Influence of preparation methods on the structure and performance of CaO–ZrO$_2$ catalyst for the synthesis of dimethyl carbonate via transesterification

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Abstract

CaO–ZrO$_2$ catalysts, which were prepared by physical mixing, impregnation and coprecipitation methods, were developed for the synthesis of dimethyl carbonate from propylene carbonate and methanol. It was found that the CaO–ZrO$_2$ catalyst prepared by the coprecipitation method showed high performance for the reaction, which was greatly dependent on the calcination temperature. The XRD and CO$_2$-TPD measurement of the catalysts revealed that both catalytic activity and stability were strongly influenced by the structure of CaO–ZrO$_2$. The aggregated CaO on the support as well as highly dispersed CaO showed poor catalytic stability, but Ca^{2+} ion substituted for Zr^{4+} ions in the host lattice to form homogeneous CaO–ZrO$_2$ solid solution, which led to the strong interaction between CaO and ZrO$_2$ and then high stability.
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Keywords: Preparation method; Calcinations temperature; Dimethyl carbonate; CaO–ZrO$_2$; Solid solution

1. Introduction

Dimethyl carbonate (DMC) is an environmentally benign chemical product and versatile intermediate [1–3]. It finds extensive uses as a precursor for polycarbonate resins as well as a starting material for organic synthesis via carbonylation and methylation, replacing poisonous phosgene and dimethyl sulfate [4–7]. It is also considered to be a promising gasoline octane enhancer and an electrolytic solution in a secondary lithium battery. To date, there have mainly been three large-scale production of DMC. Among them, the transesterification between methanol and propylene carbonate (PC) or ethylene carbonate (EC) is an attractive route in which there is no waste or corrosion to equipment [8]. Both acid and base catalysts catalyzed the reaction, and base catalysts were reported to be more effective [9]. However, homogeneous basic catalysts, such as alkali alcoholates or hydroxide [10] and trialkyl amine [11], gave rise to the problems of the products separation and catalyst reuse,

and consequently, solid base catalysts had gained much interest. Among solid bases, CaO showed unique catalytic activity for the transesterification of propylene carbonate and methanol with high yield and selectivity [12]. Unfortunately, when CaO based catalyst was employed in the continuous synthesis of DMC, its activity gradually decayed with time-on-stream due to leaching of calcium [13]. Thus, the stability of CaO based catalysts was the key problem for the continuous production of DMC via transesterification.

In our previous work, CaO–ZrO$_2$ mixed oxide was found to be a highly stable strong solid base, which was subjected to continuous synthesis of DMC in a reactive distillation reactor for 250 h without any obvious change of activity [14]. CaO stabilized zirconia with the cubic or tetragonal phase has been well understood to improve the toughness and wear resistance as a ceramic material and conductivity as solid electrolyte [15,16]. However, there is very little information about the usage of the CaO–ZrO$_2$ system as stable basic catalysts [17,18]. In the present work, much attention has been paid to the effect of the preparation method and calcination temperature on the structure and catalytic performance of the CaO–ZrO$_2$ system, especially the stability of catalysts. It was found that the formation of homo-

geneous CaO–ZrO$_2$ solid solution was responsible for the high stability.

2. Experimental

2.1. Preparation of catalyst

CaO–ZrO$_2$ catalysts with the same composition were prepared by three different methods. (A) Physical mixing method: pure tetragonal ZrO$_2$ and CaCO$_3$ were physically mixed and ground in an agate mortar and then calcined at 800 °C for 4 h in air. (B) Impregnation method: tetragonal zirconia precursor was impregnated by Ca(NO$_3$)$_2$·4H$_2$O followed by drying at 100 °C for 12 h and calcination at 800 °C for 4 h in air. Tetragonal zirconia was prepared as a control [19]. (C) Coprecipitation method: a mixed solution of ZrO(NO$_3$)$_2$ and Ca(NO$_3$)$_2$ was added dropwise, concurrently with a solution of ammonia at 40 °C with vigorously stirring. The pH of precipitation was controlled at around 10. The precipitation was aged in the mother liquid for 4 h, filtered out and then washed with deionized water. The resultant was dried at 100 °C for 12 h and then calcined at 500–800 °C for 4 h to produce the catalysts. The mole ratio of Ca/(Ca + Zr) was 0.30 which was determined by an AtomScan16 inductively coupled plasma atomic emission spectrometer. The catalysts prepared were crushed and sieved to a size range of 10–20 mesh (0.71–1.0 mm grain).

2.2. Characterization of catalyst

XRD was carried out on a Rigaku D/max-γ A diffractometer with Ni filtration. Diffraction patterns were obtained with the X-ray gun operated at 50 kV and 30 mA, using a scan rate 0.2° min^{-1} (2θ) from 20° to 70°.

The total basicity and base strength of the samples were measured by CO$_2$-TPD. Catalyst (0.1 g, 40–60 mesh) was placed in the quartz reactor bed. Pretreatment for TPD procedure consisted of treatment in flowing argon at assigned temperature for 2 h, and then the sample was cooled to room temperature. CO$_2$ was pulsed to the reactor using a 6-way valve till saturation was reached. After physically absorbed CO$_2$ was purged off, the TPD experiment was started with a heating rate of 10 °C min^{-1} under N$_2$ flow (50 ml min^{-1}), and the effluent was detected by a BALZAQ-mass spectrometer.

2.3. Catalytic performance

The reaction was carried out in either batch or distillation reactor. The 0.5 g catalyst which was crushed into 100–200 mesh grain beforehand was used for the catalyst performance test in a stainless batch reactor with 6:1 ratio of methanol to propylene carbonate. After the reaction proceeded for 2 h at 100–200 °C under constant stirring, the reactor was cooled down to room temperature and the products were then analyzed on a gas chromatograph with a TCD after centrifugal separation from the catalyst.

For stability investigation, the reaction was continuously carried out in a reactive distillation reactor which involved rectify-

ing, reaction and stripping columns. The rectifying and stripping columns were packed with Rashing rings and the reactive column was filled with catalyst (20–40 mesh). Before reaction, N$_2$ was introduced into the reactor and compressed to the desired pressure. The control of pressure was achieved by a backpressure regulator. The reactants, propylene carbonate and methanol, were continuously fed into the reactive column from top and bottom, respectively. The products of both tower top and bottom were taken out every 12 h for analysis by a gas chromatograph with a TCD. The 15 g catalysts were used for the distillation reaction with LHSV of 0.03 h^{-1} at 150 °C and 0.5 MPa.

3. Results and discussion

3.1. Effect of preparation method

CaO–ZrO$_2$ catalysts with the same composition were prepared by three different methods and calcinated at 800 °C. The crystal structure of CaO–ZrO$_2$ samples was greatly dependent on the preparation methods as shown by XRD in Fig. 1. For the physically mixed sample, both CaO and tetragonal ZrO$_2$ phases were detected, indicating that CaO–ZrO$_2$ consisted of the mixture of each oxide crystal. In the case of the impregnated CaO–ZrO$_2$ catalyst, perovskite CaZrO$_3$ and tetragonal ZrO$_2$ reflections were identified, which suggested that the solid reaction took place and then induced a phase separation on the surface of ZrO$_2$. However, only typical diffraction lines of tetragonal phase were observed for samples prepared by coprecipitation method. The absence of diffraction lines of CaO indicated that Ca^{2+} ions substituted for Zr^{4+} ions in the host lattice and then homogeneous CaO–ZrO$_2$ solid solution formed. It was reported that when CaO was added to ZrO$_2$, CaO either simply stayed on the surface or incorporated into the ZrO$_2$ lattice to form solid solution, depending on the preparation procedure [20].

Fig. 2 illustrated the CO$_2$-TPD of CaO–ZrO$_2$ prepared by different methods. The basicity of samples was greatly affected by preparation methods. Sample prepared by mechanical mixing method exhibited two desorption peaks—α (below 200 °C) and
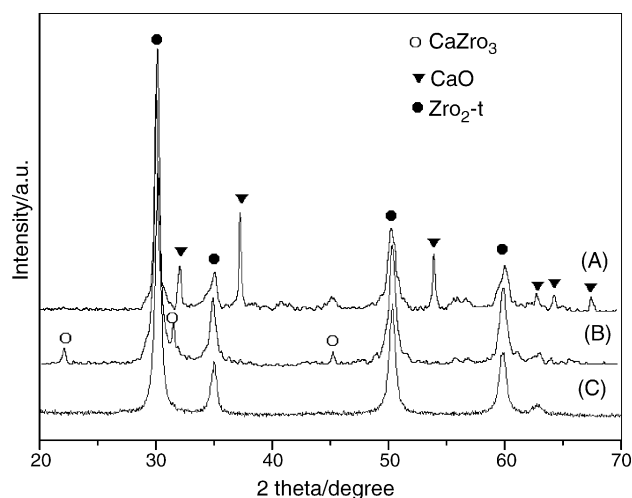

Fig. 1. XRD patterns of CaO–ZrO$_2$ catalysts prepared by different methods. (A) Physical mixing method; (B) impregnation method; (C) coprecipitation method.
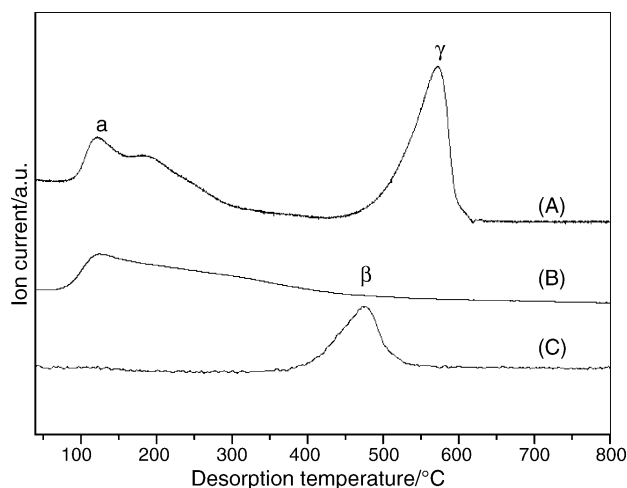
Fig. 2. CO_2-TPD profiles of CaO–ZrO$_2$ catalysts prepared by different methods. (A) Physical mixing method; (B) impregnation method; (C) coprecipitation method.

Fig. 3. Catalyst performance of CaO–ZrO$_2$ catalysts prepared by different methods in a batch reactor at different reaction temperatures. (A) Physical mixing method; (B) impregnation method; (C) coprecipitation method. Reaction conditions: methanol:PC (molar ratio) = 6:1; catalyst, 1.5 wt.%.

γ (about 570 °C). Corresponding to the results of XRD, α peak could be assigned to the weak basicity of ZrO$_2$ [21], and γ peak was ascribed to the crystalline CaO aggregated on the surface of support. For CaO–ZrO$_2$ prepared by impregnation method, only α peak was observed due to the weak basicity of ZrO$_2$ and CaZrO$_3$. However, β peak was observed at about 475 °C only for the sample prepared by coprecipitation, which could be attributed to the formation of solid solution where the presence of neighboring Ca^{2+} and Zr^{4+} improved the basicity of lattice oxygen on the surface. These implied that the mixing of ZrO$_2$ with CaO at the atomic level changed the surface basicity. Generally, the basicity of an oxide surface is closely related to the electro-donating properties of oxygen anions, which increases with the increase in the electro-positive character of combined mental ions [22]. The value for electro-negativity of Zr^{4+} is larger than Ca^{2+}; therefore, the negative charge of lattice oxygen between Ca^{2+} and Zr^{4+} would be drawn toward Zr^{4+}. Consequently, the basicity of the CaO–ZrO$_2$ solid solution was higher than ZrO$_2$ alone.

The performance of CaO–ZrO$_2$ catalysts prepared by different methods in the batch reactor at different reaction temperatures is presented in Fig. 3. The physically mixed catalyst showed extremely high catalytic activity, and the reaction reached the equilibrium even at reaction temperature as low as 120 °C, which was closely related to the strong base strength of CaO on the surface. Comparatively, the catalytic activity of the catalyst prepared by coprecipitaion was slightly lower than that of the physically mixed one, and the catalytic activity of CaO–ZrO$_2$ prepared by the impregnation method exhibited the lowest activity. The trend was analogous to the variability of basicity in CaO–ZrO$_2$ catalysts; i.e. the higher the base strength was, the higher the activity of catalyst, which was consistent with the results reported by Wei et al. [23]. However, the catalysts prepared by different methods showed different stability when they were subjected to continuous synthesis of DMC in a reactive distillation reactor (see Fig. 4). For the catalyst prepared by coprecipiion, the PC conversion was maintained at about 95%
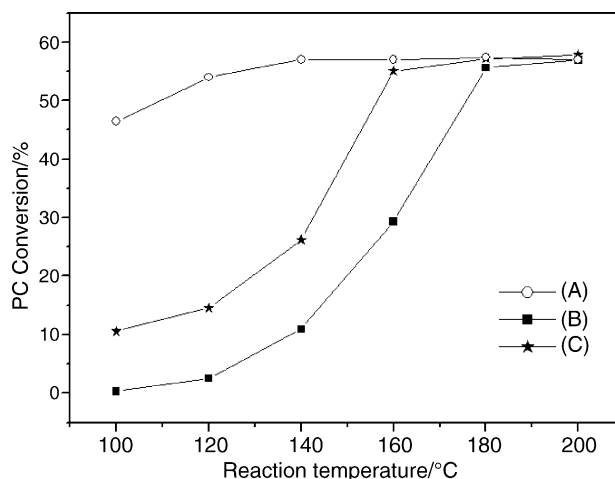
and no obvious loss of activity was observed even after 200 h. This could be due to the interaction of CaO and ZrO$_2$ in the solid solution, which strongly anchored those basic sites on the catalyst surface and led to high stability. However, the PC conversion decreased with time-on-stream for catalysts prepared by the physical mixing method, which was caused by the leaching of calcium and probably the formation of CaCO$_3$ on the catalyst surface as reported previously [13]. For catalyst prepared by the impregnation method, the PC conversion remained lowest even for a catalytic distillation. It seemed that the aggregated CaO on the support was unfavorable for high catalytic stability.

3.2. Effect of calcination temperature

Fig. 5 showed the XRD patterns of CaO–ZrO$_2$ catalyst prepared by the coprecipitation method with the calcination temper-
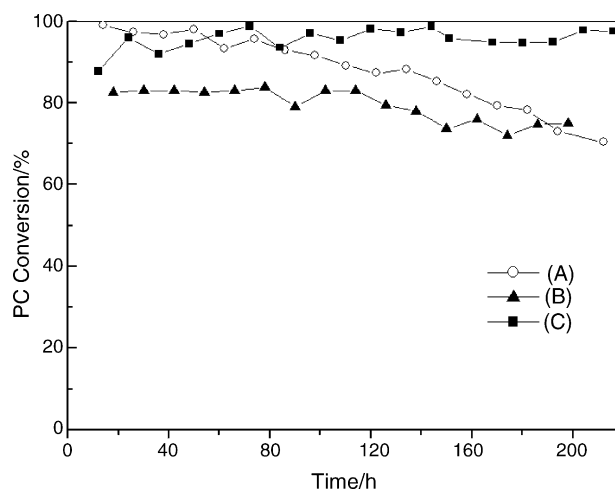

Fig. 4. Catalyst performance of CaO–ZrO$_2$ catalysts prepared by different methods in reactive distillation. (A) Physical mixing method; (B) impregnation method; (C) coprecipitation method. Reaction conditions: 15 g of catalyst with LHSV of 0.03 h^{-1}; temperature of 150 °C; pressure of 0.5 MPa and reflux ratio of 4:1.
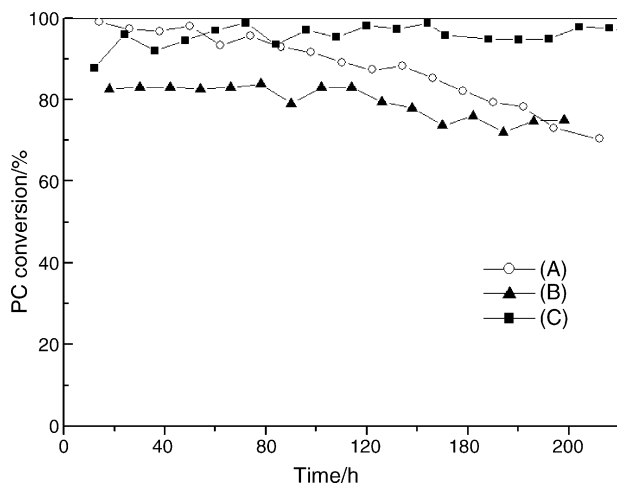
Fig. 5. XRD patterns of CaO–ZrO$_2$ catalysts calcined at different temperatures.

Fig. 7. Catalyst performance of CaO–ZrO$_2$ catalysts calcined at different temperatures in a batch reactor at different reaction temperatures. Reaction conditions: methanol:PC (molar ratio) = 6:1; catalyst, 1.5 wt.%.

atures altered from 500 to 800 °C. The patterns of the catalysts obtained at each calcination temperature were assigned to the tetragonal ZrO$_2$ phase. With the rise in calcination temperature, the intensity of peaks gradually increased and the half-width of peaks became narrower. A careful examination of the XRD pattern revealed that for the sample calcined at 800 °C, the diffraction peak shifted to lower degree which coincided with the slightly large ionic radius of Ca^{2+} in comparison with that of Zr^{4+}. This observation indicated the replacement of Ca^{2+} with Zr^{4+} and formation of solid solution at the calcination temperature of 800 °C. The formation of solid solution depended greatly on the calcination temperature and it was established that the homogeneous CaO–ZrO$_2$ solid solution was formed at 1300 °C, and at the lower temperature, CaO incorporation in ZrO$_2$ was restricted. However, the solid solution would exist at the lower temperature since a calcium ion could readily substitute for a zirconium ion due to the similarity of their ionic radii [24].

The CO$_2$-TPD profiles of samples calcined at different temperatures are shown in Fig. 6. For CaO–ZrO$_2$ calcined at
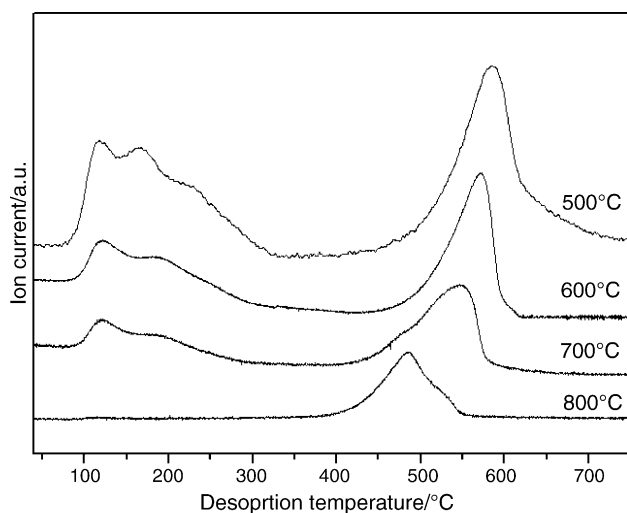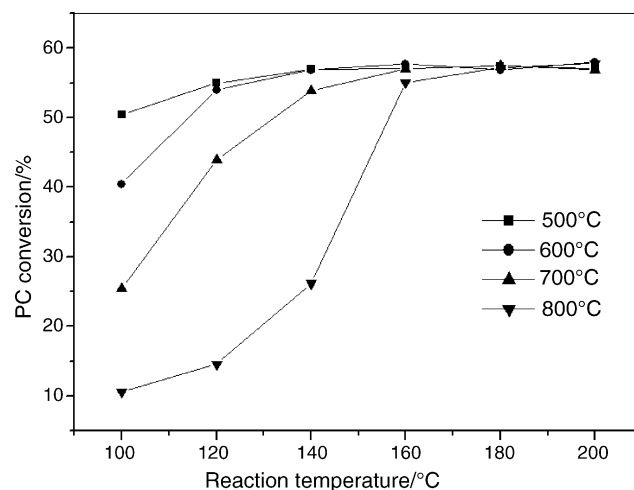
500 °C, the profiles of CO$_2$-TPD showed two peaks (below 300 °C and around 575 °C), which was almost the same as in the case of the sample prepared by the physical mixing method. But the CaO phase was not detected in XRD, which implied that CaO was well dispersed on the surface of the support. With the further increase in calcination temperature, the peak at around 575 °C shifted to a low temperature and at the same time the peaks below 300 °C decreased in its intensity and disappeared finally when the material was calcined at temperature as high as 800 °C. This indicated that highly dispersed CaO below 800 °C turned into the phase of Ca atoms incorporated ZrO$_2$ lattice at 800 °C, and this resulted in a deformed lattice and unbalanced electron charge distribution, consequently changing the base strength.

The influence of calcination temperature on the catalytic activity and stability of CaO–ZrO$_2$ catalyst is shown in Figs. 7 and 8, respectively. It could be seen that activity slightly decreased by enhancing the calcination temperature.

Fig. 6. CO$_2$-TPD profiles of CaO–ZrO$_2$ catalysts calcined at different temperatures.
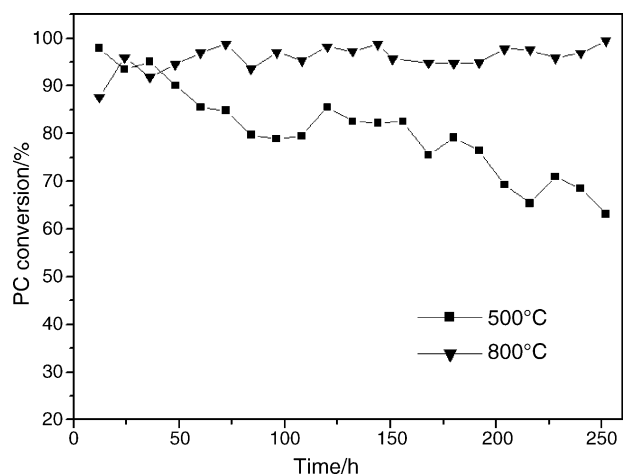

Fig. 8. Catalyst performance of CaO–ZrO$_2$ catalysts calcined at different temperatures in reactive distillation. Reaction conditions: 15 g of catalyst with LHSV of 0.03 h^{-1}; temperature of 150 °C; pressure of 0.5 MPa and reflux ratio of 4:1.

The dispersed CaO showed higher activity than the incorporated one, but its activity decayed with time-on-stream (see Fig. 8). It seemed that the highly dispersed CaO on the support was not favorable for the high catalytic stability either. Thus, it could be deduced that the formation of homogeneous CaO–ZrO$_2$ solid solution played a crucial role in determining the catalytic stability toward the transesterification reaction between methanol and propylene carbonate.

4. Conclusions

The activity and stability of CaO–ZrO$_2$ catalysts for the synthesis of dimethyl carbonate via transesterification was greatly influenced by the preparation method and calcination temperature. Three kinds of calcium phase were obtained by three different preparation methods: CaO aggregated on the support in the sample prepared by the physical mixing method, CaZrO$_3$ segregated at the boundary in the sample prepared by the impregnation method, and Ca incorporated into the ZrO$_2$ lattice prepared by the coprecipitation method. At the same time, highly dispersed CaO on the surface was obtained by calcining the sample prepared by the coprecipitation method below 800 °C. Both aggregated and highly dispersed CaO had the strongest base strength and then the highest activity but the poor stability, and CaZrO$_3$ segregated at the boundary suppressed the activity; however, the homogeneous CaO–ZrO$_2$ solid solution exhibited both excellent activity and stability because of the strong interaction between active sites and support.

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