



Effect of MgO on the catalytic performance of MgTiO₃ in urea alcoholysis to propylene carbonate



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HIGHLIGHTS

- Preparation and characterization of MgTiO₃ catalyst.
- Synergistic effect between MgTiO₃ and MgO improved the catalytic activity.
- The amount of aggregated MgO on the surface of MTO-1.0 was the maximum.
- The loss of MgO led the catalytic activity to decrease.

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ABSTRACT

The perovskite MgTiO₃ catalyst was prepared by the sol–gel method and characterized by X-ray diffraction (XRD), temperature-programmed desorption of CO₂ (CO₂-TPD) and energy dispersive spectroscopy (EDS). The catalytic behavior was also investigated for the urea alcoholysis to propylene carbonate (PC). It was found that the preparation conditions of MgTiO₃, including calcination temperature, calcination time and Mg/Ti molar ratio, affected the aggregation of MgO on the surface of MgTiO₃. Aggregated MgO could promote a synergistic effect with MgTiO₃ to change the basic performances on the surface, which resulted in the activity difference. When MgTiO₃ was prepared at calcination temperature of 700 °C, the calcined time of 3 h and the Mg/Ti molar ratio of 1.0, the synergistic effect was the strongest, which led to the highest activity. The yield and the selectivity of PC were up to 93.5% and 99.0%, respectively. An increased number of reuse of the catalyst, resulted in a loss of MgO from the catalyst surface, thereby reducing the overall catalytic activity.

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1. Introduction

Propylene carbonate (PC), an excellent polar organic solvent with high boiling point has been widely used in the fields of organic synthesis, gas separation and electrochemical techniques [1,2]. At present, PC is mostly used in the production of dimethyl carbonate (DMC) through transesterification with methanol [3–7]. The methods for the synthesis of PC include phosgene processes [2], transesterification of alkyl carbonate with propylene glycol (PG) [8], reaction of carbon dioxide with o-chloropropanol [9], cycloaddition of propylene oxide with CO₂ [10–17], and urea alcoholysis [17–22]. Among these, the urea alcoholysis, in which PC is prepared from urea and 1,2-propylene glycol (1,2-PG), shows many advantages, such as cheap and easily available raw materials, mild reaction conditions, and environment friendly that

conform to the development of green chemical industry requirements [18,19].

Su and Speranza [20] first reported the production of alkylene carbonates from urea and alkylene glycol over tin-containing catalyst, where the conversion of alkylene glycol was 66%. Doya et al. [21] improved the yield of PC to 97% by using a catalyst of zinc, magnesium, lead, calcium or their compounds under vacuum. Zhao et al. [22,23] used zinc acetate and supported zinc acetate catalyst in this reaction and showed that the yield of PC was 94% over zinc acetate and 78% over supported zinc acetate catalysts. Wu et al. [24] reported that for the monolith supported zinc–chromium mixed oxide catalyst, the monolithic stirrer reactor performs very well, and the highest yield of propylene carbonate reaches 97.8%. Gao et al. [25] used zinc chloride and magnesium chloride as catalyst and the yield of PC was 96.5% under vacuum. Li et al. [26,27] found that metal oxide (ZnO, CaO, MgO, PbO, La₂O₃) catalysts with appropriate acidity and basicity were favorable for the synthesis of cyclic carbonate. Previously, we have found that the base

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properties on the surface of M/HAP (M = Li, K, Mg, La) play an important role in the alcoholysis of urea [28].

Oxides with a perovskite structure (ABO_3) are attracting great attention as catalysts in oxidation, hydrogenation and hydrogenolysis reactions due to great flexibility in their crystal lattice to accommodate cation substitutions, high redox properties and control of their base properties, and a variety of metal ions can be introduced into the perovskite structure [29]. Mg, Ca, Pb and Zn, which showed high catalytic activity in the alcoholysis of urea, are traditionally used as the A elements in ABO_3 perovskite-type composite oxide. When A is a metal taking a divalent state in ABO_3 , B is commonly Ti or Zr in tetravalent state. Because Ti is cheaper than Zr, $ATiO_3$ is selected as the matrix, and Mg, Ca, Sr, Ba, Pb or Zn was introduced into the A position in $ATiO_3$ to obtain the catalysts with different acid-base properties. Our preliminary studies showed that $MgTiO_3$ was superior to other catalysts with respect to the PC yield of 93.5% and selectivity of 99.0%, so its catalytic performance in the alcoholysis of urea was investigated in detail.

2. Experimental

2.1. Chemical reagents

All reagents with A.R. (Analytical Reagent) purity were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification.

2.2. Preparation of the catalysts

The catalysts were prepared by a sol-gel method. The detailed procedure is as follows: Tetrabutyl titanate (0.02 mol) dissolved in 40 mL glacial acetic acid was marked as the solution A. Magnesium nitrate (0.02 mol) dissolved in 30 mL deionized water was marked as the solution B. Under vigorous stirring, solution B was first added drop wise slowly into solution A, followed by the addition of 10 mL anhydrous ethanol to the mixture. On concentrating the mixture solution in a rotavapor, a yellow colored gel formed. The yellow gel was dried at 110 °C for 12 h and further calcined successively at 600, 700, 800 and 900 °C in air to obtain $MgTiO_3$.

2.3. Characterization of the catalyst

2.3.1. X-ray diffraction

X-ray diffraction patterns of samples were obtained on a Bruker D8 ADVANCE instrument with $Cu K\alpha$ radiation at 40 kV and 30 mA.

2.3.2. Temperature-programmed desorption of CO_2

Carbon dioxide was used as the probe molecule to determine the basicity of the prepared catalyst. CO_2 -TPD experiment of catalysts was conducted on a Micromeritics 2920 apparatus using thermal conductivity detector (TCD). Before each measurement, the sample was pretreated by temperature programmed desorption (TPD) procedure under flowing helium at 300 °C for 60 min, followed by cooling to room temperature. The sample was then exposed to carbon dioxide for 30 min. After the completion of adsorption, the gas flow was switched to pure He. A stable baseline was established after a flow of He for 1 h and the catalyst was heated linearly to 800 °C at a heating rate of 10 °C/min. Carbon dioxide in effluent was recorded continuously as the function of temperature.

2.3.3. EDS measurement

The samples were measured by EDAX-FALCON in points scanning mode at 30 kV.

2.4. Catalytic test

The reaction was performed under atmospheric pressure in a 100 mL three-neck round-bottomed flask, equipped with a nitrogen inlet, cycle reflux condenser and a thermometer. Propylene glycol (30 mL, 0.4 mol), urea (6 g, 0.1 mol) and the catalyst (0.025 g) were added into the flask successively under nitrogen, and the mixture was heated to 170 °C for 2 h. After the reaction, the mixture was cooled to room temperature and the solid catalyst was separated from the liquid centrifugation. During the reaction, NH_3 formed was removed by the N_2 flow.

The products were identified by an Agilent 7890A/5975C GC-MS spectrometer, equipped with a DB-5 capillary column (15 m × 250 μm × 0.1 μm). The flow rate of He carrier gas was 0.8 mL/min, and at a heating rate of 10 °C/min, the temperature was raised to 200 °C, where it was held for 5 min. A GC-MS identification of the product mixtures revealed that the major components were 1,2-propanediol, propylenecarbonate, and 2-hydroxypropyl carbamate. The external standard method and a gas chromatograph (GC-2014), equipped with a Rtx-5 capillary column and a flame ionization detector (FID) were used for a quantitative analysis of the products. The flow rate of N_2 carrier gas was 30 mL/min, and the temperature of the capillary column was 210 °C. The temperatures of the injector and the detector were 250 °C and 300 °C, respectively. The selectivity and the yield of PC were adopted as the evaluation indices of the catalyst activity, and they were calculated as follows:

$$\text{Selectivity (\%)} = \frac{\text{moles of urea synthesised PC}}{\text{moles of urea reacted}} \times 100$$

$$\text{Yield (\%)} = \frac{\text{moles of PC produced}}{\text{moles of urea in feed}} \times 100$$

3. Results and discussion

3.1. Effect of calcination temperature on alcoholysis

Fig. 1 shows the XRD patterns of $MgTiO_3$ calcined at different temperature for 2 h. All samples exhibited the characteristic peaks at $2\theta = 19.11^\circ, 21.23^\circ, 24.01^\circ, 32.87^\circ, 35.49^\circ, 40.64^\circ, 49.15^\circ, 50.40^\circ, 53.61^\circ, 55.90^\circ, 56.98^\circ, 63.72^\circ$, which were in agreement with that of standard $MgTiO_3$ (JCPDS 06-0494) and proved that $MgTiO_3$ was successfully synthesized. However, MgO phase was also

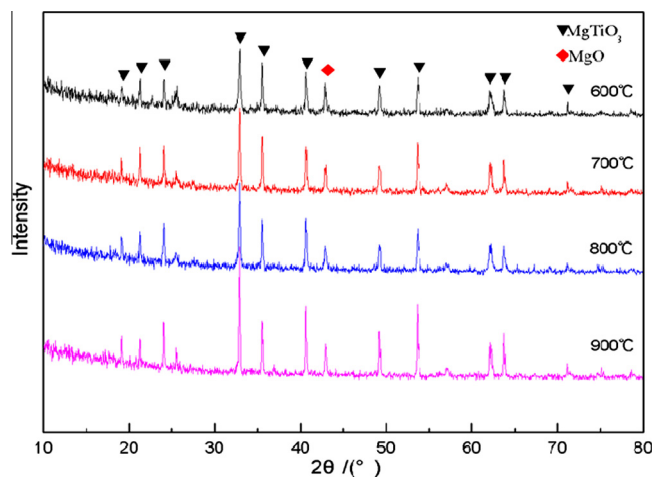


Fig. 1. XRD patterns of $MgTiO_3$ calcined at different temperature.

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