

Synthesis of CaO-CeO₂ catalysts by soft template method for biodiesel production

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Abstract. Biodiesel has recently gained extensive attention. Catalysts play an important role in producing biodiesel by transesterification reaction. In this study, CaO-CeO₂ catalysts are developed as the solid base catalyst. Using PDMS-PEO as a structure-directing agent, the prepared CaO-CeO₂ catalysts have a three-dimensional interconnected porous structure, which benefits the transesterification reaction. While the added Ce slightly decreases the catalytic activity, the stability of the catalyst shows remarkable improvement. Considering the catalytic activity and stability, the best catalyst is determined to be catalyst 0.15-1073 (Ce/Ca molar ratio of 0.15 and calcination temperature of 1073 K). Under optimum reaction conditions, the biodiesel yield reaches to 97.5% and metal leaching is 117.7 ppm. For catalyst 0.15-1073 regenerated after four reaction cycles, the biodiesel yield is 94.1%. The results reveal that the CaO-CeO₂ catalyst has good potential for application in large-scale biodiesel production in the future.

1. Introduction

Nowadays, the overuse of petroleum resources has led to serious environmental pollution everywhere in the world. People are searching for an alternative fuel, and biodiesel has gained considerable attention [1,2]. Compared to traditional petroleum fuel, biodiesel is biodegradable, renewable, non-toxic, has a higher flash point and can be blended with fossil diesel fuel [3]. Due to the fast reaction rates and less corrosive properties, base catalysts are preferred to acid ones. However, removal of the base catalysts after homogeneous reaction is a problem. Therefore, efforts in recent years have been made towards to the development of solid base catalysts in the production of biodiesel.

While there has been much progress using solid base catalysts for producing biodiesel, it remains a challenge to prepare solid base catalysts with high catalytic activity and stability. With extensive studies, the soft template method has become a popular method to synthesize nano-catalysts [4,5], but there are still no reports of CaO-CeO₂ prepared by soft template method for producing biodiesel.

In this study, CaO-CeO₂ catalysts were prepared as solid base catalysts to produce biodiesel. The synthesis of catalysts with high catalytic activity and stability was explored. The structural, textural and basic properties of CaO-CeO₂ catalysts were characterized. The best performing catalyst was obtained



by optimizing the Ce/Ca molar ratio and calcination temperature. Furthermore, the deactivation and regeneration of the best catalyst were investigated.

2. Experimental

2.1. Materials

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), HNO_3 (68%), methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were AR and purchased from Sinopharm Chemical Reagent Co. Ltd. As a soft template, PDMS-PEO was provided by Polysciences Inc. The average molecular weight is 3000 g/mol and the volume ratio of PDMS:PEO is 2:8. Refined soybean oil was obtained from Haishi Co. Ltd.

2.2. Catalyst preparation

The CaO-CeO_2 catalysts are prepared using the EISA (Evaporation Induced Self Assembly) method. First, an aqueous solution of CaO-CeO_2 precursor was prepared by dissolving $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with different Ce/Ca molar ratio in 50 mL ethanol, then PDMS-PEO, citric acid and HNO_3 were added into the solution. It was stirred for 2 h to get a transparent colorless solution. Next, the solution was placed in a drying oven at 333 K for 48 h to induce self-assembly. In the end, the CaO-CeO_2 catalyst was achieved by calcination of the gel-like solid for 2 h with different calcination temperatures under static air atmosphere. The catalysts prepared by this method mentioned above are hereafter denoted as A-B, where A is the Ce/Ca molar ratio and B is the calcination temperature (K).

2.3. Catalyst characterization

The powder X-ray diffraction patterns (XRD) of the samples were recorded on a D8 Advance A25 powder diffractometer using Cu K α radiation (40 kV and 40 mA). The diffractograms were recorded in the 2θ range of 20 to 80 ° with a 2θ step size of 0.02 ° and a step time of 0.12 s.

The specific surface area, pore volume and porosity of the samples were evaluated from nitrogen adsorption isotherms obtained at 77 K in a Quantachrome IQ instrument using the BET and BJH methods. The degasification was performed under vacuum at 473 K for 24 h before the adsorption measurements.

The SEM images were obtained using a SEM instrument of EVO MA15. The magnification was from 5 to 100,000. The samples were gold-coated in a vacuum for 40 s to prevent charging.

The TEM and HRTEM images were obtained on a model JEM 2100 (UHR) equipped with an Oxford INCA Energy Dispersive Spectrometer (EDS) unit, which was operated at an accelerating voltage of 200 kV. The samples suspended in ethanol were supported onto a carbon coated Cu grid.

X-ray photoelectron spectra (XPS) experiments were carried out on an ESCALAB 250Xi (Thermo Fisher Scientific) with Al K α radiation ($h\nu=1486.6$ eV). The sample was directly pressed to a self-supported disk (10×10 mm), mounted on a sample holder, then transferred into an analyzer chamber. The whole spectra (0-1350 eV) and the narrow spectra of all of the elements with high resolution were both recorded by using Thermo Advantage 5.948 Software. Binding energies were calibrated using containment carbon ($\text{C}_{1s}=284.6$ eV).

To investigate the leaching of metal (Ca and Ce) in the FAME phase, the catalyst was separated and centrifuged from the liquid reaction mixture after reaction completion, and the liquid mixture was then analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES, NexIon 300x).

2.4. Catalytic testing

All of the transesterification reactions were performed in a 100 mL three-neck round bottom flask equipped with a reflux condenser and a stirrer. The reaction temperature was controlled by a water bath. The reaction procedure was performed by first dispersing the catalyst in methanol. The soybean oil was then added into the flask. The reaction procedure was heated with stirring. After reaction, the catalyst was separated from the biodiesel product by centrifugation and then the excess methanol was evaporated under reduced pressure in a rotary evaporator. After the methanol was evaporated, washing with hot distilled water was performed in the biodiesel refining process. The moisture remaining from the washed

biodiesel was subsequently removed using anhydrous sodium sulfate. The biodiesel yield was analyzed using a gas chromatograph (FULI9790, China) equipped with a flame ionization detector (FID). Helium was used as the carrier gas and methyl undecanoate was used as an internal standard.

3. Results and discussion

3.1. Influence of the Ce/Ca molar ratio

The influence on catalytic activity and stability from different Ce/Ca molar ratio is shown in table 1. With the improvement of Ce/Ca molar ratio, FAME yield is gradually reduced. According to table 2, with the increase of Ce, the specific surface area and pore volume of catalysts decrease, which reduces catalytic active sites. In addition, the catalytic activity of CaO is better than that of CeO₂, and the increase of Ce means that the relative content of CaO in the catalyst is reduced. Those may cause the decrease of catalytic activity. From the metal leaching in table 1, it can be seen that adding Ce makes the catalysts more stable. The reason will be discussed in subsequent sections. Although CaO has high catalytic activity, the metal leaching of Ca is 330 ppm, which leads the reaction system to be homogeneous. In other words, homogeneous reaction makes a big contribution to FAME yield. Correspondingly, catalyst 0.15-1073 has higher catalytic activity as FAME yield is 97.5% and lower metal leaching (117.7 ppm), so it has the best comprehensive properties.

Table 1. The catalytic activity and metal leaching of catalysts.

Catalyst	FAME yield (%) ^a	Metal leaching of Ca (ppm) ^b	Metal leaching of Ce (ppm) ^b
0-1073 (CaO)	99.3%	330	0
0.10-1073	98.5%	160	13
0.15-1073	97.5%	110	7.7
0.20-1073	92.7%	98	6
0.15-973	75.5%	210	10
0.15-1173	87.5%	91	4.2
0.15-1273	60.5%	83	2

^a Reaction condition: temperature of 333 K, methanol/oil of 30:1, catalyst amount of 10 wt% (based on oil weight), reaction time of 6 h, and stirring speed of 600 rpm.

^b Measured by ICP-AES.

Table 2. Physical properties of CaO and CaO-CeO₂ catalysts.

Catalyst	BET (m ² /g)	Mesopore size (nm) ^a	Pore volume (cm ³ /g) ^a	Lattice Parameter a of CaO (Å)	Average crystallite size of CaO (Å)
0-1073 (CaO)	12.54	1.62	0.089	4.811	30.6
0.10-1073	14.16	32.50	0.169	4.808	21.2
0.15-1073	11.85	31.69	0.155	4.818	19.3
0.20-1073	11.30	32.92	0.141	4.815	15.1
0.15-973	22.63	33.70	0.207	4.809	24.8
0.15-1173	9.84	3.05	0.055	4.815	34.0
0.15-1273	7.60	1.74	0.031	4.814	40.0

^a By N₂ adsorption isotherm branch based on BJH model.

Figure 1 shows the SEM image of catalyst 0.15-1073. It has a three-dimensional interconnected porous structure, which includes microscale macropores and from tens of to hundreds of nanoscale mesopores. The porous structure with both macropores and mesopores is quite helpful to the

transesterification reaction. Those macropores allow high-molecular-weight triglycerides to penetrate deeply into catalyst so that they can reach basic active sites on the catalytic surface. Additionally, the mesopores enhance the specific surface area and pore volume of catalyst, which improves the total amount of basic active sites.

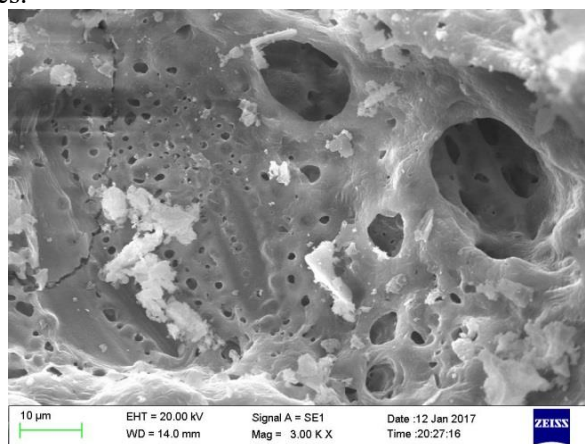


Figure 1. The SEM images of catalyst 0.15-1073.

Figure 2 demonstrates the XRD patterns of the CaO-CeO₂ catalysts with different Ce contents. Compared with CaO, the diffraction peaks of CeO₂ were clearly observed for the catalysts with added Ce. With the increase of Ce, the relative intensity of diffraction peaks of CeO₂ and CaO increases and decreases respectively. Table 2 shows that with the raising of Ce, average crystallite size of CaO phase becomes small, which may be caused by the added Ce inhibiting the growth of the crystal of CaO phase. According to ionic radius in crystals listed by Shannon, the ionic radius of Ca²⁺ in CaO ($r_{\text{Ca}^{2+}}=1 \text{ \AA}$) is slightly bigger than that of Ce⁴⁺ in CeO₂ ($r_{\text{Ce}^{4+}}=0.97 \text{ \AA}$). Therefore, if substitution of Ce⁴⁺ for Ca²⁺ in the CaO structure happens, it will cause the contraction of CaO lattice and the formation of strongly basic anionic vacancies. However, the changes of “a value” in table 2 are slight, indicating no detectable structural modification of the CaO lattice with Ce additions. Moreover, Lu synthesized MgO-Li₂O mixed oxides as base solid catalyst. By DFT, they found out that when Li was doped there was substitution of Li⁺ for Mg²⁺ in the MgO structure, which results in the decline of stability [6]. But in table 1, the stability of catalysts is improved so that it is uncertain whether there is substitution. The reason why stability improves can be described as following: the increase of Ce means that the relative content of CaO in the catalyst is reduced, and CaO is much easier to react with methanol than CeO₂, so metal leaching decreases when Ce increases.

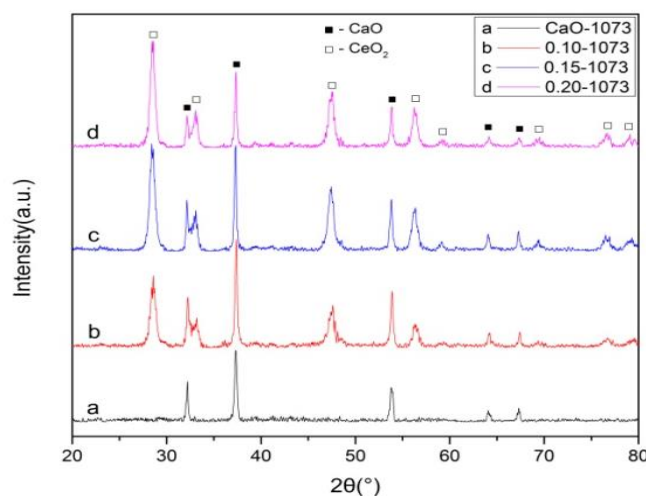


Figure 2. XRD patterns of catalysts with different Ce/Ca molar ratio.

As shown in figure 3, the morphologies and structural details of catalyst CaO and 0.15-1073 were examined by TEM. The HRTEM image of CaO in figure 3 (b) illustrates that the lattice spacing between the adjacent atomic planes of 0.277 nm can be assigned to the interplane distance between the (111) planes of CaO crystal structure. There are no diffraction peaks of SiO₂ detected by XRD, and the EDS result of CaO confirms the existence of Elemental Si in the catalyst surface, but no SiO₂ nanocrystals can be found in the image of HRTEM. These results indicate there is the presence of amorphous SiO₂ in CaO due to its amorphous nature. Likewise, Jeon found a similar result [5]. They synthesized the meso-macroporous TiO₂/SiO₂ thin film using PDMS-g-POEM and did not find SiO₂ crystallites in the film. When Ce is added, like CaO, there is the presence of amorphous SiO₂ in catalyst 0.15-1073. And as shown in figure 3 (d), there are many nanoparticles with sizes ranging from 10 nm to 20 nm uniformly scattered on the surface of catalyst 0.15-1073. The lattice spacing between the adjacent atomic planes of 0.312 nm can be assigned to the interplane distance between the (111) planes of the CeO₂ crystal structure. These nanoparticles are CeO₂. CaO and CeO₂ nanoparticles are evenly distributed in the catalyst.

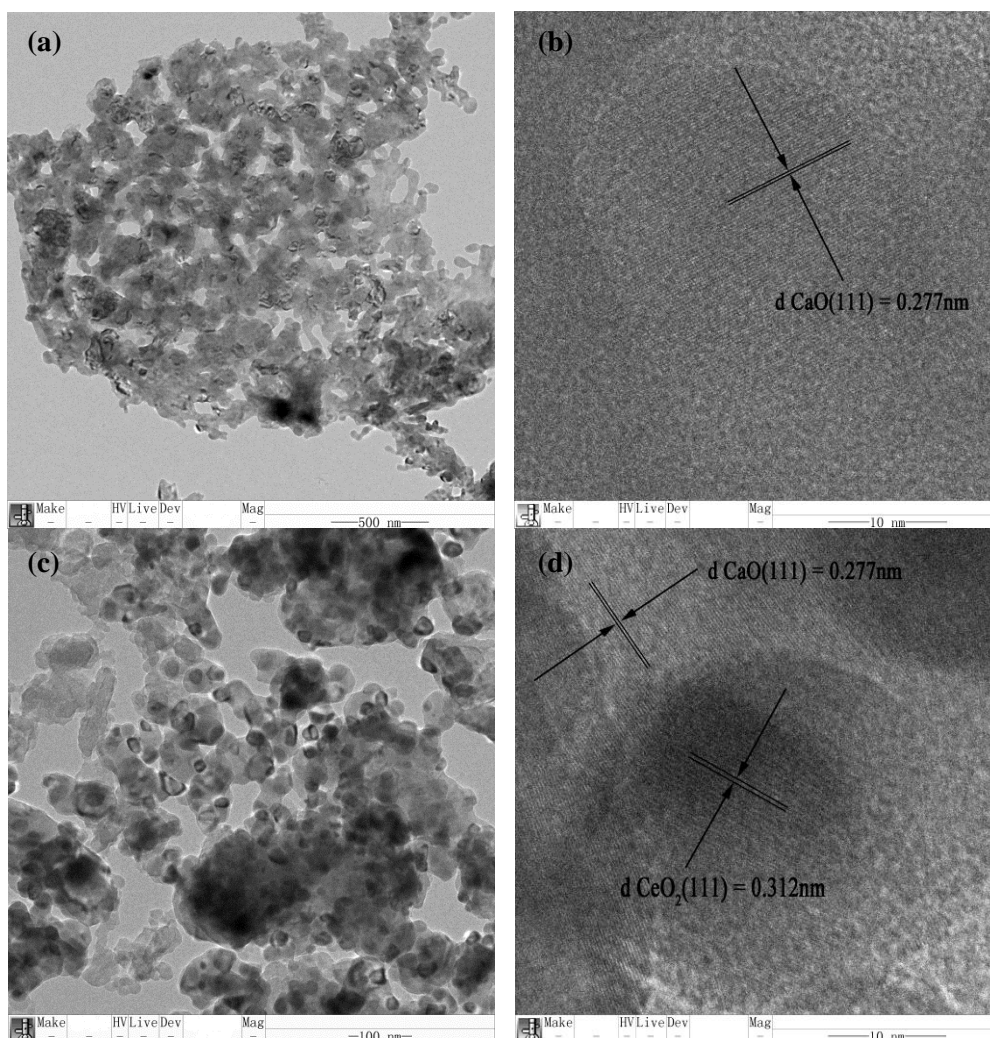


Figure 3. TEM images of CaO (a, b) and catalyst 0.15-1073 (c, d).

The binding energy (BE) of oxygen by XPS can represent the basic strength of catalysts. Generally speaking, when the BE of O_{1s} declines to a lower value, it means that the ability of electron pair donation becomes stronger. So the basic strength increases due to prevailing of their ionic state with the enhanced electron density [7]. Figure 4 shows the BE of O_{1s} of catalysts CaO and CaO-CeO₂. For the CaO, the BE of O_{1s} is 531.6 eV, which is highest. So the basic strength of CaO is the smallest. When Ce is added,

the BE of O_{1s} decreases with increasing Ce, which means the basic strength is enhanced. According to table 2, as added Ce makes crystallite size of CaO phase become small, it leads to the result that the number of low-coordination O^{2-} anions of crystallite of CaO increases. The low-coordination O^{2-} anions, which are on the edge and in the corner of crystallite, have strong basic strength. Similar results are found by Wen [8] and Marian [9]. The BE of O_{1s} of catalysts with different Ce is near. For catalyst 0.20-1073, the BE of O_{1s} is 531.1 eV, which is lowest, so it has the strongest basic strength.

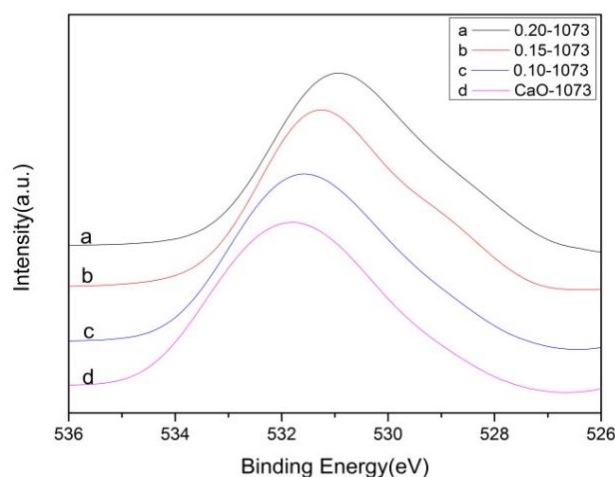


Figure 4. XPS spectra (O_{1s}) of catalysts with different Ce/Ca molar ratio.

3.2. Influence of calcination temperature

Generally speaking, most catalysts need to be calcined to produce the catalytic activity, so the calcination temperature is crucial to the catalytic activity for the transesterification reaction. As demonstrated above, the best Ce/Ca molar ratio is 0.15. This study investigates the influence of calcination temperature on catalytic activity and stability within the range of 973 to 1273 K.

As shown in table 1, the catalytic activity of catalyst 0.15-973 is lower. The reason is that there is still some remaining organics, causing the decrease of catalytic active sites in the catalyst. When calcination temperature rises from 1073 to 1273 K, catalytic activity is gradually reduced while catalyst stability is improved. According to above table 2, with the increase of calcination temperature, the specific surface area and pore volume of catalysts decreases significantly. Additionally, the average crystallite size of CaO phase increases. These factors reduce the catalytic active sites so that the catalytic activity is reduced. For improving stability, higher calcination temperature makes crystallite size of CaO phase bigger, which decreases the number of low-coordination O^{2-} anions. This enhances the difficulty of leaching into methanol for CaO. Therefore, considering catalytic activity and stability, the best calcination temperature is determined to be 1073 K.

3.3. Catalyst reusability and regeneration

Much literature has reported that the catalytic activity of catalysts is high upon initial use, but decreases significantly following several cycles, and therefore is not conducive to commercial and industrial applications. So reusability is one of the most important features for the heterogeneous catalysts [10]. The reusability studies were carried out under optimum reaction conditions (methanol/oil molar ratio of 30:1, catalyst amount of 10 wt%, reaction temperature of 333 K and reaction time of 6 h). After the reaction finished, the catalyst 0.15-1073 was recovered by centrifugation, then washed three times with methanol and dried at 393 K for 3 h. The result of FAME yield is shown in figure 5. The FAME yield decreases from 97.5% to 72.8% when the reaction is repeated four times. It is mainly due to poisoning of the catalyst surface and blockage of pores. This may cause the low accessibility of the catalytic active sites to the reactants, which reduces the FAME yield.

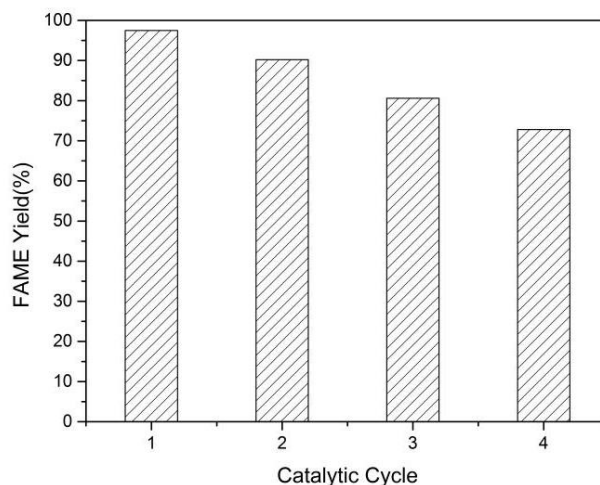


Figure 5. Reuse results of catalyst 0.15-1073.

The regeneration of catalyst 0.15-1073 is investigated after its fourth reuse. The catalyst 0.15-1073 is separated, washed, dried and calcined at 1073 K in air for 2 h. Under the optimum reaction conditions mentioned above, the FAME yield returns to 94.1% with the regenerated catalyst 0.15-1073, slightly less than that of the fresh catalyst. From this result, it indicates that the CaO-CeO₂ catalysts have good potential for large-scale biodiesel production in the future.

4. Conclusions

With soft template method, CaO-CeO₂ catalysts were successfully used to produce biodiesel. The CaO-CeO₂ catalysts have a three-dimensional interconnected porous structure, which benefits the transesterification reaction. The added Ce slightly decreases the catalytic activity, but the stability of catalyst shows a remarkable improvement. Considering the catalytic activity and stability, the best performed catalyst is 0.15-1073 (Ce/Ca molar ratio of 0.15 and calcined at 1073 K) and the biodiesel yield reaches 97.5%. The results reveal that the catalysts CaO-CeO₂ have good potential for large-scale biodiesel production.

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