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Synthesis of dimethyl carbonate from propylene carbonate and methanol using CaO–ZrO_2 solid solutions as highly stable catalysts

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Abstract

CaO–ZrO_2 catalysts were prepared by coprecipitation and their catalytic performances were evaluated in the synthesis of dimethyl carbonate from propylene carbonate and methanol. The characterization by XRD, N_2 adsorption, XPS and CO_2–TPD indicated that Ca^{2+} ion substituted for Zr^{4+} ions in the host lattice to form homogeneous CaO–ZrO_2 solid solution when Ca/(Ca + Zr) ratio changed from 0.1 to 0.3, and CaO segregated at grain boundaries with Ca/(Ca + Zr) ratio from 0.4 to 0.5. As a result, the catalysts showed different activity and stability towards the transesterification of propylene carbonate and methanol into dimethyl carbonate. The activity of catalysts was improved with increase in Ca content, whereas high stability was shown with Ca/(Ca + Zr) ratio below 0.3. The formation of homogeneous CaO–ZrO_2 solid solution was responsible for the stability of catalysts.

Keywords: Dimethyl carbonate; Transesterification; CaO–ZrO_2; Solid solution

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1. Introduction

The development of environmentally benign process based on the utilization of naturally abundant carbon resources, such as carbon dioxide, has gained considerable attention in recent years [1,2]. The synthesis of dimethyl carbonate (DMC) using carbon dioxide is considered as one of promising reaction from this viewpoint [3,4]. Due to its versatile chemical property and low toxicity, DMC finds extensive applications 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 [5–8].

Generally, DMC has been mainly produced through two environmentally compatible routes: oxidative carbonylation of methanol and transesterification between methanol and propylene carbonate (PC) or ethylene carbonate (EC). Transesterification of cyclic carbonate and methanol was a green process, which used naturally abundant CO_2 as a starting material as shown in Scheme 1. In the first step, cyclic carbonate could be synthesized with conversion and selectivity close to 100% under moderate conditions [9]. Therefore, much attention has been paid to the transesterification of cyclic carbonate and methanol. Both acid and base catalysts catalyzed the reaction, and base catalyst was reported to be more effective [10]. However, homogeneous basic catalysts, such as alkali alcoholates or hydroxides [11] and trialkyl amine [12], gave rise to the problems of the product separation and catalyst reuse, and consequently, solid base catalysts have gained much interest. Among solid bases, CaO showed unique catalytic activity for the transesterification of propylene carbonate and methanol with high yield and selectivity [13]. 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 [14]. For supported catalysts, the search for perfectly stable anchored active species on carriers without the problem of leaching, has focused on active species grafted in mesoporous materials, encapsulated by ship-in-a-bottle techniques or ion exchanged in layered structure [15].

In the present work, highly stable strong solid bases were obtained by the formation of solid solution of CaO–ZrO_2. The relationship between catalytic performance in this transesterification reaction and physical–chemical properties of CaO–ZrO_2 catalysts was investigated in detail.

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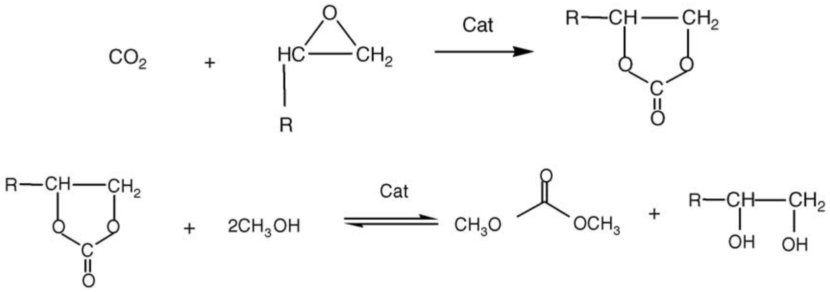

Scheme 1. Synthesis of DMC by transesterification.

2. Experimental

2.1. Preparation of catalysts

CaO–ZrO_2 catalysts were prepared by coprecipitation method. In a typical procedure, a mixed solution of $ZrO(NO_3)_2$ and $Ca(NO_3)_2$ was added dropwise, concurrently with a solution of ammonia at 313 K with vigorously stirring. The pH of precipitation was controlled at around 10. The precipitate was aged in mother liquid for 4 h and filtered and washed with deionized water. The resultant was dried at 373 K for 12 h and then calcined at 1073 K for 4 h to obtain the catalyst. For comparison, zirconia of tetragonal phase was prepared as Ref. [16] and calcined at 1073 K for 4 h. Pure CaO was prepared from $CaCO_3$ calcined at 1073 K for 2 h in a N_2 atmosphere. The mole ratio of Ca/(Ca + Zr) (denoted with x in this paper) of samples was determined by the inductively coupled plasma atomic emission spectrometer (ICP-AES) of AtomScan16.

2.2. Characterization of catalysts

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 (2θ) from 20° to 70°.

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 with a Micromeritics ASAP-2000.

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

X-ray photoelectron spectroscopy data was obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. An estimated error of ±0.2 eV can be assumed for measurements.

2.3. Catalytic performance

The reaction was carried out in either batch or distillation reactor. A 0.5 g catalyst which was powered into 0.2–0.3 mm 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 373–573 K 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 rectifying column, reaction column and stripping column. The rectifying and stripping columns were packed with Rashing rings and the reactive column was filled with 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 methanol, were continuously fed into the reactive column from top and bottom, respectively. The products of both tower top and bottom were taken out each 12 h for analysis by gas chromatograph with a TCD. A 15 g catalysts were used for the distillation reaction with LHSV of 0.03 h^{-1} at 423 K and 0.5 MPa.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows the X-ray diffraction spectra of CaO–ZrO_2 samples with different Ca/(Ca + Zr) ratios. Only typical

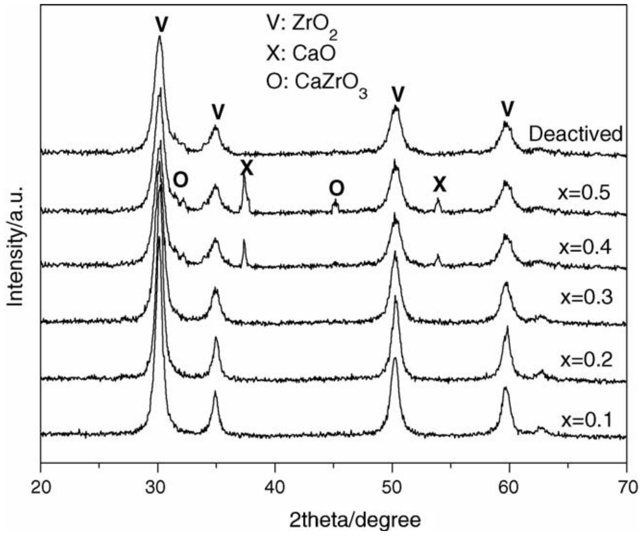

Fig. 1. XRD patterns of CaO–ZrO_2 catalysts with different Ca/(Ca + Zr) ratios (x = 0.1, 0.2, 0.3, 0.4, 0.5) and deactivated catalyst (x = 0.5).

Table 1
Textural structure and composition of samples

Samples	S_{BET} ($m^2\ g^{-1}$)	V_P[a] ($cm^3\ g^{-1}$)	D_P[a] (nm)	Ca/(Ca + Zr) (atomic ratio)	
				Surface[b]	Bulk[c]
ZrO_2	55.2	0.1	5.3	–	–
0.1	31.6	0.06	8.0	0.12	0.10
0.2	12.9	0.03	7.6	0.10	0.21
0.3	2.2	0.01	26.1	0.28	0.30
0.4	3.9	0.02	15.8	0.45	0.38
0.5	9.6	0.05	12.3	0.60	0.49
CaO	12.3	0.03	6.3	–	–
Deactived	8.9	0.05	12.1	0.32	0.36

[a] Calculated by the BJH method from the desorption isotherm.
[b] Measured by XPS.
[c] Measured by ICP-AES.

diffraction lines of tetragonal phase were observed for catalysts with $x \leq 0.3$, and very weak $CaZrO_3$ and CaO reflections were identified at $x = 0.4$, but apparent CaO diffraction peaks appeared at $x = 0.5$. It was well known that when CaO was added into ZrO_2, CaO either segregated at grain boundaries or Ca^{2+} ions substituted for Zr^{4+} ions in the host lattice to form homogeneous solid solution, the difference of which depended on the content of calcium oxide [17]. At low CaO content, CaO was incorporated into the lattice of ZrO_2 and the homogeneous CaO–ZrO_2 solid solutions were formed, but Ca species were presented on the surface of ZrO_2 for the samples with high CaO content.

Table 1 gives the surface area and pore structure of the CaO–ZrO_2 samples. The surface areas showed a minimum at $x = 0.3$ with the addition of CaO. Pure ZrO_2 had a specific area of 55.2 $m^2\ g^{-1}$. With the increase of the x from 0.1 to 0.3, the specific surface area of the samples decreased from 31.6 to 2.2 $m^2\ g^{-1}$, whereas with the further increase of x from 0.4 to 0.5, the surface area increased a little and approached to the surface area of CaO. The dispersion of Ca species on the surface of samples might be responsible for this increase. The dependence of the pore volume on the CaO content in the samples was consistent with the BET area. However, the average pore size decreased when x increased from 0.4 to 0.5, which could be due to the presence of Ca species on the pore wall.

The surface composition of CaO–ZrO_2 catalysts, determined by XPS, is also shown in Table 1. When x was below 0.4, the Ca/(Ca + Zr) ratios on the surface nearly equalled to those of bulk, which further confirmed the formation of homogeneous CaO–ZrO_2 solid solution. However, with further increasing Ca content, the surface Ca/(Ca + Zr) ratios were larger than the bulk, indicating an enrichment of Ca species on the surface. Thus, the XPS measurements supported the conclusions of XRD.

The CO_2–TPD profiles of catalysts are shown in Fig. 2 and the corresponding CO_2 uptakes are listed in Table 2. The CO_2 desorption peaks could be roughly divided into three parts: below 473 K, from 473 to 788 K and around 820 K, which were named α, β and γ, respectively. The α peaks at about 391 and 442 K were assigned to the weak basicity of ZrO_2 [15], and were observed for the catalysts with low CaO content ($x \leq 0.2$). The desorption temperature of β peak increased with the increasing of CaO content, whereas the intensity of β peak initially increased until $x = 0.3$ and then reduced gradually with the further increase of Ca content. This demonstrated that the β peak was related to the formation of solid solution in which the presence of neighboring Ca^{2+} and Zr^{4+} affected the basicity of lattice oxygen on the surface. However, γ peak observed at high desorption temperature only existed at high CaO content ($x \geq 0.4$). This indicated that γ desorption peak was probably contributed to the adsorption of dissociate Ca species on the surface of the catalysts. As a result, the formation of solid solution greatly affected the surface base properties of CaO–ZrO_2 catalysts.

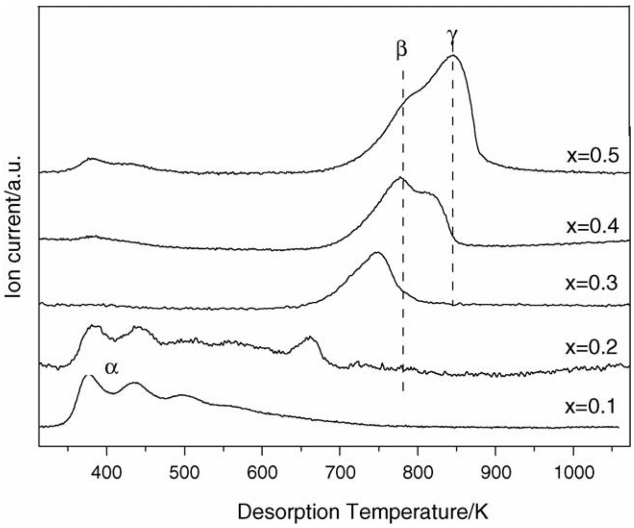

Fig. 2. CO_2–TPD profiles of CaO–ZrO_2 catalysts with different Ca/(Ca + Zr) ratios (x = 0.1, 0.2, 0.3, 0.4, 0.5).

3.2. *Catalytic performance*

The performance of CaO–ZrO_2 catalysts in the batch reactor at different reaction temperatures from 373 to 473 K was presented in Fig. 3. It can be seen that the activities of the catalysts increased with increasing CaO content. Taking the CO_2–TPD results into account, the strength and amount of base played important roles in the synthesis of dimethyl carbonate from propylene carbonate and methanol—the catalytic activities of the catalysts were improved by increasing the strength and amount of base sites, which was consistent with the results reported by Wei et al. [18].

Table 2
The CO_2 uptakes of CaO–ZrO_2 catalysts with different Ca/(Ca + Zr) ratio (x = 0.1, 0.2, 0.3, 0.4, 0.5)

Ca/(Ca + Zr) ratios	CO_2 uptake ($\mu mol\ g^{-1}$)		
	Site (α)	Site (β)	Site (γ)
0.1	4.4	1.2	–
0.2	7.3	5.4	–
0.3	–	9.0	–
0.4	–	8.8	15.7
0.5	–	8.2	25.2

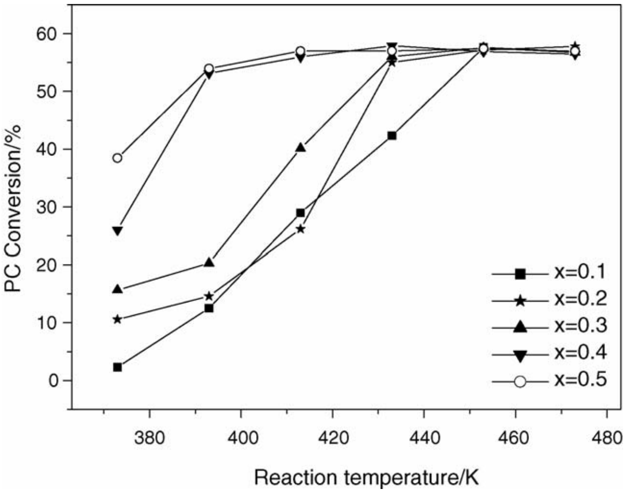

Fig. 3. Catalyst performance of CaO–ZrO_2 catalysts with different Ca/(Ca + Zr) ratios ($x = 0.1$, 0.2, 0.3, 0.4, 0.5) in a batch reactor at different reaction temperatures.

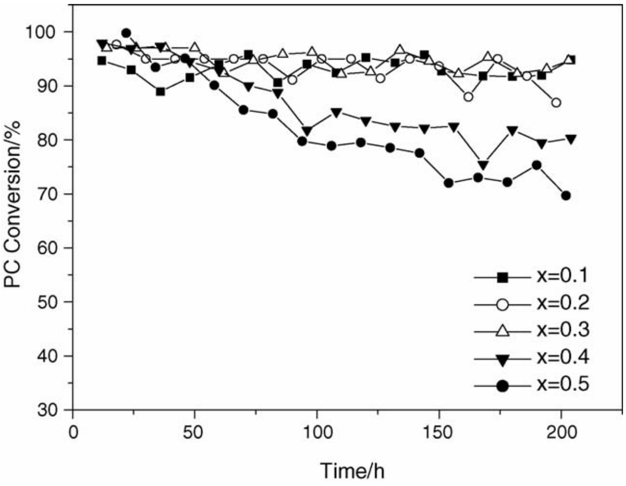

Fig. 4. Catalytic performance of CaO–ZrO_2 catalysts with different Ca/(Ca + Zr) ratios ($x = 0.1$, 0.2, 0.3, 0.4, 0.5) in reactive distillation.

The catalysts showed different stability with different CaO contents when they were subjected to continuous synthesis of DMC in reactive distillation reactor (see Fig. 4). For the catalyst with x from 0.1 to 0.3, 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 with high CaO content.

Analysis by XRD, BET, ICP-AES and XPS measurements of deactivated catalyst ($x = 0.5$) revealed that the leaching of calcium was mainly responsible for such a change. The probable formation of well-dispersed $CaCO_3$ on the catalyst surface, which could not be detected by XRD, was another reason, as reported previously [14]. Thus, the stability of CaO–ZrO_2 catalysts came from the formation of homogeneous solid solution.

4. Conclusions

CaO–ZrO_2 catalysts were obtained by coprecipitation. When CaO–ZrO_2 catalysts were subjected to the synthesis of dimethyl carbonate from propylene carbonate and methanol, the activity and stability depended greatly on the Ca/(Ca + Zr) ratios. The activity of catalysts increased with the increase of CaO content, which was ascribed to the improvement of base strength of catalysts. But high stability was only obtained for the catalysts with Ca/(Ca + Zr) ratio from 0.1 to 0.3. This was due to the formation of homogeneous CaO–ZrO_2 solid solution.

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