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Synthesis of dimethyl carbonate over waste eggshell catalyst

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ABSTRACT

Dimethyl carbonate is an important methylating and carbonylating agent. Eggshell catalysts, prepared from eggshell waste, were tested in the synthesis of dimethyl carbonate from propylene carbonate and methanol. The eggshell-derived catalyst was characterized by using techniques of nitrogen physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and energy dispersive X-ray spectroscopy (EDS). The effects of calcination temperature on structure and activity of eggshell catalysts were investigated. The reusability of eggshell catalysts was also examined. It was found that highly active, reusable solid catalyst was obtained by just calcining eggshell. Dimethyl carbonate yield of 75% can be achieved at 25 °C and 1 atm pressure. Utilization of eggshell as a catalyst for dimethyl carbonate production not only provides a cost-effective and environmental friendly way of recycling this solid eggshell waste, but also makes the process of dimethyl carbonate production economic and fully ecologically friendly.

1. Introduction

Eggs are consumed worldwide because they contain all essential amino acids, vitamins, and minerals. Eggshell weighs approximately 10% of the total mass (ca. 60 g) of hen egg, and eggshell is the significant solid waste produced from food processing and manufacturing plants [1]. In China, for example, it is estimated that annually about 4,000,000 tonnes is generated and this will continue to grow in future [2]. Most of the eggshell waste is commonly disposed in landfills without any pretreatment because it was traditionally useless. However, the waste management is not a desirable practice in view of the environmental odor from biodegradation [3,4]. Eggshell has a little porosity and pure $CaCO_3$ as an important constituent. The chemical composition (by weight) of eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [1]. In recent years, a great deal of effort has been conducted for the application of eggshell as value-added products. These major applications included a possible bone substitute [5], the starting material for preparing calcium phosphate bioceramics (e.g. hydroxyapatite) [6], coating pigments for inkjet printing paper [7], and a low-cost adsorbent for removal of ionic pollutant and dyes from the aqueous solution [3,8].

In our recent work, we found that waste eggshell could be used as an active heterogeneous catalyst for biodiesel synthesis [9]. It was proved that eggshell was an interesting unconventional heterogeneous basic catalyst for biodiesel synthesis [10,11]. Except for the reaction of biodiesel synthesis, only one other reaction, lactose isomerization, was reported utilizing eggshell as a basic catalyst [12]. However, base catalysis is important in chemical industry where it is widely applied [13]. Investigation of eggshell as a catalyst for base-catalyzed reaction is not only helpful recycling this solid eggshell waste, but also could make the reaction process environmentally benign. Though it was already demonstrated that CaO is the active phase of the eggshell waste-derived catalysts [9], there is no report to date comparing of pure CaO and eggshell waste-derived materials.

Dimethyl carbonate (DMC) is considered as an environmentally benign chemical due to negligible ecotoxicity, low bioaccumulation and low persistence [14]. Therefore, the production and chemical application of DMC have attracted much attention in the view of so-called 'sustainable society' and 'green chemistry', mainly for replacing dimethylsulfate and methylhalides in methylation reactions and for replacing harmful phosgene in polycarbonate and isocyanate syntheses [15]. 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 is a green process, which uses naturally abundant CO_2 as a starting material as shown in Scheme 1. In the first step, cyclic carbonate can be synthesized with conversion and selectivity close to 100% under moderate

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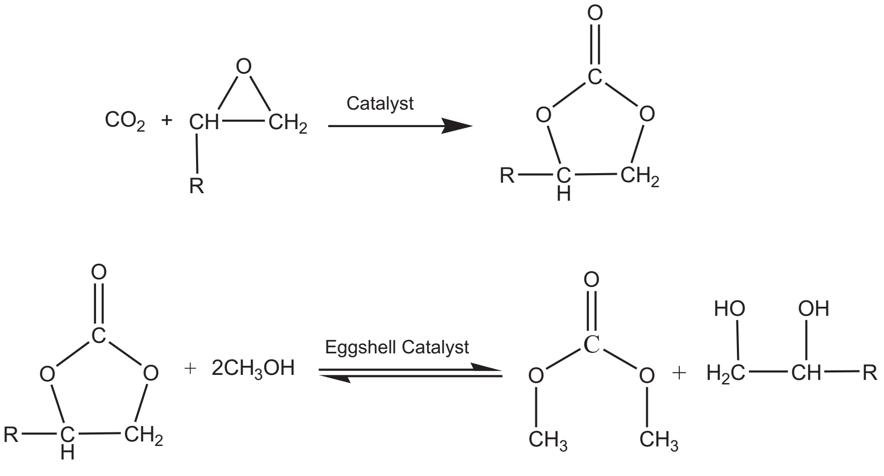


Scheme 1. Synthesis of DMC by transesterification.

conditions. Therefore, much attention has been paid to the transesterification of cyclic carbonate and methanol. Both acid and base catalysts catalyzed the reaction, and base catalysis was reported to be more effective. However, homogeneous basic catalysts, such as alkali alcoholates or hydroxides and trialkyl amine, give rise to the problems of product separation and catalyst reuse, and consequently, solid base catalysts are of much interest [16–19].

In this paper, we studied the catalytic properties of eggshell-derived catalyst for DMC synthesis from the transesterification of PC and methanol. One aim of this investigation was to examine the feasibility of using eggshell as a solid base catalyst for DMC synthesis. The other aim was to compare the catalytic activity of pure CaO and eggshell catalysts.

2. Experimental

2.1. Materials

Eggshell was collected from local bakeries. The preparation method of eggshell catalyst was described elsewhere [9]. To remove impurity and interference material, the eggshell was rinsed several times with deionized water. Then, the eggshell was dried at 100 °C for 24 h in the dry oven. Calcination was performed in the muffle furnace at 1000 °C for 2 h under static air after crushing the dried eggshell.

Pure CaO (analytical reagent, 98.0%) used was a commercial sample (Sinopham Chemical Reagent Co., Ltd., China). It was activated at 1000 °C for 2 h in static air before the reaction test.

2.2. Catalyst characterizations

XRD patterns were recorded using a D/Max-3C X-ray powder diffractometer (Rigaku Co., Japan), using a Cu-Kα source fitted with an Inel CPS 120 hemispherical detector.

Elemental analysis was determined by an FEI Quanta 200 scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (EDS).

The surface area and pore characteristics of the catalysts were determined using a Micromeritics ASAP 2020 instrument. The sample was degassed at 250 °C for 4 h in N_2 prior to surface area measurement. Nitrogen adsorption and desorption isotherms were measured at −96 °C, and the specific surface areas of the catalysts were determined by applying the BET (Brunauer–Emmett–Teller) method to nitrogen adsorption data obtained in the relative pressure range from 0.06 to 0.30. Total pore volumes were estimated from the amount of nitrogen adsorbed at a relative pressure of 0.995. Pore volume and pore-size distribution were obtained from analysis of the desorption branches of the nitrogen isotherms using the BJH (Barrett–Joyner–Halenda) method.

TGA experiments were carried out using a Q600 SDT thermal analysis machine (TA Instruments, USA) under a flow of nitrogen. The sample weight used was about 20 milligrams, and the temperature ranged from 38 to 1000 °C with a ramping rate of 20 °C/min.

2.3. Reaction procedure

The reactions were carried out in a standard round bottom flask at 25 °C temperature and 1 atmosphere pressure under vigorous stirring. During the experiments, the flask was equipped with a ground-glass stopper. Except the stopper, no special management was conducted to control the effect of CO_2 from the atmosphere. Typical reactions were performed with 1.63 g of PC and 5.64 g of methanol using 0.8 wt% (catalyst to PC weight ratio) of eggshells catalyst for the specified time (2 h). The products were analyzed on a Shimadzu GC-2014 gas chromatograph with a flame ionization detector. A Rtx-Wax capillary column ($30\,m \times 0.32\,mm \times 0.5\,\mu m$) was used for separation. N-butanol was used as internal standard for analysis.

Using the standard calibration curves that were prepared for all the components, the integrated areas were converted to moles percentages for each component present in the sample. For each data point, selectivity of DMC, conversion of PC, and yield of DMC were calculated. Selectivity is defined as the ratio of the number of moles of the product formation to that of the PC consumed in the reaction, taking into account the stoichiometric coefficient. Conversion of PC is defined as the ratio of number of moles of PC in the reaction to total moles of PC initially present. Yield of DMC is defined as the ratio of the number of DMC produced to the theoretical number of moles of DMC.

3. Results and discussion

3.1. Characterization of eggshell waste-derived catalysts

3.1.1. BET surface area and pore size

Table 1 presents the nitrogen physisorption data of natural eggshell, calcined eggshell and pure CaO (A.R.). The surface area and pore volume of natural eggshell were $0.84\,m^2\,g^{-1}$ and $0.0049\,cm^3\,g^{-1}$, respectively (Table 1, entry 1), which indicated that natural eggshell processed low porosity [20]. Both the surface area and pore volume of other samples (i.e. calcined eggshell and pure

Table 1
Nitrogen physisorption data of natural eggshell, calcined eggshell and pure CaO (A.R.).

Entry	Sample	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Average pore width (Å)
1	Natural eggshell	0.84	0.0049	32.15
2	Eggshell calcined at 600 °C	3.26	0.0559	53.30
3	Eggshell calcined at 1000 °C	0.21	0.0053	7.82
4	CaO (A.R.)	5.35	0.0064	6.53

CaO) were similar to that of natural eggshell (Table 1, entries 2–4). They also processed low porosity.

3.1.2. *Chemical composition of eggshell waste-derived catalysts*

Element analysis by EDS reveals that natural eggshell contains calcium, carbon and oxygen, as well as two minor constituents (i.e. Mg, and P) (Fig. 1a). The composition of eggshell was consistent to the results reported by Stadelman [1]. The composition of calcined eggshell was similar to that of natural eggshell, but with a difference in the content of carbon (Fig. 1b). The calcined eggshell contained less carbon, which may result from the decomposition of organics and calcium carbonate. Pure CaO (A.R.) contained only calcium and oxygen (Fig. 1c).

3.1.3. *TGA analysis*

In order to explain the effect of calcination temperature, we investigated the calcination process of eggshell with thermal gravimetric analysis (Fig. 2). TGA result showed the temperatures, at which the eggshell precursors decomposed when heated in a controlled environment at a given ramp rate. Between 38 °C and 600 °C, the weight loss was less than 3%. There is one distinguished weight loss peak between 600 °C and 812 °C. Water and organics were removed from the precursors below 600 °C, whereas carbon dioxide was lost between 700 and 800 °C.

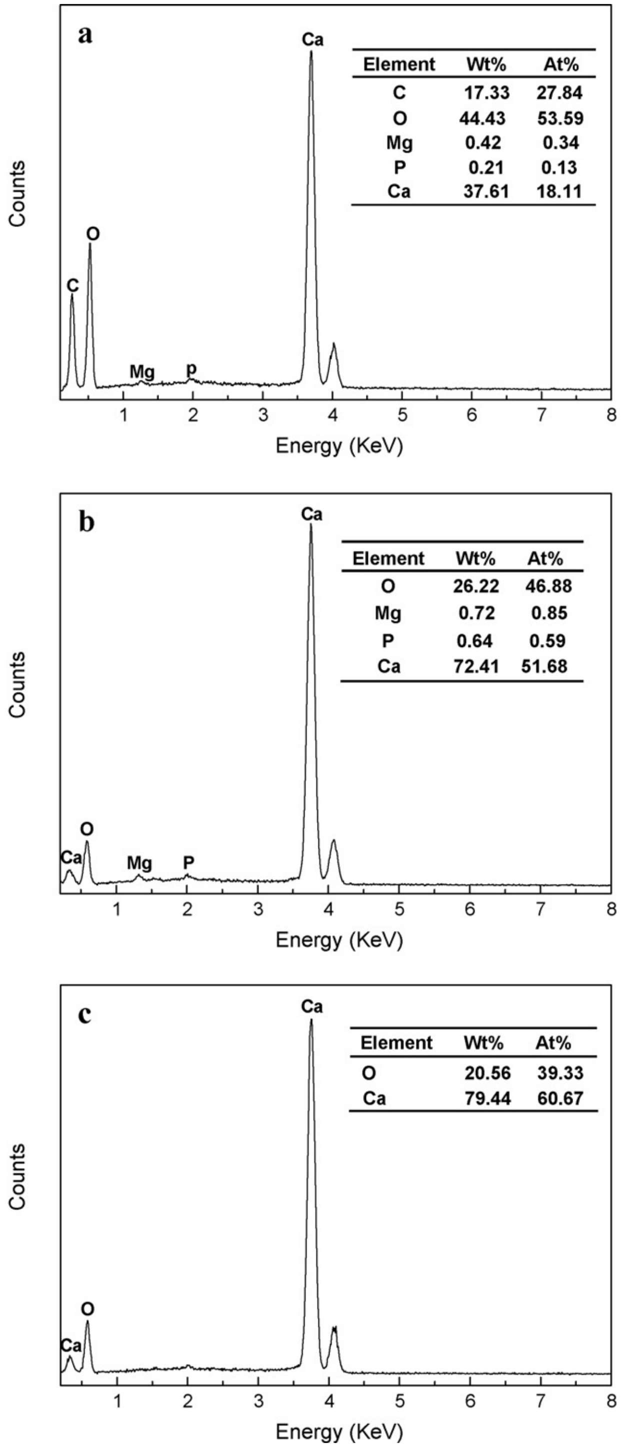
3.1.4. *XRD analysis*

Fig. 3 shows the XRD patterns of natural eggshell, calcined eggshell, and pure CaO (A.R.). The natural eggshell displayed diffraction reflections characteristic of $CaCO_3$ [9]. Thermal pre-treatment resulted in a change in the X-ray diffraction pattern, caused by the removal of CO_2 from the starting material. The diffraction patterns of the samples heated at temperatures <700 °C were characteristic of $CaCO_3$, while samples activated at temperatures >700 °C displayed diffraction reflections characteristic of CaO. Samples calcined at 700 °C for 2 h contain $CaCO_3$ as the major phase and CaO as a minor phase. Pure CaO (A.R.) exhibited diffraction reflections characteristic of CaO.

3.2. *Transesterification over eggshell waste-derived catalysts*

3.2.1. *Effect of calcination temperature*

To determine the influence of the calcination temperature on the activity of the eggshell-derived catalyst, eggshell was calcined at different temperatures between 300 °C and 1000 °C and then tested for the transesterification of PC and methanol to produce DMC (Table 2). The results show that eggshell sample calcined above 800 °C was the most active catalyst. A DMC yield of 80% was obtained in the presence of the eggshell sample calcined above 800 °C (Table 2, entries 5 and 6). When the calcination temperature was 700 °C, a DMC yield of 16% was achieved (Table 2, entry 4), whereas, a low level of activity was observed when the calcination temperature was <600 °C. The PC conversion was <7% and no apparent DMC yield was gained in the presence of eggshell sample calcined <600 °C (Table 2, entries 1–3). As shown in Table 2 and Figs. 4–6, the selectivity to DMC was less than 100%. The side reaction of this reaction might be the slow polymerization of PC after equilibrium [21].



Element	Wt%	At%
C	17.33	27.84
O	44.43	53.59
Mg	0.42	0.34
P	0.21	0.13
Ca	37.61	18.11

Element	Wt%	At%
O	26.22	46.88
Mg	0.72	0.85
P	0.64	0.59
Ca	72.41	51.68

Element	Wt%	At%
O	20.56	39.33
Ca	79.44	60.67

Fig. 1. EDS spectrum of (a) natural eggshell, (b) eggshell calcined at 1000 °C, and (c) pure CaO (A.R.).

The changes observed in the XRD patterns (Fig. 3) coincided with a change in the catalytic activity (Table 2). Calcination below 700 °C did not lead to the formation of CaO, and, consequently, the catalytic activity was very low. The best catalytic performance was obtained for calcination temperatures above 800 °C, when the XRD patterns corresponded to a crystalline CaO. Samples calcined at 700 °C contain $CaCO_3$ as the major phase and CaO as a minor phase, hence

Table 2
The catalytic activity of natural eggshell, calcined eggshell and pure CaO (A.R.).

Entry	Catalyst	Conversion of PC (%)	Yield of DMC (%)	Selectivity to DMC (%)	Yield of 1,2-propanediol (%)
1	Natural eggshell	4	–	–	–
2	Eggshell calcined at 300 °C	7	–	–	–
3	Eggshell calcined at 600 °C	7	–	–	–
4	Eggshell calcined at 700 °C	40	16	39	12
5	Eggshell calcined at 800 °C	83	80	96	60
6	Eggshell calcined at 1000 °C	81	79	97	66
7	CaO (A.R.)	83	77	93	64

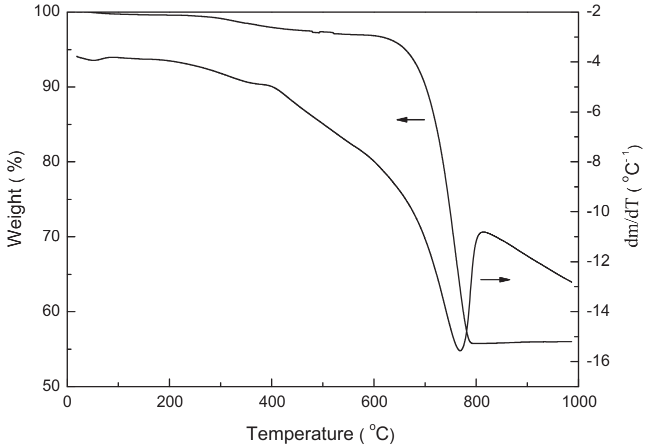


Fig. 2. TGA curves of eggshell.

middle yield were obtained. Therefore it can be concluded that CaO is the active phase of the eggshell derived catalysts.

3.2.2. *Effect of reaction variables*

The stoichiometric ratio for transesterification is 2:1 (methanol/PC). Because this is an equilibrium reaction, an excess of methanol will increase the PC conversion by shifting this equilibrium to producing DMC. The effect of methanol to PC molar ratio on transesterification of PC with methanol was investigated. The DMC yield and PC conversion increased with increasing the molar ratio of methanol to PC, reaching the maximum when the ratio was above 9 (Fig. 4). The molar ratio above 9 did not increase the DMC yield and PC conversion, suggesting that the reaction has reached equilibrium.

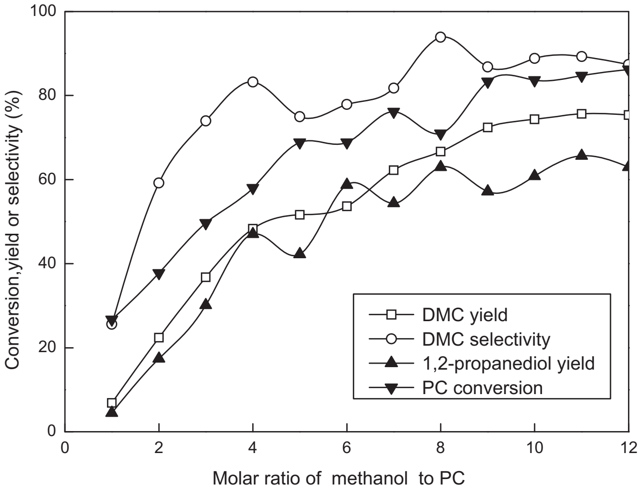


Fig. 4. Effect of methanol to PC molar ratio on transesterification of PC with methanol. Reaction conditions: catalyst amount, 0.8 wt%; reaction temperature, 25 °C; pressure, 1 atm; reaction time, 2 h.

When a small amount of catalyst was used the maximum product yield could not be reached. However, increasing the amount of catalyst lead to the slurry (mixture of catalyst and reactants) becoming too viscous, giving rise to a problem of mixing and higher power consumption for adequate stirring. To avoid this kind of problem, an optimum amount of catalyst loading was determined. As shown in Fig. 5, the yield increased with increasing the

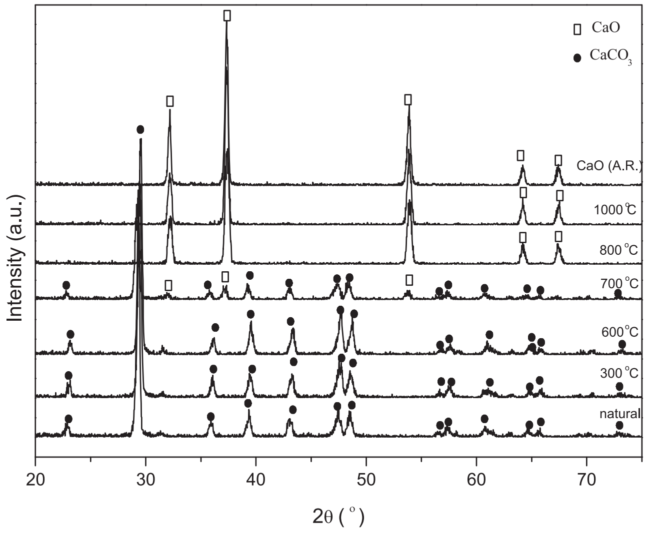


Fig. 3. XRD patterns of natural eggshell, the materials obtained by calcining natural eggshell in the range of 300–1000 °C, and the pure CaO (A.R.).

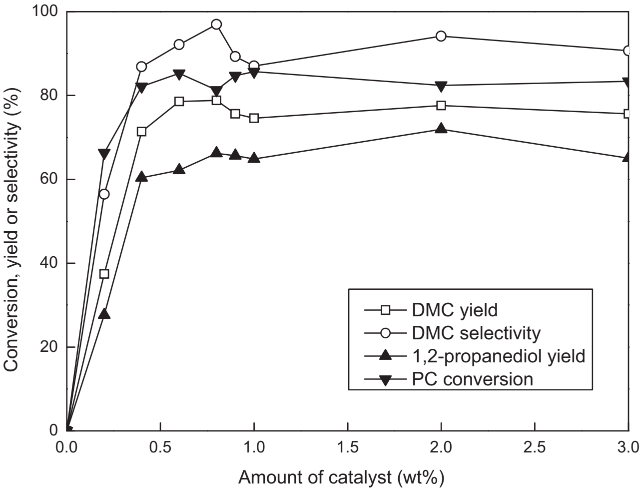


Fig. 5. Effect of catalyst amount on transesterification of PC with methanol. Reaction conditions: methanol to PC molar ratio, 10:1; reaction temperature, 25 °C, pressure, 1 atm; reaction time, 2 h.

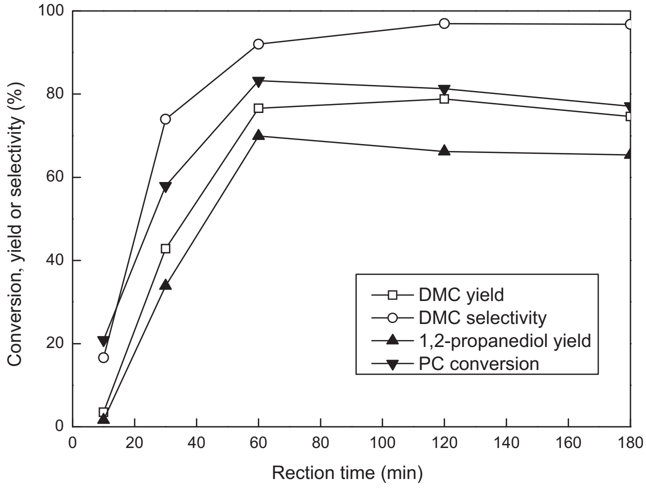


Fig. 6. Effect of reaction time on transesterification of PC with methanol. Reaction conditions: catalyst amount, 0.8 wt%; methanol to PC molar ratio, 10:1; reaction temperature, 25 °C; pressure, 1 atm.

Table 3
Recycling experiments for eggshell catalyst.[a]

Reused times	Conversion of PC (%)	Yield of DMC (%)	Selectivity to DMC (%)	Yield of 1,2-propanediol (%)
First use	81	79	97	66
Second use	79	77	97	67
Third use	85	75	89	60
Fourth use	84	75	89	69

[a] Reaction conditions: methanol to PC molar ratio, 10:1; catalyst amount, 0.8 wt%; reaction temperature, 25 °C; pressure, 1 atm; reaction time, 2 h.

catalyst loading weight up to 0.6 wt%. Above 0.6 wt%, the yield did not increase.

Conversion of PC was also studied with reaction time using eggshells as catalyst. As shown in Fig. 6, it was observed that conversion of PC and yield of DMC increased with time, reaching maximum value (PC conversion >80%) after 1 h. Above 1 h, the conversion of PC remained constant with increasing reaction time.

3.2.3. Comparison of eggshell waste-derived catalysts with pure CaO

The data in the previous section have shown that CaO is the active phase of the eggshell derived catalysts. In order to compare the activity of the eggshell derived catalyst with pure CaO, the activity of pure CaO (A.R.) were investigated. As shown in Table 2, the eggshell (entry 6) and pure CaO (entry 7) have comparable catalytic performance. The composition analysis by EDS indicated that eggshell contained, beside calcium and oxygen, minor constituents (i.e. Mg and P), while pure CaO possessed only calcium and oxygen. Since eggshell and pure CaO have similar catalytic performance, it was concluded that the impurities in the eggshell derived catalyst did not affect activity.

3.2.4. Reusability of eggshell waste-derived catalysts

Recovery and reuse of the catalyst is an important factor in the economics of the use of the heterogeneous catalytic process for DMC manufacture. We attempted to reuse the catalyst by the following method. The used eggshell catalyst was separated from the reaction solution by centrifugation. It was then applied as the catalyst for the repeated reactions. Repeat reactions were run under the same reaction conditions. As shown in Table 3, the eggshell catalyst can be reused at least four times with little deactivation.

4. Conclusion

This is the first report of the synthesis of DMC by transesterification through the use of eggshell-derived catalyst. The eggshell-derived catalyst was active and reusable for DMC synthesis. CaO was proved to be the active phase of eggshell catalysts. The experimental results showed that under the optimum conditions, a 10:1 molar ratio of methanol to PC, addition of 0.8 wt% eggshell catalysts, room temperatures and 1 atm pressure gave the best results, and conversion of PC and yield of DMC reached maximum value (PC conversion = 80%, DMC yield = 75%) after 1 h. In addition, this work further demonstrates that the eggshell-derived material is an effective solid base catalyst.

Acknowledgments

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References

[1] W.J. Stadelman, Encyclopedia of Food Science and Technology, 2nd ed., John Wiley and Sons, New York, 2000, pp. 593–599.
[2] Ministry of Agriculture (MOA) of the People's Republic of China, Yearbook of Agriculture Statistics in China, MOA, Beijing, 2006, pp. 3–5.
[3] W.T. Tsai, K.J. Hsien, H.C. Hsu, C.M. Lin, K.Y. Lin, C.H. Chiu, Bioresour. Technol. 99 (2008) 1623–1629.
[4] W.T. Tsai, J.M. Yang, H.C. Hsu, C.M. Lin, K.Y. Lin, C.H. Chiu, Micropor. Mesopor. Mater. 111 (2008) 379–386.
[5] L. Dupoirieux, D. Pourquier, F. Souyris, J. Craniomaxillofac. Surg. 23 (1995) 187–194.
[6] C. Balázsi, F. Wéber, Z. Kovér, E. Horváth, C. Németh, J. Eur. Ceram. Soc. 27 (2007) 1601–1606.
[7] S. Yoo, J.S. Hsieh, P. Zou, J. Kokoszka, Bioresour. Technol. 100 (2009) 6416–6421.
[8] D. Liao, W. Zheng, X. Li, Q. Yang, X. Yue, L. Guo, G. Zeng, J. Hazard. Mater. 177 (2010) 126–130.
[9] Z. Wei, C. Xu, B. Li, Bioresour. Technol. 100 (2009) 2883–2885.
[10] Y.C. Sharma, B. Singh, J. Korstad, Energy Fuels 24 (2010) 3223–3231.
[11] N. Viriya-empikul, P. Krasae, B. Puttasawat, B. Yoosuk, N. Chollacoop, K. Faungnawakij, Bioresour. Technol. 101 (2010) 3765–3767.
[12] A. Montilla, M.D. del Castillo, M.L. Sanz, A. Olano, Food Chem. 90 (2005) 883–890.
[13] G. Busca, Chem. Rev. 110 (2010) 2217–2249.
[14] N. Keller, G. Rebmann, V. Keller, J. Mol. Catal. A: Chem. 317 (2010) 1–18.
[15] M. Sankar, S. Satav, P. Manikandan, ChemSusChem 3 (2010) 575–578.
[16] H. Wang, M. Wang, W. Zhang, N. Zhao, W. Wei, Y. Sun, Catal. Today 115 (2006) 107–110.
[17] R. Juárez, A. Corma, H. García, Green Chem. 11 (2009) 949–952.
[18] S.R. Jagtap, M.D. Bhor, B.M. Bhanage, Catal. Commun. 9 (2008) 1928–1931.
[19] G. Stoica, S. Abelló, J. Pérez-Ramírez, ChemSusChem 2 (2009) 301–304.
[20] W.T. Tsai, J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin, C.W. Yeh, Bioresour. Technol. 97 (2006) 488–493.
[21] T. Wei, M. Wang, W. Wei, Y. Sun, B. Zhong, Green Chem. 5 (2003) 343–346.