According to the identification of mixture products by GC-MS, the major components were 1,2-propanediol, propylene carbonate, and 2-hydroxypropyl carbamate. The reaction for synthesis of propylene carbonate from urea and 1,2-propanediol appeared to proceed in two steps. 2-hydroxypropyl carbamate was formed in the first step, and then propylene carbonate was formed by the loss of ammonia from 2-hydroxypropyl carbamate. The by-product (4-methyl-2-oxazolidone) was produced over some catalysts by the dehydration of 2-hydroxypropyl carbamate.

Among the catalysts, ZnO showed the best performance. Fig. 4 shows the influence of the reaction time without and with the presence of ZnO, respectively. Without ZnO, the selectivity of 2-hydroxypropyl carbamate was higher than that of propylene carbonate. In the presence of ZnO, the selectivity of 2-hydroxypropyl carbamate decreased rapidly with the reaction time prolonged, and the selectivity of propylene carbonate increased swiftly. Therefore, the synthesis of propylene carbonate from urea and 1,2-propanediol was a typical stepwise reaction. At the initial stage, there produced a large amount of 2-hydroxypropyl carbamate, it indicated that the formation of 2-hydroxypropyl carbamate was fast. The catalytic performance of ZnO was remarkable during the conversion of 2-hydroxypropyl carbamate to propylene carbonate. Hence the second step was the rate-determined step. Furthermore, without the catalysts, the yields of propylene carbonate and 2-hydroxypropyl carbamate were 40.7% and 48.6%, respectively (see Table 2). With the presence of Al_2O_3, ZrO_2 and ZnS, the yields of propylene carbonate only reached 38.9%, 40.1% and 39.5%, respectively. This implied that the reaction was suppressed at a certain extent over acidic oxides. Among the others, amphoteric ZnO showed high activity for the synthesis of propylene carbonate with the yield up to 98.9%, and MgO, La_2O_3 and CaO gave the yields of propylene carbonate of 92.9%, 86.8% and 74.6%, and the yields of 4-methyl-2-oxazolidone of 1.4%, 2.2% and 3.8%, respectively. Thus, the strong basic oxides were inclined to promote the formation of by-product.

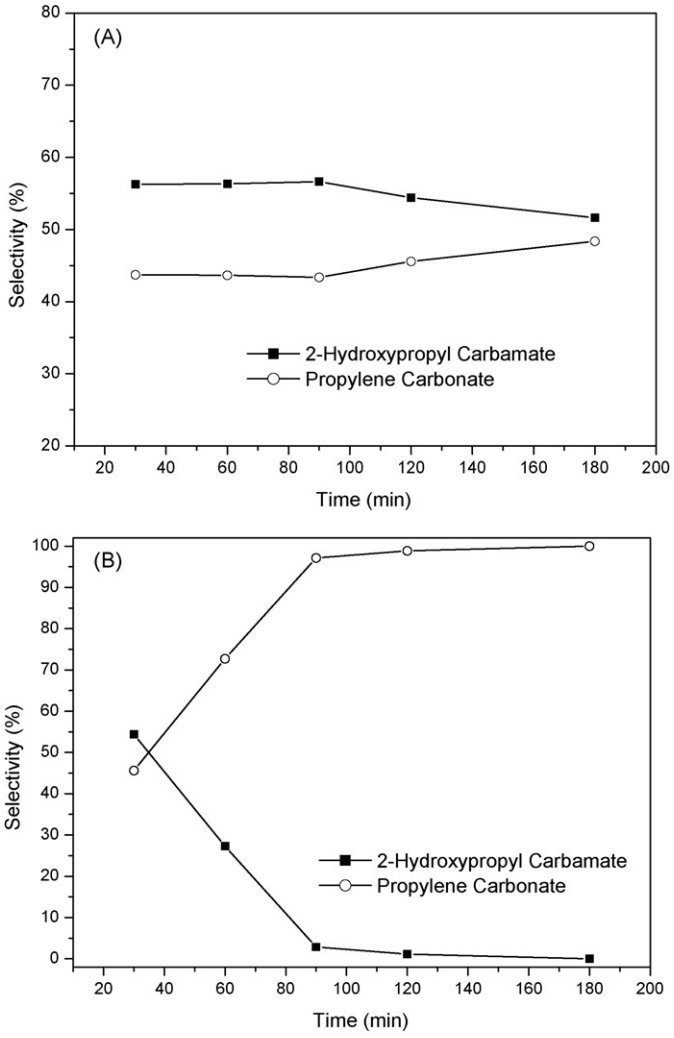


Fig. 4. Influence of reaction time without and with ZnO catalyst (A, without catalyst; B, ZnO catalyst).

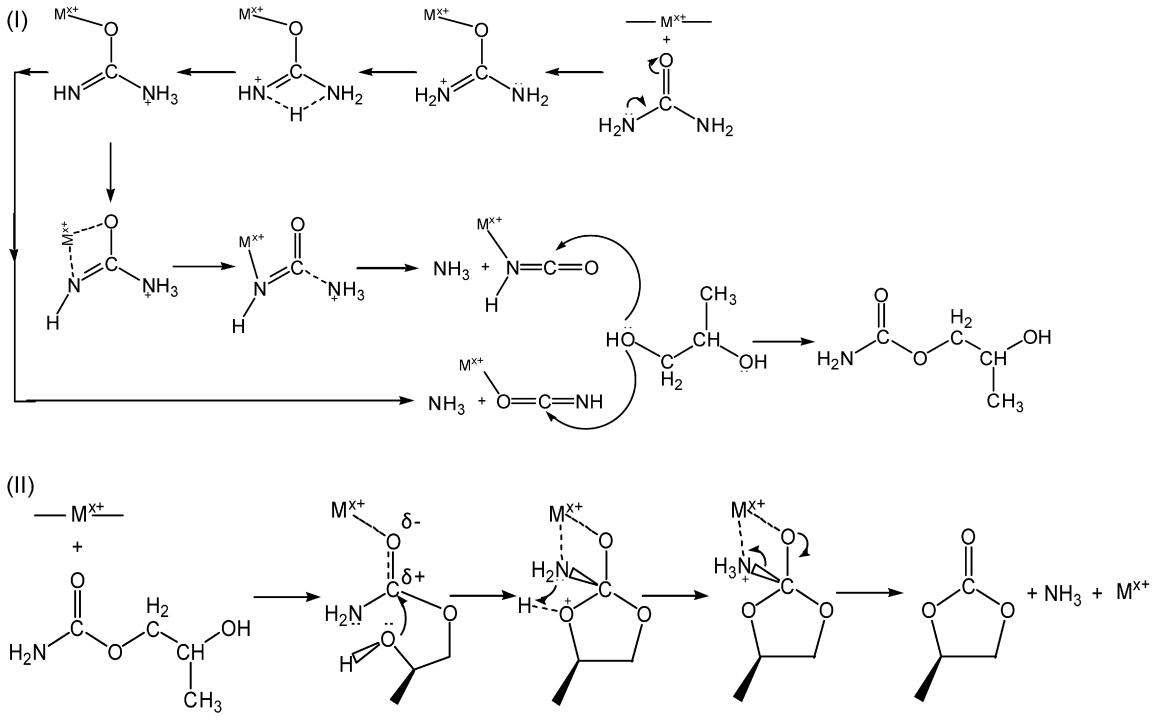
4. Discussion

4.1. Activated decomposition of urea

Urea, had three coordination sites (one oxygen and two nitrogen atoms) [29], and was commonly considered as basic substance [30]. The charge numbers of O and N atom in the urea

Table 2
Catalytic performance of metal oxides for synthesis propylene carbonate

Catalysts	Conversion (%) urea	Yield (%)		
		2-Hydroxypropyl carbamate	Propylene carbonate	4-Methyl-2-oxazolidone
Blank	89.3	48.6	40.7	0
Al_2O_3	90.4	51.5	38.9	0
ZrO_2	92.8	52.7	40.1	0
ZnS	89.8	50.3	39.5	0
ZnO	100.0	1.1	98.9	0
MgO	97.7	2.8	92.9	1.4
La_2O_3	94.3	5.6	86.8	2.2
CaO	85.6	7.2	74.6	3.8



Scheme 1. The mechanism of synthesis propylene carbonate over metal oxides.

molecule were −0.492 and −0.375, respectively, which were calculated by HyperChem 7 based on ZINDO/1 semi-empirical method. On the basis of these, the molecule of urea could be considered as the donor of electron-pair. The metal cations of oxides exhibited different electrophilicity, and they were the acceptor of electron-pair. Thus, the urea molecule could be interacted with metal cations to form the coordination structure.

FTIR of urea over oxides indicated that the metal cations of amphoteric and basic oxides with strong electrophilicity were favorable to the formation of isocyanate species, and acidic oxides hardly showed any catalytic activation toward urea decomposition. As well-known, urea was stable due to its resonance structures [31], and then the direct decomposition of urea to isocyanic acid was not easy. When amphoteric oxide or basic oxide interacted with urea, the resonance stabilization was decreased through metal cation of oxide coordinating with O atom in urea molecule. This promoted the formation of isocyanate species by expulsion of ammonia over a series of electron transformation [32]. And then 1,2-propanediol added to isocyanate species to produce 2-hydroxypropyl carbamate. The detailed reaction mechanism of this process was listed in Scheme 1 (I). As for acidic oxides, the electrophilicity of metal cation was extra-strong. They interacted with O and N atom in urea molecule simultaneously to form a steady ligand, which restrained the electron transformation and then the loss of ammonia became difficult. Thus, acidic oxides hardly had any catalytic activity toward urea decomposition.

4.2. Synthesis of propylene carbonate

The relationship between the area of isocyanate species in FTIR and the yield of propylene carbonate over oxides (see Fig. 5) indicated that the activity of catalytic urea decomposition appeared to parallel with the catalytic performance for synthesis of propylene carbonates except for CaO. The acidic oxides had no activity, amphoteric ZnO showed the highest activity, and the basic oxides were active towards the reaction as well. But CaO showed the lowest catalytic performance for synthesis of propylene carbonate. Besides the formation of 4-methyl-2-oxazolidone, the decomposition of propylene carbonate by strong base should be another negative factor [33]. It was considered that there were similar in the reaction mechanism between the catalytic decomposition urea and the conversion of 2-hydroxypropyl carbamate to propylene carbonate on the basis of their consistency. Thus, the mechanism for synthesis of propylene carbonate was proposed in Scheme 1(II). First the

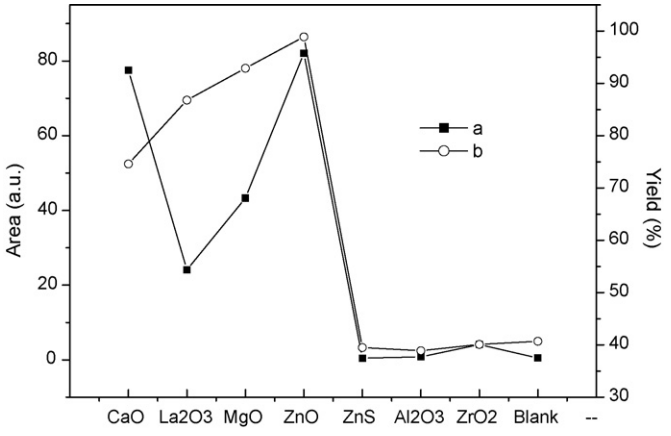


Fig. 5. The relationship between the area of isocyanate species in FTIR and the yield of propylene carbonate over oxides (a, isocyanate species in FTIR; b, propylene carbonate).

oxygen in carbonyl of 2-hydroxypropyl carbamate interacted with metal cation of oxide, and increased the electropositivity of carbon in carbonyl. Then oxygen in hydroxyl attacked carbon in carbonyl to form the tetrahedron transition state, and the metal cation had a tendency to close with the group of NH_2. Simultaneously, NH_2 combined with proton hydrogen to form the positive ion group of NH_3. In the end the propylene carbonate was produced by expulsion of ammonia. ZnO showed the best catalytic activity in the process, while the activity decreased for basic oxides with strong basic sites. The strong basic site (oxygen in oxide) was inclined to interact with hydrogen in hydroxyl of 2-hydroxypropyl carbamate, and then the nitrogen with unshared electron-pair attacked the carbon close to hydroxyl. It promoted the dehydration reaction to form 4-methyl-2-oxazolidone. For acidic oxides, the metal cation with extra-strong electrophilicity coordinated with the oxygen in hydroxyl of 2-hydroxypropyl carbamate, and restrained the formation of tetrahedron transition state. Thus, they had no catalytic activity.

5. Conclusions

The synthesis of propylene carbonate from urea and 1,2-propanediol was stepwise reaction, and the second step was rate-determined. The acid–base properties of metal oxides had a great influence on the catalytic performance for the reaction. The amphoteric ZnO had the best catalytic activity, while the activity decreased for basic oxides with strong basic sites, and acidic oxides showed no activity. Urea was catalyzed decomposition to form the isocyanate species in the process of alcoholysis at first. The metal cations of amphoteric and basic oxides with strong electrophilicity were favorable to the formation of isocyanate species. The acidic oxides hardly had any catalytic activity toward urea decomposition. There were consistency between the catalytic performance for synthesis of propylene carbonate and the catalytic activity of urea decomposition. The formation of isocyanate species played an important role in the reaction. The catalysis in the conversion of 2-hydroxypropyl carbamate to propylene carbonate was also the key. When the formation of tetrahedron transition state was promoted, the yield of propylene carbonate increased.

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