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RESEARCH PAPER

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

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 latter 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°C 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 of mL ammonia water was then trickled constantly into the solution. After that, the mixed solution was heated at 80°C for 3 h and then filtered to obtain a gel. The gel was dried at 120°C for 12 h to obtain $Zn(OH)_2$, which was

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finally calcined at 500°C 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°C; HNO_3 was dropped into the mixture until the pH value reached 2.5. The mixture was stirred at 80°C for 5 h and then evaporated to obtain a gel. The gel was dried at 120°C for 12 h and then calcined at 550°C 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 = 0.154056 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°C/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°C 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°C 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°C and helium was used as carrier gas with a flow rate of 20 mL/min; the column temperature was kept in 35°C for 17 min and then increased to 230°C at a heating rate of 10°C/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.

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].

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°C 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