

Preparation of Solid Superacid $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ and Its Action on Synthesis of Dimethyl Carbonate from Urea and Methanol

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ABSTRACT: $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ catalyst was prepared by sulfating ZnO-TiO_2 powders with H_2SO_4 solution. The catalyst was characterized by XRD, IR and Hammett indicator. The catalyst showed strong acidity ($H_0 \leq -16.0$). The optimum conditions are found that the calcination temperature is 823K and the soaked consistency of H_2SO_4 is 1 mol/dm³. Then $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ was applied as the catalyst in the catalytic synthesis of dimethyl carbonate (DMC) from urea and methanol under the optimum conditions and revealed higher catalytic activity. On condition that the reaction time is 6h, the reaction temperature is 433K, the mass percent of the catalyst used in the reactants is 5wt.%, and the molar ratio of methanol to urea is 14, the yields of DMC can reach 27.9%.

KEY WORDS: Preparation, Solid superacid, Synthesis, Dimethyl carbonate, Catalytic activity.

INTRODUCTION

DiMethyl Carbonate (DMC) has been considered as an environmentally benign compound and unique intermediate with versatile chemical reactivity. Since DMC contains several active basic groups like CH_3 -, CH_3O -, $\text{CH}_3\text{O-CO}$ -, $-\text{CO}$ - groups, it shows excellent reaction activity in carbonylation, carbomethoxylation and methylation, replacing toxic phosgene, dimethyl sulfate, etc [1-3]. The synthesis of DMC has attracted much attention in recent years. And the synthesis techniques reported mainly consist of phosgenation of methanol, oxidative carbonylation of methanol and transesterification of ethylene carbonate with methanol, etc [4-6]. However, each of the above mentioned processes has either commercial or technical disadvantage, which make it desirable in the industry to develop a new

process which avoids such setbacks. The alcoholysis of urea for producing DMC is a new process developed recently [7]. In this method, DMC is prepared from urea and methanol under a definite temperature, pressure and the existence of catalyst, the starting materials have abundant resources and low cost. The most active catalysts reported in the prior literatures are organotin derivatives and metal oxides. But there exist some problems such as low DMC yield, difficult to handle the homogeneous production and so on, which is far from satisfactory. In order to overcome the problems, many researchers had carried out a great deal of work. Wang *et al.* [8] had used heterogeneous solid bases catalysts to prepare DMC by urea methanolysis method and discussed the function of solid base catalysts.

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Wu et al. [9] carried out comprehensive research on the catalytic property of Zn-based catalyst for the reaction of urea and methanol to DMC. Lin et al. [10] proposed a new route for producing dimethyl carbonate (DMC) from urea and methanol catalyzed by the organotin. Wu et al.' experimental results showed that the modified V_2O_5 catalysts were effective for the direct and selective synthesis of DMC from carbon dioxide and methanol [11]. However, to the best of our knowledge, few studies on synthesis of dimethyl carbonate using solid acid catalyst have been reported. SO_4^{2-}/M_xO_y solid acid has many advantages, such as easy separation, strong acidity and high activity, well thermal stability and low corrosiveness, which has attracted great attentions and has been applied in many aspects [12].

In this paper, $SO_4^{2-}/ZnO-TiO_2$ catalyst was prepared and characterized by XRD, IR and Hammett indicators. The $SO_4^{2-}/ZnO-TiO_2$ solid acid was applied as the catalyst to synthesis dimethyl carbonate at the first time. During the experiment, according to Sun's experimental results, CO_2 was applied to pressurize the autoclave to restrain the side reaction and a small amount of polyphosphoric acid was used as the absorbent for the ammonia to simplify the technical process [13]. The effects of catalyst preparation conditions and reaction conditions on DMC yield were systematically discussed in the experiments.

EXPERIMENTAL SECTION

Materials and measurements

Methanol(A.R), urea(A.R) were commercial reagents, which were purchased from Tianjin Chemical Reagents of China. PPA(C.R. $P_2O_5 \geq 80.0\%$, high viscosity colorless liquid), also commercial reagent, was purchased from Chengdu Chemical Reagents of China. DMC was purchased as analytically pure reagents from Shanghai Chemical Reagent. Titanium dioxide(HR3), average particle size: 20 ± 5 (nm), specific surface area: 640 ± 30 (m^2/g). All other chemicals were commercial products of reagent grade.

X-ray powder diffraction patterns of the catalysts were carried out on a Japanese D/max-2400 X-ray diffraction system with $CuK\alpha$ radiation at room temperature. This diffractometer was operated at 40 KV and 60 mA. The range of the spectra in 2θ was from 10° to 90° .

InfRared (IR) spectra were recorded using a Bruker Equinox55 Fourier Transform InfRared (FT-IR) spectrophotometer equipped with a DTGS detector.

The acid strength of $SO_4^{2-}/ZnO-TiO_2$ was determined by Hammett indicators.

The distilled part contained DMC and methanol was analyzed by a gas chromatograph (GC 2000) using a Rtx-1 capillary column ($15m \times 0.53mm \times 1.5\mu m$, column temperature: 333 K) and hydrogen Flame Ionization Detector (FID). The external standard method was adapted to the quantitative analysis of DMC.

Preparation of $SO_4^{2-}/ZnO-TiO_2$ solid acid catalyst

The ZnO-TiO₂ composite oxide was prepared by homogeneous precipitation method. $Zn(NO_3)_2$ aqueous solution mixed with nano-TiO₂ was ultrasonic vibrated for 20min, then 28% ammonia water was dropped into the mixed aqueous solution under stirring at 343K until the pH reaches to 7~8. The obtained precipitate was dried at 373K, followed by calcination at 673K for 1h. The above obtained powders were sulfated with a solution of sulfuric acid ($1.0 \text{ mol} \cdot \text{dm}^{-3}$) for 1 h. Finally the sample was dried under atmosphere at 373K and calcinated at 823K for 3 h to get the $SO_4^{2-}/ZnO-TiO_2$ catalyst.

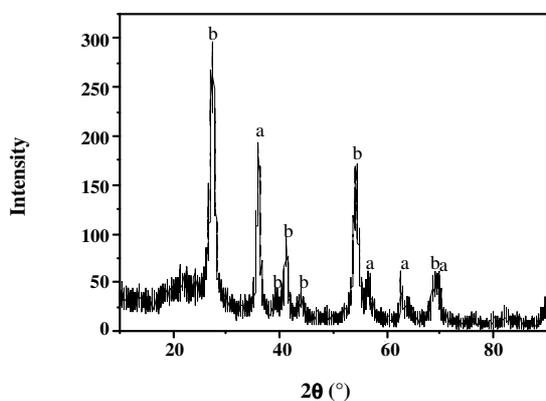
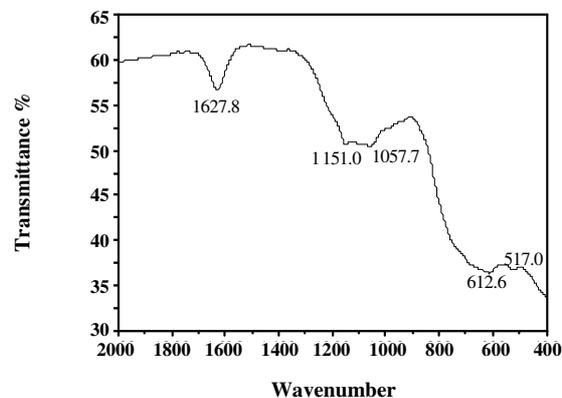
Catalytic activity test

The experiments were carried out in a stainless steel 100mL autoclave with electric heating and dynamoelectric stirring. Urea(0.1mol), $SO_4^{2-}/ZnO-TiO_2$ powder, methanol and PPA(3mL) were added to the autoclave in turn. The autoclave was firstly flushed with carbon dioxide to replace air within the reactor, then the autoclave was pressurized with carbon dioxide to the pressure of about 0.6 MPa and was heated to the desired temperature with stirring (the stirring speed was adjusted to about 900 rpm). After the reaction was completed, the reaction mixture was formed into two phases by centrifugal separation. The upper layer was liquid phase containing DMC, methanol and the excess PPA. The under layer was solid phase containing ammonium polyphosphate. The mixture of DMC and methanol was obtained after the liquid phase part was simply distilled at a temperature of 337–373K under atmospheric pressure. The distilled part involved DMC and methanol.

Table 1: Acid strength of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ catalyst samples.

H_2SO_4 concentration ($\text{mol}\cdot\text{dm}^{-3}$)	0.2	0.6	1.0	1.5
2,4-DNFB ($H_0 = -14.5$)	-	+	+	-
1,3,5-TNB ($H_0 = -16.0$)	-	-	\pm	-

+: color changed clearly; \pm : color changed unclearly; -: color was unchanged.

**Fig. 1: The XRD spectra of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$.****Fig. 2: The FT-IR spectra of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$.**

RESULTS AND DISCUSSION

Catalyst characterizations

X-ray powder diffraction analysis of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$

Fig. 1 shows the X-ray powder diffraction spectra of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ solid acid calcinated at 823K. Compared the spectra with standard card, a points shown in Fig. 1 corresponds to ZnO (Standard diffraction card JCPDS 36-1451), b points shown in Fig.1 corresponds to TiO_2 (Standard diffraction card JCPDS 21-1276). This result suggests that ZnO- TiO_2 composite oxide is formed. After introducing SO_4^{2-} ions, the thermal stability of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ is increased.

Infrared spectrum of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$

Fig. 2 shows the IR spectrum of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$. As can be seen in Fig.2, the vibration peak at 1627.8 cm^{-1} contributes to the vibration mode of adsorbed water, the vibration peak at 1151.0 cm^{-1} contributes to the vibration mode of Ti-OH. The peaks at 1150.9 cm^{-1} and 1057.7 cm^{-1} contribute to asymmetry and symmetrical flex vibration mode of O-S-O, respectively. The peaks at 612.6 cm^{-1} and 517.0 cm^{-1} contribute to adsorb vibration mode of rutile TiO_2 and Ti-O, respectively.

Acid strength of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$

The acid strength of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ catalyst

was tested by means of Hammett indicators. As shown in Table 1, the change of color of two adsorbed indicators could be observed on $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ when the soaked concentration of H_2SO_4 was $1.0\text{ mol}\cdot\text{dm}^{-3}$, showing that it was super acid and its acidity achieved -16.0 .

Effect of the preparation conditions of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ solid acid

Effect of the soaked concentration of H_2SO_4 on DMC yield

Table 2 shows the effect of the soaked concentration of H_2SO_4 on DMC yield. From Table 2, it can be found that DMC yield reaches 27.9% when the soaked concentration of H_2SO_4 is $1.0\text{ mol}/\text{dm}^3$. The soaked concentration of H_2SO_4 is higher or lower, DMC yield will decline. Thus, the soaked concentration of H_2SO_4 of $1.0\text{ mol}\cdot\text{dm}^{-3}$ was selected in the following experiments.

Effect of calcination temperature on DMC yield

Table 3 shows the effect of calcination temperature of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ solid acid on DMC yield. According to Table 3, it can be observed that DMC yield reaches 27.9% when the calcination temperature is 823K. The calcination temperature is higher or lower, DMC yield will decrease. Hence, the calcination temperature of 823K was selected in the experiments.

Table 2: Effect of the soaked concentration of H_2SO_4 on DMC yield.

H_2SO_4 concentration (mol/dm ³)	0.2	0.6	1.0	1.5
DMC yield (%)	18.6	23.4	27.9	21.7

Table 3: Effect of calcination temperature on DMC yield.

Calcined temperature (K)	623	723	823	923
DMC yield (%)	19.7	22.5	27.9	20.3

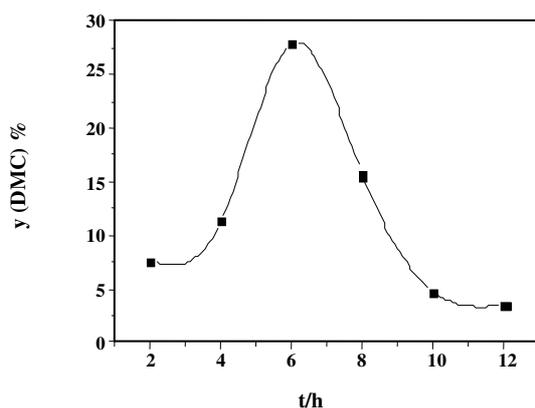


Fig. 3: The effect of reaction time on DMC yield. Reaction temperature: 433K, the mass percent of catalyst: 5wt.%, methanol/urea molar ratio:14, the stirring speed: 900rpm.

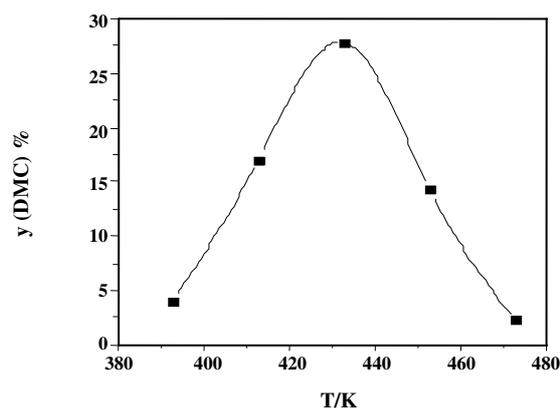


Fig. 4: The effect of reaction temperature on DMC yield. The mass percent of catalyst: 5wt.%, reaction time:6h, methanol/urea molar ratio:14, the stirring speed: 900rpm.

Effect of the reaction conditions on DMC yield

Effect of reaction time on DMC yield

Fig. 3 shows the effect of reaction time on DMC yield. According to Fig.3, it can be observed that DMC yield increases rapidly before 6h and the DMC yield reaches 27.9% at 6 h. Then, the DMC yield decreases with reaction time of increasing. This is the reason that the side reactions will be serious and lead to DMC concentration fall after reaction time of 6h. Thus, the optimal reaction time of 6h was selected.

Effect of reaction temperature on DMC yield

The reaction temperature affects the DMC synthesis reaction as shown in Fig. 4. Obviously, the DMC yield sharply increases in a range of 393–433K. The DMC yield decreases when reaction temperature exceeds 433K. This is due to that the higher temperature can lead to the decrease of carbon dioxide absorption on catalysts [14]. Also higher reaction temperature can cause thermal decomposition of urea and MC, and increase in the rate of side reactions of DMC with urea and MC. Hence, 433K is the optimal reaction temperature for the synthesis of DMC.

Effect of $SO_4^{2-}/ZnO-TiO_2$ amount on DMC yield

The effect of catalyst amount on DMC yield is shown in Fig. 5. From Fig. 5, the DMC yield increases with increasing catalyst amount. However, when the catalyst amount reaches 5wt.%, the DMC yield will decline with the increasing catalyst amount. For this reaction, higher catalyst concentration can lead to the consuming of DMC by secondary reaction earlier. Therefore, the mass percentage of catalyst 5wt.% was selected in this process.

Effect of methanol/urea molar ratio on DMC yield

The effect of methanol/urea initial molar ratio on DMC yield is shown in Fig.6. It can be known that DMC yield increases with increasing molar ratio of initial methanol/urea. When the molar ratio of methanol/urea is lower, the urea concentration will become higher and the decomposition of urea and MC will take place in a higher reaction temperature. When the molar ratio of initial methanol/urea is higher than 14:1, the DMC yield begins to fall. The reason is that the higher methanol/urea initial molar ratio would result in lower urea concentration and it would reduce the reaction rate. Thus, the methanol/urea initial molar ratio 14:1 was selected.

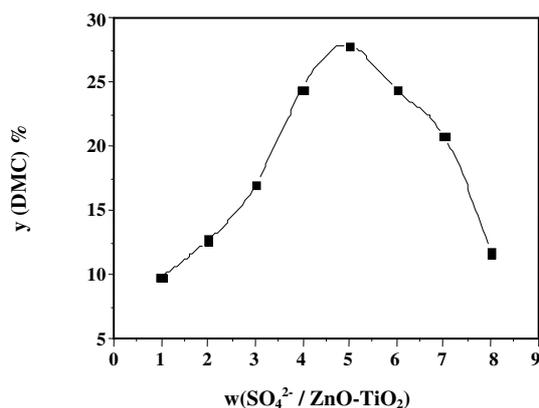


Fig. 5: The effect of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ amount on DMC yield. Reaction temperature:433K, reaction time:6h, methanol/urea molar ratio:14, the stirring speed: 900rpm.

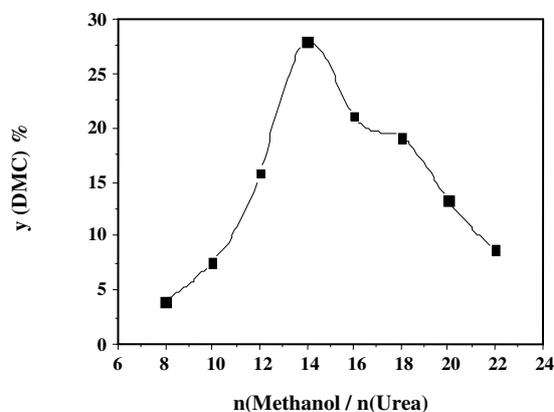


Fig. 6: The effect of methanol/urea molar ratio on DMC yield. Reaction temperature:433K, reaction time:6h, the mass percent of catalyst:5wt.%, the stirring speed: 900rpm.

CONCLUSIONS

In this paper, $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ solid acid catalyst was prepared by sulphating ZnO-TiO_2 powders with H_2SO_4 solution and its catalytic activity was investigated by the synthesis of DMC from urea and methanol in a batch autoclave. The catalyst showed strong acidity ($\text{H}_0 \cong -16.0$). The factors, such as the calcination temperature, the soaked concentration of H_2SO_4 , reaction temperature, reaction time, the molar ratio of methanol/urea and catalyst mass percent on the activities of $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ catalyst, were systematically investigated in the experiment. The optimal reaction conditions were obtained.

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