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# Preparation of nano-CaO and catalyzing tri-component coupling transesterification to produce biodiesel

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#### ABSTRACT

Nano-CaO with different particle sizes and crystallinity was prepared by sol-gel method. A tri-component coupling transesterification of rapeseed oil/dimethyl carbonate (DMC)/methanol was used to determine the viability of prepared nano-CaO as a basic catalyst for biodiesel synthesis. Nano-CaO exhibits better catalytic performance than commercial CaO for biodiesel production under same reaction condition. At 1:1:8 molar ratio of oil to DMC to methanol, 5 wt% nano-CaO catalyst (calcined at 800 °C), and 65 °C reaction temperature, the reaction gave the best results, and the fatty acid methyl ester yield exceeded 92% at 4 h which was 2 h shorter than that of commercial CaO. The catalyst calcined under different temperature has been characterized by BET, CO2-TPD, TGA, XRD, and SEM. As the results shows that nano-CaO calcined at 800 °C exhibited the most active which should be contributed to the presence of good dispersivity, large surface area and pore volume.

An efficient transesterification reaction has been developed over nano-CaO which possessing good dispersivity, larger surface area and pore volume. Dimethyl carbonate as a green methylating reagent, has been added aiming to turn rapeseed oil to biodiesel with no glycerol by-product.

#### Introduction

Associated with the diminishing fossil fuel supplies and increasing environmental concerns, researchers have focused on the renewable energy resources.<sup>[1]</sup> Biodiesel has been considered as a renewable fuel derived from triglycerides by transesterification of triglycerides, typically of chain lengths with 16, 18 or 20 carbon atoms, or their mono-alkyl esters with alcohols.<sup>[2]</sup> The prevailing commercial method of biodiesel production is transesterification of glycerol triglyceride with short-chain alcohols, such as methanol or ethanol, in the presence of soluble inorganic bases as catalysts, such as sodium or potassium methoxides.<sup>[3]</sup> Although the reaction rates for this process are high, recovery of catalysts is difficult and treatment of wastes containing catalysts, water, glycerol and oils presents challenges.<sup>[4]</sup> Furthermore, these heterogeneous catalytic process still produces glycerol byproduct, and its separation from the fatty acids and esters adds to overall cost of biodiesel production. Glycerin, as a by-product, is not very valuable as that obtained from biodiesel production simply adds to the over-supply of the commodity from other sources and thus contribute to a depression of its price.<sup>[5,6]</sup> Glycerol production can be

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avoided if rapeseed oil and DMC are reacted to produce glycerol carbonate as a secondary product that is not required to be separated from the fatty acid esters. Some researchers have used enzymes as catalyst to produce biodiesel by introducing DMC as reactant.<sup>[7]</sup> In our previous research, an indirect reaction between DMC and triglycerides can be established if methanol is added as a third reacting component.<sup>[8]</sup>

The application of calcium oxide as transesterification catalyst for biodiesel production is restricted due to the requirement of long reaction time and high molar ratio of methanol to oil.<sup>[9]</sup> To solve these problems, we expanded the specific surface area of CaO to obtain a relatively high fatty acid methyl ester (FAME) yield.<sup>[10]</sup> Presented in this article are results on the application of nano-CaO prepared by sol-gel method as catalysts for the coupling transesterification of rapeseed oil, dimethy carbonate and methanol to produce biodiesel at moderate condition. The catalytic activities were investigated and the effect of nano-CaO preparation condition on the yield of biodiesel was examined.

#### Experimental

#### **Materials**

Refined rapeseed or canola oil was purchased from Xi'an Coal Co., Ltd. Dimethyl carbonate (DMC), methanol, absolute ethyl alcohol, cyclohexnae,  $Ca(NO_3)_2$ , citric acid (analytical grade).

# **Catalyst preparation**

The mixture that absolute ethyl alcohol/Ca(NO<sub>3</sub>)<sub>2</sub>/citric acid/water was prepared in a 100 mL round-bottomed flask and was heated to gelatinous by water bath. Then the production was aging at room temperature for 24 h and was dried in vacuum oven. Finally, the nano oxide catalyst was obtained after calcinating for 6 h at 900 °C in muffle stove.

#### Preparation of biodiesel

The coupling transesterification of rapeseed oil, dimethy carbonate and methanol to produce biodiesel has been established based on our previous research work as shown in Scheme 1. The reaction was performed in a three necked round bottomed flask equipped with a reflux condenser and methanol were charged into the flask. After 30 g rape-seed oil, 6.0 g methanol and 2.8 g DMC adding, the mixture was heated and maintained at  $65^{\circ}$ C temperature with continuous stirring for hours. Samples were taken out from the reaction mixture every one hour and quenched to room temperature, then the catalyst was separated by

centrifugation, and the excess methanol was distilled off under vacuum. Samples were analyzed for composition on an HP-7890 gas chromatograph equipped with a flame ionization detector and a fused-silica capillary column (HP-5;  $0.32 \text{ mm} \times 30 \text{m}$ ,  $0.1 \mu \text{m}$  film thickness) using methyl heptadecanoate as the standard. The nitrogen was the carrier gas at a flow rate of 20 mL/min. The oven temperature was kept constant at 260 °C. Yield of FAME was defined as a ratio of the weight of FAME in samples, as determined using the gas chromatography, to the weight of equivalent FAME that the oil used in the reaction would have contained.

#### Catalyst characterizations

Textural characteristics were investigated by means of surface area determined by BET including mean pore diameter and pore volume using desorption isotherms on a Micromeritics ASAP2010. Temperature-programmed desorption patterns of carbon dioxide (CO<sub>2</sub>-TPD) for the products were measured with an automated chemisorption analyzer (AutoChem II 2920, Micromeritics, USA) at the temperature range from 40 to 800 °C with a heating rate of 10 °C min<sup>-1</sup>. The crystalline structures of the products of calcination were analyzed using an X-ray diffraction device (JDX-3530, JEOL, Japan) with an X-ray tube that has copper Cu as target and released  $K_{\alpha}$  radiation when accelerated at 30 mA and 40 kV). Thermo gravimetric analyses (TGA) of catalyst samples were performed in the static air condition 20-1000 °C with a heating rate of 5 °C min<sup>-1</sup>, using a thermo-gravimetric analyzer/simultaneous differential thermal analyzer (TGA/SDTA 851e, Mettler-Toledo, Switzerland). Scanning Electron Microscopy (SEM) was used for the investigation of surface morphology of catalyst samples. Before being submitted to SEM characterization, the solid sample was coated with gold in order to achieve sufficient conductivity.

# **Results and discussion**

#### The comparative study

The catalytic performances of 10 wt% nano-CaO powder for biodiesel production have been investigated at refluxing temperature (65 °C) with a molar oil/DMC/methanol ratio of 1:1:8. For comparison, FAME yield of commercial CaO has also been investigated. As indicated in Figure 1, over 90% yield of FAME can be obtained over nano-CaO after 4 h which is better than that of commercial CaO with the yield of FAME below 80%. Similar result has been proved by other researchers that commercial CaO catalyst shows a lower catalytic activity in normal reaction condition for



Scheme 1. The tri-component coupling transesterification to produce biodiesel.



Figure 1. Catalytic performance comparison of different CaO samples.

2

biodiesel production.<sup>[11]</sup> This results indicated that large surface area of nano powder provided more active sites which gave great chance for the high transesterification reaction rate.

3

Time/(h)

4

5

6

# Effect of catalyst amounts

1

FAME yield/(%)

0

0

To explore the influence of the amount of catalyst in the reaction, catalytic performance in presence of various concentration nano-CaO catalysts were tested under the same reaction condition at refluxing temperature (65°C) with a molar oil/DMC/methanol ratio of 1:1:8 and the results were shown in Figure 2. From the results summarized in Figure 2, it can be seen that the yield of FAME markedly increased at the beginning with the increase of catalyst dosage from 1 to 5% (weight to oil). The yield of FAME attained the maximum value of 85.5% when 5% catalyst was introduced at 4 h. However, with further increase of the catalyst content, the FAME yields decrease due to the decrease of contact between the reactants and the catalyst as a result of agglomeration of nano particle catalyst. Moreover, the higher viscosity of the reaction system due to the more the dosage of the nano particle catalyst leads to the influence of the mass transfer so as to the difficulty of the reaction.<sup>[12,13]</sup> So the optimum amount of the catalyst was selected as 5%.

#### Effect of calcination temperature

To study the influence of the calcination temperature of nano-CaO in FAME yield, the catalytic performances of nano-CaO calcinated under various temperatures have been investigated under the optimal conditions obtained in the previous section ( $65^{\circ}$ C refluxing temperature, a molar oil/DMC/methanol ratio of 1:1:8 and 5 wt% nano-CaO catalysts). From the result as shown in Figure 3, it was found that the yield of FAME varied from 38.7 to 90.8% with rising of calcination temperature from 600 to 900°C and reaches the optimal value of 92.82% after 4 h at 800°C. These results may be due to the high thermal stability of the



Figure 2. Effect of the amount of catalyst on biodiesel yield.



Figure 3. Effect of calcination temperature on biodiesel yield.

formed complex of citric acid and  $Ca^{2+}$  during catalyst preparation process. The organic matter failed to decompose completely led to less effective constituent CaO at low calcination temperature, on the contrary, catalytic surface was sintered leading to covering active sites at high calcination temperature.<sup>[14,15]</sup> By drawing on the results, the optimum calcination temperature was selected as 800 °C.

#### Effect of alcohol solvent

Since the amount of alcohol has great effect on the structure of formed gel so as to the physic-chemical properties of obtained nano-CaO particles, the influence of alcohol content on catalytic properties was investigated under the optimal reaction conditions and shown in Figure 4. From the results, it was found that biodiesel yield varied from increase to decrease with the increasing of absolute molar ratio of ethyl alcohol/Ca(NO<sub>3</sub>)<sub>2</sub>/citric acid/water from 0.2/5/5/50 to 2/5/5/50, and the high ratio of ethanol at 1/5/5/50



Figure 4. Effect of the alcohol solvent on biodiesel yield.

indicating low ratio of Ca(NO<sub>3</sub>)<sub>2</sub>/citric acid/water gave the highest biodiesel yield of 92.4%. It is concluded from this results that a critical concentration of water should be noted which affecting the formation of gel probably due to the excess of water causes a very fast hydrolysis of the alcoxide by consuming all the disposable alcoxide groups. The nearcomplete removal of alcoxide groups from the molecular structure causes the condensation of the particles in these systems, because the presence of a small amount of alcoxide groups is necessary to produce the solubility in alcohol.<sup>[16]</sup> However, as the molar ratio of ethanol increases, an occlusion of ethanol and water inside the pores happened. Hence, the pores of formed nano-CaO precursor would be blocked which lead to a decrease in the values of surface area and pore volume of formed gel so to its catalytic performance.<sup>[17,18]</sup>

## Effect of molar ratio

The influence of the molar ratio in the proposed transesterification of rapeseed oil was investigated at refluxing temperature ( $65 \,^{\circ}$ C) using 5 wt% nano-CaO and the results were shown in Figure 5. In general, such a high proportion of methanol, usually 15:1 molar ratio of methanol to oil, was used in transesterification between methanol and oil to promote thigh equilibrium conversion of vegetable oil to esters. However, in this work, from Figure 5, it showed that the optimal proportion of the feed reactants, on a molar basis, is oil: DMC: methanol of 1:1:8 under the refluxing condition. The results suggested that the proposed method containing three reactants greatly reduce the amount of methanol, which gives more potential to the widely application for biodiesel production.

#### **Characterizations of samples**

#### XRD

The X-ray diffraction patterns for all calcium oxide samples calcined under different temperature have been shown in Figure 6. The plots show that the crystal structures of all



Figure 5. Effect of the amount of the methanol on biodiesel yield.



Figure 6. CO<sub>2</sub>-TPD curves of different CaO samples.

nano-CaO particles are similar with major diffraction peaks for CaO at  $2\theta$  angles of  $32.3^{\circ}$ ,  $37.4^{\circ}$ ,  $53.9^{\circ}$ ,  $64.2^{\circ}$ , and  $67.4^{\circ}$ .<sup>[19]</sup> Peaks of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> were also visible that obtained nano-CaO is partially hydrated and carbonated. Furthermore, the characteristic diffraction peaks of CaCO<sub>3</sub> were still existed even the calcination temperature was set at 900 °C, which indicated that the complete decomposition of CaCO<sub>3</sub> required high temperature.

#### BET

The BET surface, pore size and average volume of different nano-CaO are characterized and listed in Table 1. As shown, a reasonable increase of the  $S_{BET}$  and the pore volume were observed over nano-CaO, which benefit the mass transform between catalysts and reactants in the heterogeneous reaction. Therefore reasons for the tremendous variation in the catalytic efficiency of the sample prepared using sol-gel

Table 1. Pore structure property of the CaO samples.

	BET surface area (m²/g)	Pore volume (cm <sup>3</sup> /g $\times$ 10 <sup>-2</sup> )	Pore size (nm)
CaO	443.3695	0.4414	39.8189
Nano-CaO	659.3303	0.5868	35.5979

method in this experiment. Moreover, pores in both samples belong to the mesopores class with their dimension of magnitude larger than the triglyceride dimensions,<sup>[20]</sup> thus any significant diffusion restriction should not be expected. According to Figure 7, the hysteresis curve of common CaO is more similar to Type H1 and put up adsorption limit in the low relative pressure, while the hysteresis curve of nano-CaO is corresponding to Type H3 with more obvious hysteresis loop, which shows that the pore pattern is vary from narrow seam pore to ampuliform pore with small caliber and large lumen.<sup>[7,21]</sup>

# CO<sub>2</sub>-TPD

For solid basic catalysts, the amount of  $CO_2$  irreversibly adsorbed reflects the population of basic sites on exposed surfaces. The desorption temperature indicates that the strengths of adhesion at the base site. Results for temperature-programmed desorption are presented in Figure 8. According to the result, above 615 °C desorption peak indicated that nano oxides exhibit stronger base than commercial oxides. With increasing of calcination temperature, desorption curves of nano-CaO move to high temperature attributed to the strong basic sites of  $O^{2-}$  anions, which indicated that the low calcination temperature led to weak effect of  $O^{2-}$ , while the effect of  $O^{2-}$  was strengthened with increasing calcination temperature.<sup>[22]</sup> This is similar to previously claimed that the required calcination temperature to generate maximum amounts electron donating sites on CaO surface should be high than 700 °C.<sup>[23]</sup>

# TGA

In order to investigate the influence of temperature of the catalyst activation on biodiesel yield, the thermal behavior of the prepared samples were investigated using TGA from room temperature to 800 °C. Figure 9 exhibits TGA curves of nano-CaO and commercial CaO. In the thermograph of both samples two major steps for the mass loss with changing temperature indicating two endothermal effects. The first step from 350 to 420 °C is due to loss of decomposing Ca(OH)<sub>2</sub>, known to perform less efficiently in the transesterification reaction in comparison to its counterpart oxide. The second step occurred in the range of 500-600 °C corresponding to the release of CO<sub>2</sub> from CaCO3 due to the easily react of CaO with carbon dioxide as it was exposed to the air. Based on these thermogravimetric properties it seems that a much more pronounced endothemic effect at 400 °C for prepared nano-CaO particles indicating much more hydration of this sample. The decompose temperature for CaCO3 around 600 °C suggest that the complete decarbonation of carbonates over nano-CaO requires higher temperature and the thermal stability of nano-CaO has been improved.



Figure 7. N<sub>2</sub> adsorption curves of the catalyst.



Figure 8. CO<sub>2</sub>-TPD curves of different CaO samples.



Figure 9. TGA plot for different CaO samples.

# FT-IR

The Fourier transform infrared spectra of the commercial CaO and nano-CaO calcinated at different temperatures were shown in Figure 10. The absence of the band at  $1645 \text{ cm}^{-1}$ , usually assigned to the bending of OH-groups of physisorbed water molecules, on all of nano-CaO samples, indicates that



Figure 10. IR spectra of the commercial and nano-CaO.

the complete dehydration of nano-CaO over calcination temperature of 600 °C. For all the samples, the spectra bands at 850 and 1460 cm<sup>-1</sup> correspond to vibration modes of mono and bidentate carbonates which provide the poisoning of  $CO_2$ over their surface. The nano-CaO appeared stronger vibration a mode indicates that it was eroded more easily by  $CO_2$  than commercial CaO as exposed to the air. Although results of thermal analysis presented in TGA (Figure 8) suggest that 600 °C should be the temperature high enough for the complete decarbonation, it is obvious that in reality this process requires higher temperatures. On the other side, the vibration peaks of mono and bidentate carbonates have diminished with increasing calcination temperature, which indicate the surface sintering of nano-CaO under high calcination temperature.

# SEM

The SEM images of commercial and nano-CaO samples calcined under different temperature were shown in Figure 11.



600 °C





CaO

These images of nano-CaO show a good morphology that particles are more homogeneous than commercial CaO. However, nano-CaO particles calcined at 900 °C were column like indicating sintering of the surface so as to its relatively low yield of biodiesel, while nano-CaO particles calcined at 800 °C which are concentrated in spheres and the particle size distribution is more uniform indicating the good dispersivity which have good relationship with its best catalytic performance.

# Conclusion

In this research, nano-CaO obtained by sol-gel method exhibited high activity in the transesterification of rapeseed oil with DMC and methanol to produce biodiesel. At 1:1:8 molar ratio of oil to DMC to methanol, addition of 5 wt% nano-CaO catalyst (calcined at  $800 \,^{\circ}$ C), gave the best results with FAME yield exceeded 92% at 4 h under  $65 \,^{\circ}$ C reaction temperature, which shorten 2 h of reaction time than commercial CaO at the same reaction condition. The large surface area and strong basic properties results in a remarkable high activity of nano-CaO. Based on this highly efficient and low-cost catalyst, the production of biodiesel could be greatly enhanced and the production cost could be reduced.

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