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Synthesis of dimethylcarbonate from urea and methanol catalyzed by various metal oxides and salts

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Abstract: Various metal oxides and metallic salts were used as a catalyst in the synthesis of dimethyl carbonate (DMC) from urea and methanol in an autoclave. The results indicated that the hydrated metallic salt is most catalytically active in DMC synthesis among various metal oxides and salts considered in this work. Furthermore, a binary catalyst, viz, $Zn(NO_3)_2$ combined with hydroxyl containing compounds, can noticeably enhance the yield of DMC, in comparison with the single catalyst of both $Zn(NO_3)_2$ and the hydroxyl containing compound, which may be ascribed to a synergistic effect between $Zn(NO_3)_2$ and the hydroxyl group. Among various binary catalysts, $Zn(NO_3)_2$-SiO_2 exhibits the best catalytic performance; the yield of DMC reaches 4.5% over $Zn(NO_3)_2$-SiO_2 with a $Zn(NO_3)_2$ to SiO_2 weight ratio of 2.

Keywords: dimethyl carbonate; urea; methanol; methanolysis; binary catalyst; metallic salt; metal oxide; hydroxyl
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Dimethyl carbonate (DMC), as an environmentally benign building block, becomes more and more important in the chemical industry[1,2]. It can be used as a methylating and carbonylating agent to replace the extremely toxic ones such as phosgene and dimethyl sulphate (DMS). In addition, it is also an ideal additive for gasoline due to its high oxygen content and octane value[3]. Industrially, DMC is mainly produced through methanol oxy-carbonylation and trans-esterification[4~6]. Recently, urea methanolysis has been developed to produce DMC, which has several advantages such as the abundant resource and low cost for raw materials, and especially the convenience for product separation, as no water is formed in this process and then the formation of ternary methanol-water-DMC azeotrope can be avoided.

For the synthesis of DMC from urea and methanol, urea is firstly converted into methyl carbamate (MC) (Eq. (1)) with a yield over 90%, and MC is then converted further with methanol into DMC (Eq. (2)); the later is the rate-controlling step. Because of the thermodynamic restriction, the conversion is in general rather low. Due to the endothermic nature of the second step, one may shift the reaction equilibrium to the direction of DMC by removing NH_3 from the reacting system or increasing temperature, to enhance the yield of DMC.

$$NH_2CONH_2+CH_3OH=NH_2COOCH_3+NH_3 \quad (1)$$

$$NH_2COOCH_3+CH_3OH=CH_3OCOOCH_3+NH_3 \quad (2)$$

A number of catalysts have been used for the synthesis of DMC from urea and methanol, including organotin, alkali oxide, polyphosphoric acid, Lewis acids, Lewis bases, mixed metal oxides, and so on[7~10], in which both nucleophilic site and electrophilic site were considered catalytically active.

In this work, various metal oxides and metallic salts were used as a catalyst in the synthesis of DMC from urea and methanol in an autoclave. The roles of various components such as metal and hydroxyl group in the catalytic reaction were investigated.

1 Experimental

1.1 Catalyst preparation

Aluminum hydroxide was purchased from Tianjin Damao Chemical Reagent Company and Phenol-formaldehyde resin (ab. PR) from Fushun Weite Chemical Co., Ltd.

CaO was obtained by thermal decomposition of calcium carbonate at 800 ℃ for 2 h. Other metal oxides were prepared through precipitation method. For an example, 31 g of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) was dissolved in 50 mL of distilled water and 45 mL of ammonia water was then trickled constantly into the solution. After that, the mixed solution was heated at 80 ℃ for 3 h and then filtered to obtain a gel. The gel was dried at 120 ℃ for 12 h to obtain $Zn(OH)_2$, which was finally calcined at 500 ℃ for 3 h in air to yield ZnO catalyst. ZnO-CeO_2 was prepared by following the similar procedures.

Silica was prepared through sol-gel method. 20.8 g TEOS and 7.4 g *n*-butanol were mixed and heated to 80 ℃; HNO_3 was dropped into the mixture

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until the pH value reached 2.5. The mixture was stirred at 80 ℃ for 5 h and then evaporated to obtain a gel. The gel was dried at 120 ℃ for 12 h and then calcined at 550 ℃ for 4 h.

1.2 Catalyst characterization

XRD patterns of ZnO, CaO and ZnO-CeO_2 catalysts were collected on a X-Ray diffractometer (Rigaku, D-MAX2500-PC) using Cu $K\alpha$ radiation (λ = 0.154 056 nm) operated at 50 kV and 100 mA. TG-DTG-DSC measurements was performed on a STA449C-QMS 403C thermal analyzer in N_2 flow (20 mL/min) with a heating rate of 10 ℃/min. FT-IR measurements was carried out on Nicolet 6700 spectrometer; the catalyst sample was heated in helium for 6 h at 120 and 170 ℃ and then the sample cell was evacuated, to get the adsorption spectrum at room temperature.

1.3 Synthesis of DMC from urea and methanol

2 L stainless steel autoclave with electric heating and stirring was used as the reactor. In a typical test, 16 g (0.267 mol) of urea was added in 162 mL (4 mol) of methanol under stirring, which was then transferred into autoclave together with 8 g of catalyst. The molar ratio of methanol to urea in the feed was 15 and the catalyst accounted for 6% of the total mass; the catalytic reaction was then conducted at 170 ℃ for 6 h. After that, the reactor was cooled down to room temperature and then depressurized. The product samples were analyzed by a gas chromatograph (HP 7820A, FID) equipped with a DB-FFAP capillary column (30 m × 0.530 mm × 1.0 μm). The injection temperature and detector temperature were both 250 ℃ and helium was used as carrier gas with a flow rate of 20 mL/min; the column temperature was kept in 35 ℃ for 17 min and then increased to 230 ℃ at a heating rate of 10 ℃/min. The external standard method was adopted for the quantitative analysis of DMC and MC.

2 Results and discussion

2.1 Urea methanolysis over different catalysts

Table 1 summarizes the reaction results for DMC synthesis from urea and methanol catalyzed by different metal oxides and salts (Entries 1 ~ 7). As $Zn(NO_3)_2 \cdot 6H_2O$ (Entry 1) and $CeCl_3 \cdot 7H_2O$ (Entry 4) are more active than other catalysts, Zn^{2+} and Ce^{3+} are probably the catalytically active centers, in view of their electrophilic attack to the reactant molecules. Meanwhile, it seems that hydrate may also play an important role in catalysis. The metallic salts without hydrate show comparatively lower catalytic activity than those with hydrate (Entries 5 ~ 7). Three metallic salts without hydrate water give a DMC yield below 2.5% (Entries 5 ~ 7), whereas those with hydrate give a DMC yield above 3.0% (Entries 1 ~ 4). As moisture adsorption may occur for the metallic salts without hydrate, only newly purchased chemicals was used to minimizing the effect of additional water adsorbed in metallic salt on the reaction.

Table 1 Catalytic performance of metallic salts and oxides in urea methanolysis

Entry	Catalyst	MC yield w/%	DMC yield w/%
1	$Zn(NO_3)_2 \cdot 6H_2O$	45.7	3.5
2	$Zn(Ac)_2 \cdot 2H_2O$	48.8	3.0
3	$Ce(NO_3)_3 \cdot 6H_2O$	45.9	3.2
4	$CeCl_3 \cdot 7H_2O$	50.1	3.4
5	$ZnBr_2$	57.9	2.4
6	$ZnCl_2$	59.2	2.4
7	$Zr(NO_3)_2$	51.2	1.6
8	CaO	44.9	1.3
9	ZnO	51.2	2.8
10	ZnO-CeO_2	55.7	3.1
11	ZnO-$CeCl_3 \cdot 7H_2O$	44.7	3.1
12	ZnO-$Ce(NO_3)_3 \cdot 6H_2O$	47.8	2.6

reaction was carried out at 170 ℃ for 4 h, with n(methanol)/n(urea) ratio of 15 and catalyst amount of 2% by weight, in Entries 10 ~ 12, the ratio of m(Zn)/m(Ce) is 1

The XRD patterns of three metal oxides used in this work are shown in Figure 1. Metal oxides have been intensively used as an active catalyst in many processes and it is then expected that they may also be catalytically effective in urea methanolysis. As given by Entries 8 ~ 10 in Table 1, the yield of DMC over these metal oxides is closely related to the basicity of metal oxide, as the basicity of a catalyst played a significant role in the formation of methoxyl from methanol[10]. On the other hand, the amphoteric

centers (acidity and basicity) on ZnO are more favorable for the formation of methoxyl[11~14]. Furthermore, ZnO doped with a proper ratio of amphoteric centers gave a better catalytic performance[14,15]. In this work, ZnO exhibits a moderate catalytic activity and ZnO-CeO_2 is most active among three metal oxides, in accordance with those observed in the literature[16]. Nevertheless, the performance of ZnO-CeO_2 is poorer than $Zn(NO_3)_2 \cdot 6H_2O$ and $CeCl_3 \cdot 7H_2O$.

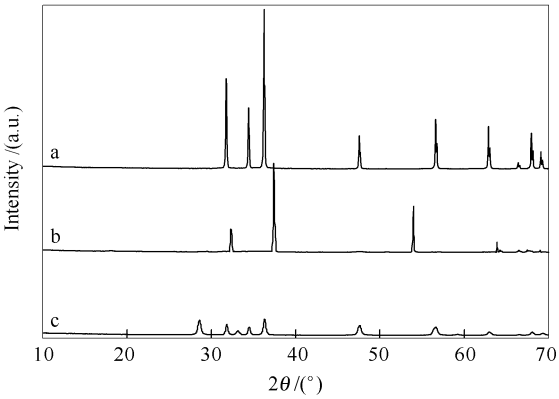

Figure 1　XRD patterns of various metal oxides
a: ZnO; b: CaO; c: ZnO-CeO_2

It should be noted that urea provides an alkaline environment in the reaction system, in which metallic salt with hydrate may be partly transformed into metal oxide. As a result, the metallic salt catalyst may actually act as a mixture of salt and oxide; to prove this suspicion, ZnO mixed with either $CeCl_3 \cdot 7H_2O$ or $Ce(NO_3)_3 \cdot 6H_2O$ was applied as the catalyst for urea methanolysis (Table 1, Entries 11 and 12). However, the results indicate that the mixture has a similar performance as the pure hydrated metallic salts; a combination of two components cannot improve their catalytic activity, viz., there is not a synergy between ZnO and hydrated metallic salt.

2.2　Urea methanolysis over different binary catalysts

A series of hydroxyl containing compounds are also used in urea methanolysis; however, as given in Table 2, no DMC was detected in the product, indicating that these hydroxyl containing compounds alone are catalytically inactive for DMC synthesis.

When these hydroxyl containing compounds are combined with the active metallic hydrate catalyst ($Zn(NO_3)_2$), however, the catalytic performance of $Zn(NO_3)_2$ in DMC synthesis is significantly altered, as illustrated in Figures 2~5.

To optimize the performance of binary catalysts, the effect of weight ratio of two components on the yields of DMC and MC in urea methanolysis for various binary catalysts was then investigated (Figures 2~5). Figure 2 displays that the catalytic activity of $Zn(NO_3)_2$ towards DMC synthesis by urea methanolysis cannot be promoted by adding $Zn(OH)_2$; highest DMC yield of 2.7% is achieved over $Zn(NO_3)_2$-$Zn(OH)_2$ with a weight ratio of 3:1, which is however almost the same as that obtained over single $Zn(NO_3)_2$. Moreover, excessive $Zn(OH)_2$ may even promote the decomposition of DMC and other side reactions and then reduce the DMC yield[16,17].

Table 2　Catalytic performance of various hydroxides in urea methanolysis to DMC

Catalyst	MC yield w/%	DMC yield w/%
$Zn(OH)_2$	54.2	0
SiO_2	55.3	0
$Al(OH)_3$	52.9	0
Phenol-formaldehyde resin	49.3	0

reaction was carried out at 170 ℃ for 4 h, with n(methanol)/n(urea) ratio of 15 and catalyst amount of 2% by weight

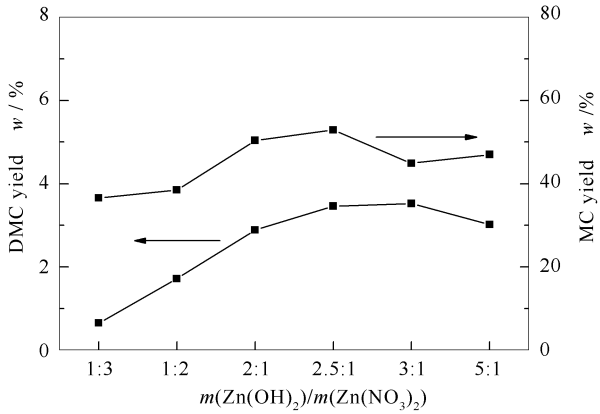

Figure 2　DMC and MC yields over the mixture of $Zn(NO_3)_2$ and $Zn(OH)_2$ with different weight ratios

$Al(OH)_3$ shows a positive effect on the catalytic performance (Figure 3). Over $Zn(NO_3)_2$-$Al(OH)_3$ with an optimal weight ratio of 6, the yield of DMC reaches 4.05%, a bit higher than that obtained over single $Zn(NO_3)_2$. Meanwhile, excessive amount of $Al(OH)_3$ promoter has little effect on the catalytic performance.

Over the binary catalysts of $Zn(NO_3)_2$-PR and $Zn(NO_3)_2$-SiO_2, PR and SiO_2 have a similar effect on the yields of DMC and MC, as shown in Figures 4 and 5. The yield of DMC increases initially with the amount of promoter, levels off at a plateau, and then decreases with further increasing the amount of promoter. The yield of MC also increases at the beginning and then reaches a plateau with the promoter amount. $Zn(NO_3)_2$-SiO_2 with a weigh ratio

of 2 provides the highest DMC and MC yields under the same reaction conditions; the yields of DMC and MC reach 4.5% and 58%, respectively. All these results indicate that there is a catalytic synergy between the hydroxyl containing compound and Lewis acid $Zn(NO_3)_2$.

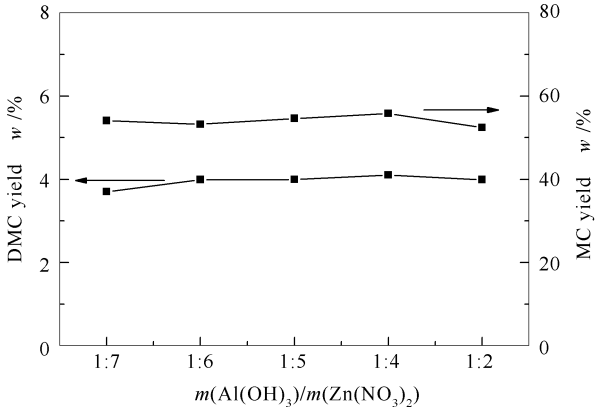

Figure 3 DMC and MC yields over the mixture of $Zn(NO_3)_2$ and $Al(OH)_3$ with different weight ratios

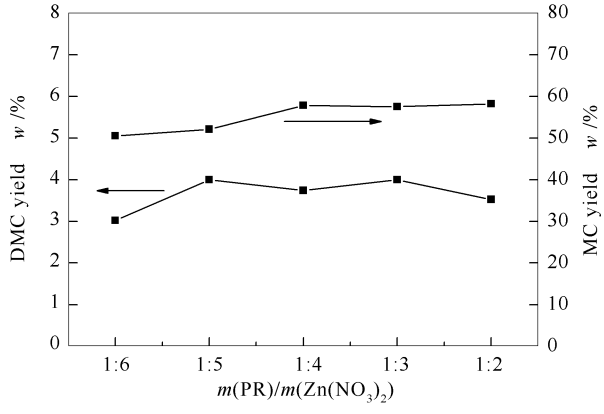

Figure 4 DMC and MC yields over the mixture of $Zn(NO_3)_2$ and PR with different weight ratios

2.3 Characterization of the hydroxyl containing compounds

TG-DTG-DSC curves of three promoters (SiO_2, $Al(OH)_3$ and $Zn(OH)_2$) are shown in Figure 6. The weight loss around 100 ℃ is attributed to the removal of adsorbed water and the weight loss between 100 and 200 ℃ to water occluded in the inner pore. The weight loss between 250 and 600 ℃ is ascribed to the removal of water produced by hydroxyl condensation reaction. No weight loss happens beyond 600 ℃. Hydroxyl can be distinguished in the promoters, as the weight losses of SiO_2 at 500 ℃, $Al(OH)_3$ at 300 and 500 ℃, and $Zn(OH)_2$ at 300 ℃. Figure 6 indicates that the OH amounts in $Al(OH)_3$ and $Zn(OH)_2$ are higher than that in SiO_2, but the strength of hydrogen bonding in SiO_2 should be stronger than those in $Al(OH)_3$ and $Zn(OH)_2$. As a result, it may be proposed that the strength of hydrogen bonding in the hydroxyl containing compounds is closely related to the performance of binary catalysts; the strong hydrogen bonding between silanol species at SiO_2 surface and MC formed by urea methanolysis may weaken the C–N bond in MC molecule and promote the formation of DMC[18].

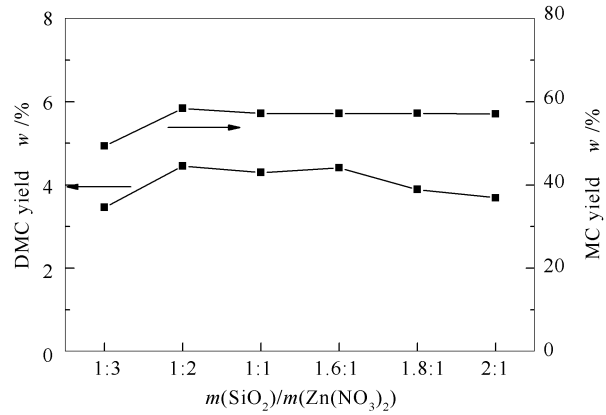

Figure 5 DMC and MC yields over the mixture of $Zn(NO_3)_2$ and SiO_2 with different weight ratios

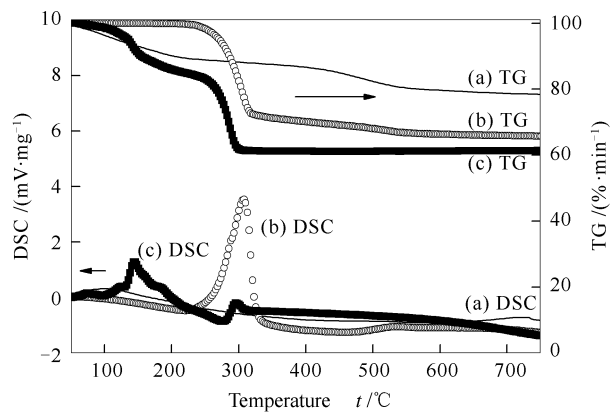

Figure 6 DTG-DSC profiles of (a) SiO_2, (b) $Al(OH)_3$ and (c) $Zn(OH)_2$

3 Conclusions

Various metal oxides and metallic salts were used as a catalyst in the synthesis of DMC from urea and methanol. The results indicated that the hydrated metallic salt is most catalytically active in DMC synthesis among various metal oxides and salts considered in this work.

Furthermore, a binary catalyst, viz, $Zn(NO_3)_2$ combined with hydroxyl containing compounds, can noticeably enhance the yield of DMC, in comparison with the single catalyst of both $Zn(NO_3)_2$ and the hydroxyl containing compound, which may be ascribed to a synergistic effect between $Zn(NO_3)_2$ and the hydroxyl group.

Among various binary catalysts, $Zn(NO_3)_2$/

SiO_2 exhibits the best catalytic performance; the yield of DMC reaches 4.5% over $Zn(NO_3)_2/SiO_2$ with a $Zn(NO_3)_2$ to SiO_2 weight ratio of 2. Such a catalytic system may be potential in the urea methanolysis to produce DMC.

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金属氧化物和盐催化剂上尿素与甲醇合成碳酸二甲酯

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摘　要: 在高压釜中采用金属氧化物和盐作为催化剂由尿素与甲醇合成碳酸二甲酯。结果表明,含有结晶水的金属盐比无结晶水金属盐和金属氧化物具有更好的催化活性。采用羟基化合物与硝酸锌组成的二元催化剂,其催化活性显著高于单一催化剂;羟基与硝酸锌之间具有协同催化作用。其中,硝酸锌与 SiO_2 组成的二元催化剂活性最高;硝酸锌与 SiO_2 的质量比为 2 时,DMC 收率可达 4.5%。

关键词: 碳酸二甲酯; 尿素; 甲醇; 醇解; 双组分催化剂; 金属盐; 金属氧化物; 羟基

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