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CaO–ZrO_2 Solid solution: A highly stable catalyst for the synthesis of dimethyl carbonate from propylene carbonate and methanol

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CaO–ZrO_2 prepared by co-precipitation showed to be a well-performed catalyst for the transesterification of propylene carbonate (PC) and methanol. The characterization by X-ray powered diffraction (XRD) and Raman spectroscopy indicated that CaO was doped into the lattice of ZrO_2 to form CaO–ZrO_2 solid solution. Such a solid solution was a strong solid base, which was proved by CO_2 temperature program desorption (CO_2-TPD). As a result, the catalyst showed high stability towards the transesterification of propylene carbonate and methanol into dimethyl carbonate with high PC conversion, especially being subjected to the continuous production of dimethyl carbonate at reactive distillation reactor for 250 h without any obvious loss of activity at the PC conversion of 95%.

KEY WORDS: CaO–ZrO_2; solid solution; dimethyl carbonate; stability.

1. Introduction

Dimethyl carbonate (DMC), an environmentally benign and biodegradable chemical, has attracted more and more attention in recent years [1–3]. It is an important precursor of polycarbonate as well as useful carbonylation and methylation agent since it can be substituted for toxic phosgene, dimethyl sulfate or methyl iodide [4,5]. In addition, DMC is a candidate for replacing MTBE as an oxygen-containing additive for gasoline due to its high oxygen content [6,7].

Generally, DMC has been mainly produced via two environmentally compatible routes: oxidative carbonylation of methanol and transesterification using cyclic carbonate as intermediate from CO_2, epoxides and methanol. Transesterification of cyclic carbonate and methanol is a green process that there is no waste and corrosion, and it uses naturally abundant CO_2 as a starting materials as shown in Scheme 1 in which a cyclic carbonate is formed from epoxide and carbon dioxide, and subsequently transesterified to form DMC and alkylene glycol. Both acid and base catalysts catalyze the reaction, and base catalyst was reported to be more effective [8]. However, homogeneous basic catalysts such as alkali alcoholates or hydrates [9] and trialkyl amine [10], gave rise to the problems of the products separation and the catalyst reuse, and consequently, solid base catalysts have gained much attention, among which CaO showed unique catalytic activity for the transesterification of propylene (PC) with methanol with high PC conversion and DMC selectivity [11]. 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 [12]. For supported catalysts, many efforts for perfectly stable anchored active species on carries are employed to overcome the problem of leaching. For instance, active species were grafted in mesoporous materials, encapsulated by ship-in-a-bottle techniques, and ion exchanged in layered structure [13].

In the present work, CaO–ZrO_2 solid solution was prepared by co-precipitation to prevent the leaching of calcium via the strong interaction between CaO and ZrO_2 in the solid solution. So-produced solid base showed to have high stability and was subjected to continuous synthesis of DMC on reactive distillation reactor for 250 h without any obvious change of activity.

2. Experimental

2.1. Preparation of catalyst

CaO–ZrO_2 catalyst was prepared by co-precipitation method. A mixed solution of $ZrO(NO_3)_2$ and $Ca(NO_3)_2$ was added dropwise, concurrently with a solution of ammonia (the pH of which was previously adjusted to 10 with ammonia) at 313 K with vigorously stirring. The pH of precipitation was controlled at around 10. The precipitation was aged at the mother liquid for 4 h and filtered and then washed with deionized water. The resultant was dried at 373 K for 12 h and then calcined

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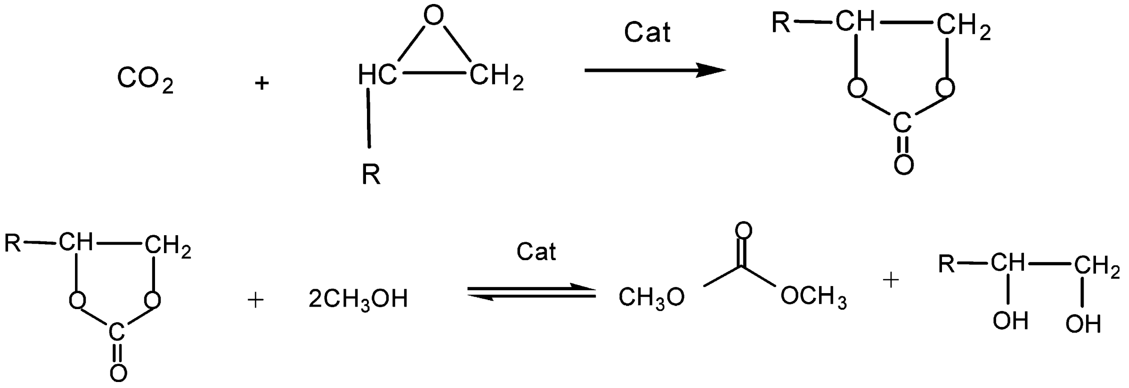

Scheme 1. Synthesis of DMC by transesterification.

at 1073 K for 4 h to obtain the catalyst. Before used the catalyst was crushed and sieved to a size range of 10–20 mesh (0.71–1.0 mm grain). The mole ration of Ca/(Ca + Zr) was 10% which was determined by the inductively coupled plasma atomic emission spectrometer of AtomScan16.

Zirconia of tetragonal phase was prepared as reference [14] and calcined at 1073 K for 4 h.

2.2. Characterization of catalyst

XRD was carried out on Rigaku D/max-γ A 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 20–70 degree.

Raman spectra were obtained at room temperature with a microscopic confocal Raman spectrometer (Perkin Elmer). The 1064 nm line from Nd: YAG laser was used as the excitation source.

The BET surface area, pore volume and pore size distribution of the samples were determined from the corresponding nitrogen adsorption–desorption isotherms (at 77 K) with the BET method through Micromeritics ASAP-2000.

The total basicity and base strength of the samples were measured by CO_2-TPD which was performed at a heat rate of 10 K/min under N_2 flow (50 ml/min), and the CO_2desorbed was detected by a BALZA Q-Mass spectrometer.

2.3. Catalytic performance

The reaction was continuously carried out in a reactive distillation reactor as shown in Figure 1. The rectifying and stripping column were packed with Rashing

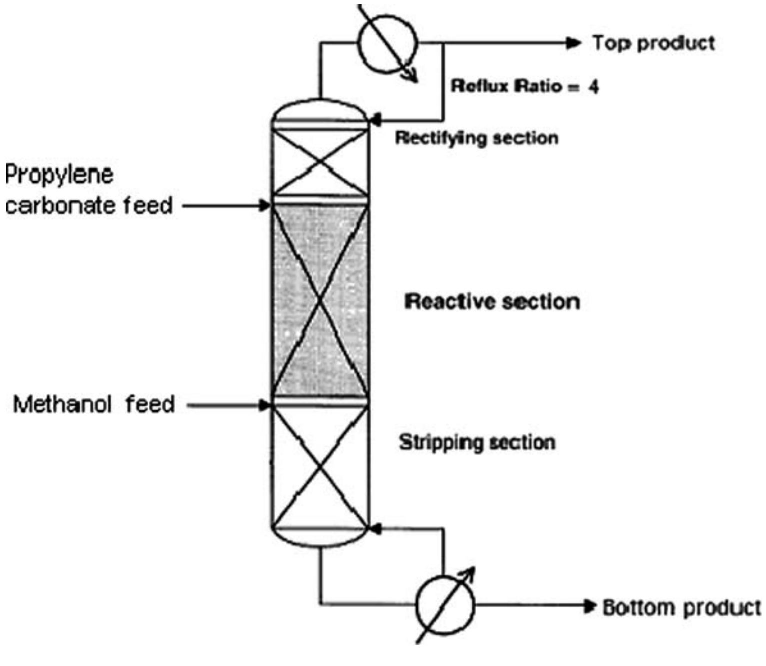

Figure 1. The reactive distillation setup for the reaction.

rings and the reactive column was filled with 15 g catalyst (0.71–1.0 mm grain). Before reaction, N_2 was introduced into the reactor and compressed to desired pressure. The control of pressure was achieved by a backpressure regulator. The reactants, propylene carbonate and excess methanol, were continuously fed into the reactive column from top and bottom, respectively. The feed rate of methanol was maintained at 15 ml/h. The product of tower top was a mixture of DMC and methanol and bottom products were mainly composed of methanol, PG, a little DMC and PC, which were both taken out each 12 h for analysis by gas chromatograph with a TCD.

3. Results and discussion

3.1. Characterization of catalyst

Table 1 gives the surface area and pore structure of the samples. It can be seen that the surface area of ZrO_2 decreased slightly when CaO was added, and the resultant CaO–ZrO_2 catalyst had the pore size of ca. 10 nm. The XRD patterns showed that CaO–ZrO_2 had either cubic or tetragonal phase (see Figure 2). This indicated that neither CaO was amorphous nor well dispersed on the surface of zirconia because the calcination at 1073 K was enough for the formation of calcium oxide crystalloid. Obviously, the surface area of 12.3 m^2/g was too small to well disperse the calcium oxide. As a result, CaO was doped into the lattice of ZrO_2, which led to the formation of CaO–ZrO_2 solid solution.

Table 1

BET surface area and pore size of ZrO_2 and CaO–ZrO_2

Sample	BET surface area/m^2 g^{-1}	Pore volume[a] /cm^3 g^{-1}	Average pore size[a]/nm
ZrO_2	24.6	0.04	8.7
CaO–ZrO_2	12.3	0.02	10.5

[a] Calculated by the BJH method from the desorption isotherm.

Six Raman-active mode of $A_{1g}+3E_g+2B_{1g}$ symmetry are usually observed for tetragonal ZrO_2 (space group $p4_2$/nmc), while for the cubic fluorite structure (space group F_{m3m}), only one F_{2g} mode centered at around 490 cm^{-1} is Raman active [15]. Tetragonal phase of ZrO_2 prepared here showed six typical Raman peaks at 190, 271, 314, 380, 475 and 639 cm^{-1}, respectively (see Figure 3). But for CaO–ZrO_2 features, only three broad peaks were observed at 288, 390 and 604 cm^{-1}, respectively. Some trace impurities, such as $NH_4{}^+$, metal ion, would not be expected to yield all bands with the above consistent peaks [16]. Thus, the appearance of three bands in CaO–ZrO_2 catalyst was an indication of some distortion of oxygen sublattice. It is well known that monoclinic zirconia is the thermodynamically stable phase at room temperature. However, the cubic and tetragonal phase can be stabilized at room temperature under several conditions. For instance, the presence of calcium oxide and magnesium oxide allowed the cubic or tetragonal phase to be stabilized [17, 18]. In the present case, the tetragonal phase of ZrO_2 was stabilized by CaO. Typically, Ca^{2+} ions substituted for Zr^{4+} ions in the host lattice, which generated oxygen vacancy. And then the broader Raman peaks of CaO-doped ZrO_2 might be related to the more defects and vacancy on the surface of CaO–ZrO_2 solid solution (see Figure 3).

The CO_2-TPD profiles of samples indicated that ZrO_2 had a shoulder peak at the range of 325–650 K (see Figure 4), which was related to its weak basic strength as reported in other documents [19]. With the incorporation of Ca^{2+} into the lattice of ZrO_2, only one peak appeared at 750 K, indicating that such a solid solution was of strong base property. This could be due to the strong basic property of CaO and the formation of CaO–ZrO_2 solid solution influenced the strong base character of CaO.

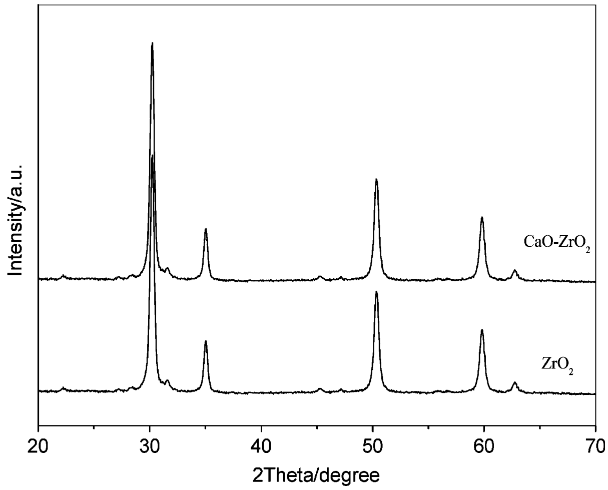

Figure 2. XRD patterns of ZrO_2 and CaO–ZrO_2.

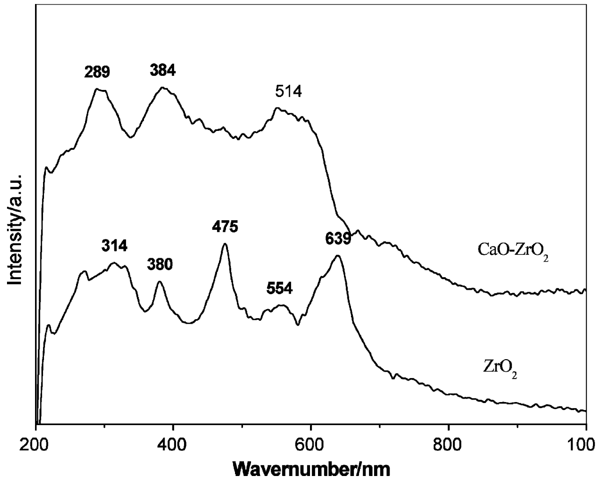

Figure 3. Raman spectra of ZrO_2 and CaO–ZrO_2.

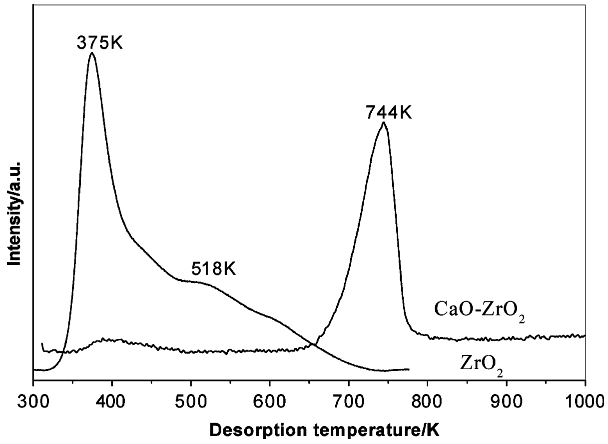

Figure 4. CO_2-TPD of ZrO_2 and CaO–ZrO_2.

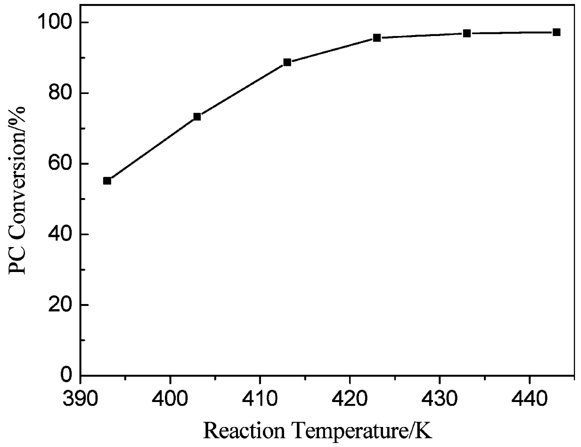

Figure 5. The effect of reaction temperature on the catalytic performance (15 g of catalyst with LHSV of 0.03 h^{-1}, pressure of 0.5 MPa and reflux ratio of 4:1).

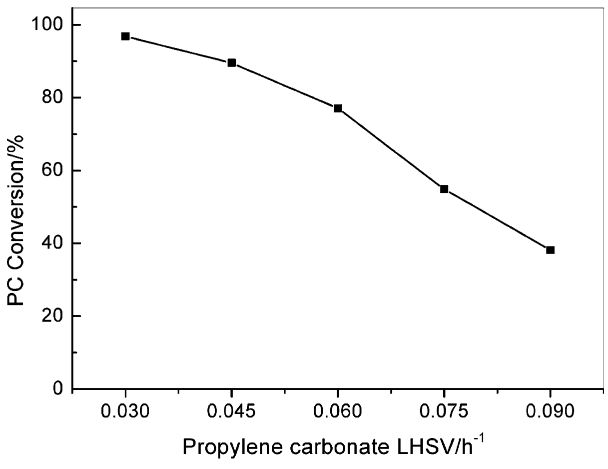

Figure 6. The effect of LHSV of propylene carbonate on the catalytic performance (15 g of catalyst with temperature of 423 K, pressure of 0.5 MPa and reflux ratio of 4:1).

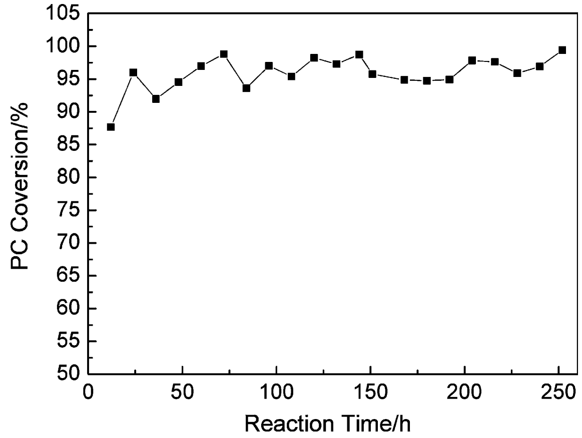

Figure 7. Catalytic performance of CaO–ZrO_2 catalyst in catalytic distillation (15 g of catalyst with LHSV of 0.03 h^{-1}, temperature of 423 K, pressure of 0.5 MPa and reflux ratio of 4:1).

3.2. Catalytic performance

The transesterification of propylene carbonate and methanol was employed in the catalytic distillation reactor to investigate the activity and stability of CaO–ZrO_2 catalyst. The conversion of propylene carbonate was found to increase sharply with the rise of the temperature from 393 to 423 K and then change a little (see Figure 5). When the reaction temperature was higher than 430 K, the side reaction such as decomposition and polymerization took place [20]. However, even at 393 K, the conversion of propylene carbonate reached 55%, indicating that the catalyst performed well in the transesterification. With the increase of LHSV the conversion of propylene carbonate decreased (see Figure 6). The conversion of propylene carbonate reached 97% at LHSV of 0.03 h^{-1}, but decreased to 38% at LHSV of 0.09 h^{-1} at the same reaction temperature. This could be ascribed to the less residence time of the reactants in the reactor.

At the optimal reaction conditions, CaO–ZrO_2 showed high stability towards the transesterification of propylene carbonate with methanol (see Figure 7). The conversion of propylene carbonate remained at about 95% even for 250 h. When the catalyst was subjected to the continuous reactive distillation, no obvious loss of activity was observed. This should originated from the strong action of CaO and ZrO_2in CaO–ZrO_2 solid solution, which strongly anchored those basic sites on the catalyst surface and led to high stability.

4. Conclusions

CaO-doped ZrO_2 was prepared by co-precipitation, and the characterization of XRD, Raman spectra confirmed that Ca^{2+} was doped into the lattice of ZrO_2 to form the solid solution. Such a solid solution had strong base properties measured by CO_2-TPD, and showed to be a well performed catalyst for the synthesis of dimethyl carbonate from propylene carbonate and methanol. The reaction temperature and LHSV remarkably influenced the performance of the catalyst in the reactive distillation. However, CaO–ZrO_2 catalyst showed high stability at high conversion of propylene carbonate, which could be directly related to the strong interaction of CaO and ZrO_2 in the solid solution.

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