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## Hydrothermal effect on synthesis, characterization and catalytic properties of calcium methoxide for biodiesel production from crude *Jatropha curcas*

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Hydrothermal synthesis is a well-suited approach for preparing bulk metal catalysts with high purity as it is cost-effective and easy to control in terms of temperature and time. In the current study, an effective catalyst for transesterification of high fatty acid content of crude Jatropha curcas oil (JCO) was appraised. Calcium methoxide  $(Ca(OCH_3)_2)$  has been successfully synthesized via a green and economical hydrothermal process at different synthesis times. CaO was used as a precursor as it is abundant, inexpensive and environmentally friendly. Ca(OCH<sub>3</sub>)<sub>2</sub> can form on the surface of CaO and its active basic surface is very well developed. This facile experimental strategy without any surfactant or template produced porous Ca(OCH<sub>3</sub>)<sub>2</sub> with a high surface area and high basicity, which leads to a superior catalytic reaction and is a promising alternative for short-reaction-time solid-based catalysts in biodiesel production in terms of excellent transesterification performance and long durability. The performance of synthesized Ca(OCH<sub>3</sub>)<sub>2</sub> was examined by characterizing it using analytical techniques such as TG-DTA, XRD, BET, FT-IR, TEM and SEM. Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts had three types of morphologies, i.e. (a) irregular round shape particles, (b) a well arrangement of plate-like structures with rough surface and (c) a cluster of tiny plate-like architectures with smooth surfaces. The correlation between synthesis time, surface area and morphology of catalysts and the biodiesel yield was studied. Ca(OCH<sub>3</sub>)<sub>2</sub> was able to maintain the FAME content above 86% after a fifth cycle, at optimum reaction conditions of 2 h reaction time, 12:1 methanol/oil molar ratio, 2 wt% catalyst loading and 65 °C reaction temperature. Ca(OCH<sub>3</sub>)<sub>2</sub> is a solid heterogeneous catalyst for the transesterification reaction of non-edible Jatropha curcas oil for biodiesel production. The catalyst can be separated easily from the reaction mixture and reused to give a consistent transesterification activity.

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## Introduction

Biodiesel, also called fatty acid methyl ester (FAME), is a promising alternative energy source for the transportation sector. Numerous advantages are associated with biodiesel, such as renewability, low/zero net CO<sub>2</sub> emission, low sulfur and higher biodegradability.<sup>1</sup> Additionally, biodiesel is superior to fossil diesel fuel in terms of cetane number, flash point and lubricity characteristics. Biodiesel can be produced by the transesterification with alcohol of various feedstocks such as vegetable oils (Europe), palm oil (South East Asia), *Jatropha* oil, Kranjar oil (India) and soybean oil (USA). In order to solve the problems related to food-based biodiesel, non-edible oils have attracted increasing attention as potential feedstocks.<sup>2</sup>

The *Jatropha curcas* L. seed kernel has about 60% oil content. *Jatropha curcas* L. is attracting increasing attention as a potential feedstock as it is non-edible and easy to produce, it has low cost and its seeds are available in abundance. Therefore, this makes its use as an energy or fuel source very attractive, especially for biodiesel production. The overall reaction of methanolysis of vegetable oil is shown in Scheme 1.

$H_2C$ —COO— $R_1$ HC—COO— $R_2$ + H <sub>2</sub> C—COO— $R_3$	3CH <sub>3</sub> OH <u>catalyst</u>	H <sub>3</sub> C—COO—R <sub>1</sub> H <sub>3</sub> C—COO—R <sub>2</sub> H <sub>3</sub> C—COO—R <sub>3</sub>	H₂C—ОН   + НС—ОН   H2C—ОН
triglyceride	methanol	mixture of alkyl esters (FAME)	glycerol

 $R_1$ ,  $R_2$ ,  $R_3$  = hydrocarbon chains ranging from 15 to 21 carbon atoms

Scheme 1 Transesterification of triglyceride with methanol.

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Due to their advantages of corrosion resistance, environmental benignancy and easy separation from liquid products, heterogeneous solid catalysts are being widely used for the transesterification of triglycerides. Calcium oxide (CaO) is the most widely used and exhibits good catalytic properties for transesterification of triglycerides to biodiesel from an economic point of view.<sup>3,4</sup> However, the reaction rate is slow and it seems not to be adaptable for industrial application, because extensive leaching of, for example, Ca<sup>2+</sup> may reduce the reusability and the environmental sustainability of the catalyst.<sup>5,6</sup>

Recently, hydrothermal synthesis has turned out to be wellsuited for the preparation of bulk metal catalysts with high purity as it is low-cost and easy to control (i.e. temperature and time). The variety of micro/nano-materials with unique morphologies can be obtained, such as nanocable,<sup>7</sup> nanorod,<sup>8</sup> star-shaped and flower-like9 products. Up to now, this technique has been successfully applied in preparing Ca(OCH<sub>3</sub>)<sub>2</sub> solid catalyst.<sup>10-12</sup> However, morphology and structurecontrolled growth of micro/nanoarchitectures of Ca(OCH<sub>3</sub>)<sub>2</sub> has not been achieved. The synthesized  $Ca(OCH_3)_2$  exhibited various unique physical and chemical properties, such as high surface area, ideal porosity and strong basicity. Nanoparticle catalysts could be an important factor for improving the catalytic properties by exposing catalytically active -OCH<sub>3</sub> on the surface of the catalyst, which would favor the transesterification reaction.13

Herein, we report a simple hydrothermal approach without using any surfactant or template to prepare  $Ca(OCH_3)_2$  catalyst. By varying the synthesis time, heterogeneous catalysts exhibiting different effectiveness in the transesterification of crude *Jatropha curcas* oil (JCO) with methanol have been obtained. The active phase of  $Ca(OCH_3)_2$  was characterized with data obtained from physico-chemical properties of the catalysts. The influence of varying the synthesis time on the size and structural and textural properties of the prepared  $Ca(OCH_3)_2$  is appraised. Also, the correlative effect between transesterification activity and catalyst surface area is discussed. This is the first report in which the catalytic performance of  $Ca(OCH_3)_2$  for the transesterification of non-edible crude JCO is presented. Moreover, the efficiency and reusability of the catalyst in biodiesel production is also studied.

## Experimental

#### Preparation and characterization of materials

Crude *Jatropha curcas* L. oil (JCO) was purchased from Bionas Sdn Bhd, Malaysia and was used without further treatment or purification. CaO (R&M Chemicals, 99.0%), anhydrous methanol (Merck, 99.7%) were purchased from Fisher Scientific and used for methanolysis of CaO and transesterification of oil reactions. Dichloromethane (Fisher Scientific, UK) was used as solvent for FAME yield evaluation. Methyl heptadecanoate,  $C_{18}H_{36}O_2$ , was the internal standard for gas chromatography analysis. All the chemicals used in the present study were analytical reagent grade.

The fatty acid profile of crude JCO was identified and is tabulated in Table 1. The average molecular weight (M) was

calculated based on the acid value (AV) and saponification value (SV) of crude JCO obtained using the following correlation:<sup>14</sup>

$$M = 56.1 \times 1000 \times 3/(\text{SV} - \text{AV})$$
(1)

 $Ca(OCH_3)_2$  catalyst was prepared by heating CaO in excess dehydrated methanol under 65 °C at a range of durations (2 to 12 h) under N<sub>2</sub> flow (50 ml min<sup>-1</sup>). The reaction can be expressed as shown in Scheme 2.

CaO was used without removing any hydroxide phase. Typically, 1 g of CaO was dispersed rapidly into 20 ml of anhydrous methanol in a three-neck round bottom flask equipped with a water-cooled reflux condenser and a magnetic stirrer. The resulting white suspended slurry was continuously stirred at 600 rpm to facilitate sufficient contact between the reactants. Then, the white paste precursor was formed by distilling most of the methanol using a rotary evaporator under reduced pressure and was then dried in a vacuum oven at 105 °C for 1 h. Henceforth, the catalysts are denoted as CMX, where X represents the reflux time of 2, 4, 6, 8, 10 and 12 h, respectively.

#### Catalyst characterization

Thermogravimetric and differential thermal analysis (TG/DTA) of the Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts was performed using a Mettler Toledo thermogravimetric analyzer. The heating was carried out in an air flow (100 ml min<sup>-1</sup>) with a heating rate of 10 °C min<sup>-1</sup>, from 35 to 1000 °C.

Powder X-ray diffraction analysis (XRD) was employed to identify the crystallography of the Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts. The analysis was carried out using a Shimadzu diffractometer model XRD6000. The diffractometer employed CuK $\alpha$  radiation (2.7 kW and 30 mA) with wavelength ( $\lambda$ ) of 1.54 Å to generate diffraction patterns from powder crystalline samples at ambient temperature. The data were recorded over a 2 $\theta$  range of 5–40° with steps of 0.02° and a count time of 1 s. Each sample was run for 35 minutes. The phases were identified using the power diffraction file (PDF) database (JCPDS, International Centre for Diffraction Data). The crystallite size of the catalysts can be calculated from the line broadening or FWHM (full width at half maximum) of the corresponding peaks (the most intense peaks), by using the Debye–Scherrer equation<sup>15</sup> as follows:

$$t = \frac{0.89\lambda}{\beta_{hkl}\cos\theta_{hkl}} \tag{2}$$

where *t* is the crystallite size for (*hkl*) phase (nm),  $\lambda$  is the X-ray wavelength of radiation for CuK $\alpha$ ,  $\beta_{hkl}$  is the full width at half maximum (FWHM) at (*hkl*) peak in radians and  $\theta_{hkl}$  is the diffraction angle for (*hkl*) phase.

The specific surface area, average pore size, total pore volume and pore size distribution of the  $Ca(OCH_3)_2$  catalysts were determined from the corresponding nitrogen adsorption-desorption isotherms at liquid nitrogen temperature (-196 °C) with a Thermo Finnigan Sorptomatic 1900 series. The isotherms were generated by dosing nitrogen onto the catalyst. Before the adsorption measurements, all the catalysts (0.5 g) were degassed for 8 h at 150 °C under vacuum conditions until

Table 1 Fatty acid composition of crude Jatropha curcas oil-based methyl esters (CJCOME) in comparison to other esters using GC-FID analysis

FAMEs	Carbon	CJCOME <sup>a</sup>	POME <sup>b</sup>	CiRME <sup>c</sup>	$SBME^d$	SFOME <sup>e</sup>
Lauric acid	12:0	_	0.9	_	_	_
Myristic acid	14:0	_	1.5	_	_	_
Palmitic acid	16:0	20.2	41.9	26.9	12.5	46.0
Palmitoleic acid	16:1	1.1	_	_	_	_
Stearic acid	18:0	7.2	2.7	4.6	5.2	4.0
Oleic acid	18:1	39.8	40.8	25.6	23.5	40.0
Asclepic acid	18:1(n-7)	_	_	1.2	_	_
Linoleic acid	18:2	31.2	11.9	37.7	48.8	10.0
Linolenic acid	18:3	0.3	0.3	3.8	10.0	_
Arachidic acid	20:0	0.2	_	0.2	_	_
$\sum_{SFA}^{f}$		27.6	47.0	31.7	17.7	50.0
$\sum_{\text{USFA}}^{g}$		72.4	53.0	68.3	82.3	50.0

<sup>a</sup> CJCOME (crude Jatropha curcas oil methyl esters).<sup>b</sup> POME (palm oil methyl esters).<sup>21</sup> <sup>c</sup> CiRME (Citrus reticulate methyl esters).<sup>2 d</sup> SBME (soybean methyl esters).<sup>11 e</sup> SFOME (sunflower oil methyl esters).<sup>2 f</sup> Total saturated fatty acid. <sup>g</sup> Total unsaturated fatty acid.

the pressure gradient reached an extremely low state. The total surface area ( $S_{\text{BET}}$ ), total pore volume (cm<sup>3</sup> g<sup>-1</sup>) and average pore size (nm) of the catalysts were generated from adsorptiondesorption isotherms by using the Brunauer-Emmett-Teller (BET) method, whereas the pore size distribution was evaluated from desorption branches by using the Barrett-Joyner-Halenda (BJH) plot.

Infrared spectra of the solid  $Ca(OCH_3)_2$  catalysts were measured by using attenuated total reflection-Fourier transform-infrared (ATR-FTIR) on a Perkin Elmer (PC) Spectrum 100 FTIR spectrometer to identify the surface functional groups presenting on the catalyst at room temperature. Each spectrum was an average of 128 scans analyzed over the wavelength scanning range of 650-4000 cm<sup>-1</sup> at a resolution of  $4 \text{ cm}^{-1}$ .

The morphological observations of the prepared Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts were made by field emission scanning electron microscopy (FESEM, JOEL, JSM-6700F) and transmission electron microscopy (TEM, Hitachi, H7100). For FESEM analysis, the catalysts were coated with Au (gold) for avoiding the induction of electric current using a sputter coater. Particle size of the Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts was obtained by using TEM with an accelerating voltage of 200 kV.

#### Methanolysis of triglycerides

Production of biodiesel by methanolysis of crude J. curcasderived oil, over Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst, was performed using a 100 ml two-neck round-bottom flask equipped with a watercooled reflux condenser and with continuous stirring at



calcium oxide

Scheme 2 Hydrothermal synthesis of calcium oxide with methanol.

900 rpm. The reaction proceeded at a controlled temperature, using a silicone oil bath to keep the temperature constant. Typically, CMX (X = 2-12) catalyst was suspended in the required volume (n(methanol) : n(oil) = 12 : 1) of methanol. The reaction temperature was controlled at 65 °C by the silicone oil bath. Crude JCO (10 g) was added into the mixture under vigorous stirring in the presence of catalyst (2 wt%). Once the reaction had finished (1.5 h), the mixture was then cooled to room temperature. After cooling, the catalyst was separated via centrifugation and the residual methanol and glycerol of the byproduct were eliminated by washing with water. The transesterified oil was collected after the separation process mentioned above, and was dried with a rotary evaporator under reduced pressure prior to analysis.

### Analysis of fatty acid methyl esters

The yield of FAME produced was measured using gas chromatography on a Shimazu GC-14C. A split type injector and a flame ionization detector (FID) were connected to a polar BP-20 capillary column (30 m  $\times$  0.5 mm  $\times$  0.25  $\mu$ m). The transesterified oil was injected at 140 °C with a split ratio of 1:30. FAME was separated from the transesterified oil in the column heated at 250 °C, with the heating rate at 5 °C min<sup>-1</sup>. Methyl heptadecanoate was used as an internal standard and dichloromethane was used as the solvent. The FAME content was determined in agreement with European regulated procedure EN 14103.16 FAME content (%) was calculated using the equations as following:

FAME yield (%) = 
$$[(m_{\text{FAME}}/\text{MW}_{\text{FAME}}) \times C_{\text{FAME}}]/$$
  
 $[(m_{\text{JCO}}/\text{MW}_{\text{JCO}}) \times 3] \times 100\%$  (3)

where  $m_{\text{FAME}}$  and  $m_{\text{ICO}}$  are the mass of FAME produced and JCO, respectively, and MWFAME and MWICO are the average molecular weights of FAME produced and JCO, respectively, which were calculated according to the composition of fatty acids.

Additionally,  $C_{\text{FAME}}$  is the FAME concentration and the coefficient 3 accounts for the fact that each triglyceride molecule yields three methyl ester molecules.

### Recyclability study of produced catalyst

To study the catalyst lifetime and stability, used CM8 catalyst was separated from the reaction mixture and reused in a transesterification reaction without additional treatment. In this case, crude JCO and methanol were added in the same amount into each reaction system, and the reactions were performed at the optimum conditions.

## Results and discussion

#### Properties of crude Jatropha curcas L. oil

The crude JCO was found to contain 0.091% w/w of moisture. Other analyses for the crude JCO were a density value of 0.9162 g cm<sup>-3</sup>, a saponification value of 188.4  $m_{\text{KOH}}/m_{\text{oil}}$  (mg g<sup>-1</sup>) and an acid value of 13.6  $m_{\text{KOH}}/m_{\text{oil}}$  (mg g<sup>-1</sup>). Therefore, the average molecular weight of *J. curcas* oil was calculated as 962.8 g mol<sup>-1</sup>. Moreover, the content of free fatty acids presence in crude JCO is 6.8% w/w, which is in the higher range.

The gas chromatography results showed that the FAME constituents present in *J. curcas* oil were methyl palmitate  $(C_{16:0})$ , methyl palmitoleate  $(C_{16:1})$ , methyl stearate  $(C_{18:0})$ , methyl oleate  $(C_{18:1})$ , methyl linoleate  $(C_{18:2})$  and methyl arachidate  $(C_{20:0})$ ; unsaturated methyl esters were the most prominent compounds.

The methyl ester composition of crude JCO is shown in Table 1, which shows that it consisted of 72.4% unsaturated fatty acids (USFA), whereas the level of saturated fatty acids (SFA) was 27.6%. These results conform with the profiles in the literature.<sup>10</sup> The GC data revealed the fatty acid profiles of biodiesel fuels produced from other sources were comparable to the major ester constituents derived from crude JCO. However, crude JCO exhibited a high unsaturated/saturated lipid ratio, with the sequence soybean methyl esters (SBME) > crude *Jatropha curcas* oil methyl esters (CJCOME) > *Citrus reticulate* 

methyl esters (CiRME) > palm oil methyl esters (POME) > sunflower oil methyl esters (SFOME).

#### Catalyst characterization

In thermogravimetric analysis (TGA), the weight of the synthesized catalyst was measured as a function of temperature while it was subjected to a controlled heating programme. The amount of weight loss provided a quantitative indication about the composition of the catalyst. Additionally, the temperature of thermal and oxidative degradation of the catalyst was also measured using differential thermal analysis (DTA). The curve showed the physical and chemical transitions of the sample by measuring exothermic and endothermic effects.

Fig. 1 shows the TGA and DTA thermograms of the synthesized Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst under air flow conditions. The TGA curve remained constant from 35 °C to 370 °C. Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst began to decompose at about 370 °C with a weight loss of around 17%. This phenomenon was due to a chemical reaction occurring. The DTA curve shows an exothermic peak appearing between 370 and 460 °C, which is consistent with the peak in the TGA curve. The reaction at 430 °C might be the decomposition of Ca(OCH<sub>3</sub>)<sub>2</sub> with oxygen to calcium carbonate as shown in Scheme 3.

Furthermore, the TGA curve showed evidence of thermal decomposition of calcium carbonate, with the formation of gaseous products above 600 °C. A steep slope was observed between 600 and 800 °C in the TGA curve. At 720 °C, the DTA peak showed the endothermic transformation of CaCO<sub>3</sub> to stable CaO. The thermogravimetric analysis suggested that the

Ca(OCH<sub>3</sub>)<sub>2</sub> + 3O<sub>2</sub> 
$$\longrightarrow$$
 CaCO<sub>3</sub> + CO<sub>2</sub>  $\uparrow$  + 3H<sub>2</sub>O  $\uparrow$  (exothermic)  
Scheme 3



Fig. 1 TGA and DTA thermograms of calcium methoxide catalyst.

synthesized  $Ca(OCH_3)_2$  catalyst is stable below 400 °C. Thus, the produced  $Ca(OCH_3)_2$  catalyst is extremely stable during the transesterification reaction.

The XRD patterns of all the catalysts are shown in Fig. 2. CaO had very appreciable broad peaks at  $2\theta$  of  $32.1^{\circ}$  and  $37.2^{\circ}$  (JPDS file no. 00-037-1497). Ca(OCH<sub>3</sub>)<sub>2</sub> was characterised with the presence of a peak at  $2\theta$  of  $10.8^{\circ}$  (ref. 17) for CM2–CM12 catalysts. The insignificant three peaks at  $2\theta$  of  $17.8^{\circ}$ ,  $28.6^{\circ}$ , and  $34.0^{\circ}$  suggested the existence of calcium hydroxide (JCPDS file no.: 01-84-1264), which had probably appeared due to the interaction of the catalyst with the water molecules formed as a byproduct during the synthesis reaction.

The crystallite size and surface area of the catalysts are summarized in Table 2. As can be seen, the average crystallite size for pure CaO catalyst was 66.3 nm. The CM2–CM12 catalysts had crystallite sizes of 29.0, 31.1, 30.6, 27.5, 29.7 and 31.4 nm, respectively. These results indicated that crystallite sizes of the final products were being reduced significantly to become



Fig. 2 X-ray diffraction patterns of calcium oxide and calcium methoxide catalysts. Ca(OCH<sub>3</sub>)<sub>2</sub> was prepared with methanol reflux of CaO at 65 °C (under 50 ml min<sup>-1</sup> nitrogen flow conditions) for 2, 4, 6, 8, 10 and 12 hours, and is accordingly labeled as CM2, CM4, CM6, CM8, CM10 and CM12. •, characteristic peak of calcium methoxide;  $\Delta$ , characteristic peak of calcium oxide;  $\bigcirc$ , characteristic peak of calcium hydroxide.

2 times smaller compared to pure metal oxide clusters. The results also showed that crystallite sizes of the catalysts were in agreement with the line width of the peak in which decrease of FWHM with the increment of the crystallite size.

The surface areas of all the catalysts are shown in Table 2. The surface area of the catalysts was in agreement with XRD analysis which showed that smaller crystallite sizes gave higher surface areas, as demonstrated in Fig. 3. The BET isotherm of the CM8 catalyst resembles the Type IV isotherms, with hysteresis loop of type H3 based on the IUPAC classification.<sup>18,19</sup> The measured surface area, total pore volume and average pore diameter were  $30.5 \text{ m}^2 \text{ g}^{-1}$ ,  $0.21 \text{ cm}^3 \text{ g}^{-1}$  and 31.97 nm, respectively. Therefore, this suggested that the catalyst is favourable for use in a liquid phase reaction since it can provide a sufficiently large area of active sites in a stirrer-type reactor.<sup>20</sup>

The pore size distribution of the CM8 catalyst reveals that the surface is occupied by relatively small-size mesopore structures in the range of 2 to 5 nm, as shown in Fig. 4. Mesoporous materials can serve as effective catalysts in transesterification reactions for adsorbing large organic molecules, due to their uniform pore structure and extremely high surface area. Furthermore, a large part of the surface is fully occupied by larger pore structures, with size between 6 and 100 nm. The macropore structure of the particle catalyst provides rapid mass transfer into the interstices of the catalyst and leads reagent to the ultimate reaction sites. Consequently, high surface area and porosity properties are important characteristics of solid catalysts because they are closely related with the catalytic activity.

The FTIR spectrum of the synthesized  $Ca(OCH_3)_2$  catalysts at room temperature are shown in Fig. 5, which indicates that the important features appear in the –C–O stretching vibration of primary alcohol (1070 cm<sup>-1</sup>), –OH stretching vibrations (2800– 3000 cm<sup>-1</sup>) and –C–H alkene bending (1465 cm<sup>-1</sup>).<sup>20,21</sup> Furthermore, the unusual peak that appeared at 3650 cm<sup>-1</sup> suggested the adsorption of water on the surface of all catalysts. This peak indicates the existence of –OH functional groups isolated on calcium cation.<sup>20</sup> Since water was produced as a byproduct in the catalyst synthesis reaction, these isolated –OH groups might have been produced from water, facilitated by the

Table 2	able 2 Crystallite size, BET surface area, shape and particle size of calcium methoxide catalysts					
Catalyst	2 heta (°)	FWHM	Crystallite size <sup><math>a</math></sup> (nm)	$S_{\text{BET}}^{b} \left(\text{m}^2 \text{g}^{-1}\right)$	Shape <sup>c</sup>	Particle size <sup>d</sup> (nm)
CaO	37.4701	0.1510	66.3	9.2	Cubic crystal	$137.02\pm11.30$
CM2	10.8448	0.2784	29.0	16.2	Cubic crystal & irregular round	$170.71 \pm 25.26^{e} \ \& \ 68.06 \pm 19.29$
CM4	10.8348	0.2597	31.1	18.3	Cubic crystal & irregular round	$120.07 \pm 23.32^{e} \ \& \ 34.74 \pm 3.26$
CM6	10.8248	0.3074	30.6	20.5	Plate	$267.10 \pm 35.10$ (D) $72.46 \pm 22.34$ (T)
CM8	10.8105	0.2941	27.5	30.5	Plate	$391.77 \pm 65.34$ (D) $111.38 \pm 13.12$ (T)
CM10	10.8213	0.2721	29.7	28.8	Plate & round	530.41 $\pm$ 21.69 (D) 157.38 $\pm$ 5.69 (T) &
						$302.30 \pm 46.93$
CM12	10.8223	0.2847	31.4	26.0	Irregular bulky round	$366.52\pm24.82$

<sup>*a*</sup> Determined from XRD patterns using the Scherrer equation. <sup>*b*</sup> BET surface area. <sup>*c*</sup> Observed by SEM analysis. <sup>*d*</sup> Measured by TEM technique. <sup>*e*</sup> unreacted CaO and (D): diameter and (T): thickness





Fig. 3 Crystallite size and BET surface area of calcium methoxide catalysts.

strong basic property of  $Ca(OCH_3)_2$  catalyst, as shown in Scheme 3.

The particle morphology of all the catalysts is summarized in Table 2. It was found that the difference in synthesis time leads to the different morphologies of Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst, as shown in the TEM (Fig. 6) and FESEM (Fig. 7) images. Fig. 6(a) and (b) show the TEM images of the parent and non-modified CaO as the starting material. The TEM images of CaO show clusters of well-developed cubic crystals. The particle sizes were measured from the TEM image and the average particle sizes were 137.02  $\pm$  11.30 nm in diameter. The structure of commercial CaO catalyst showed surface unevenness (Fig. 7(a) and (b)).

Fig. 6(c) and (d) show TEM images of the CM2 catalyst synthesized over 2 hours, giving cubic crystals of unreacted CaO and irregular round-shaped Ca(OCH<sub>3</sub>)<sub>2</sub> that are 170.71  $\pm$  25.26 nm and 68.06  $\pm$  19.29 nm in diameter, respectively. Increasing the synthesis time showed no significant changes in morphology for the CM4 catalyst (Fig. 6(e) and (f)). However, the TEM images revealed that the average particle sizes were



Fig. 4 Pore size distribution of CM8 catalyst.

reduced to  $120.07 \pm 23.32$  nm (unreacted CaO) and  $34.74 \pm 3.26$  nm in diameter. The shapes of the CM2 and CM4 catalysts were confirmed by FESEM, as shown in Fig. 7(c)–(f). These results are consistent with the results obtained, corroborating the conclusion from the XRD patterns about the existence of CaO and Ca(OCH<sub>3</sub>)<sub>2</sub> particles.

On the other hand, the TEM images in Fig. 6(g) and (h) show that the CM6 catalyst was composed of bundles of particles of biconvex-like structure (view from top of plate-like shape particles). The average particle sizes of CM6 as determined from the TEM images were a diameter of  $267.10 \pm 35.10$  nm and a thickness of  $72.46 \pm 22.34$  nm. Furthermore, a small amount of well arranged irregular plate-like shape particles is clearly visible on the external surface of the catalyst observed in Fig. 7(g) and (h). A minute amount of particles or patches also coexisted. The close-up view of Fig. 7(g) and (h) shows a typical plate-like structure with an overall size of about 70 nm in length; and a few small particles attached on the assembled plates formed rough surface particles. This result is consistent with the result gained from morphological studies by the FESEM technique.

Representative TEM images of the CM8 catalyst are displayed in Fig. 6(i) and (j). In the magnified TEM image in the inset, rigid biconvex-like structure particles are sufficiently revealed by the appearance of the clear edge (Fig. 6(j)). The averages sizes of CM8 determined from TEM images (Fig. 6(i) and (j)) were 391.77  $\pm$  65.34 nm in diameter and 111.38  $\pm$  13.12 nm in thickness, correspondingly. The primary particles of CM8 catalyst appeared to be formed of abundant clusters of thin plates as shown in Fig. 7(i) and (j). Increasing the synthesis time not only resulted in high quantities and uniform morphology, but also enhanced the number of pores which are visible on the surface of the catalyst. The pores and thin plate-like morphology contributed to the high surface area of the catalyst. The close-up view in the inset of Fig. 7(j) shows that the thin plate particles possessed a smooth surface state and were about 100 nm in length, almost consistent with the FESEM observations.

Fig. 6(k) and (l) shows the TEM photos of the CM10 catalyst consisting of aggregated biconvex-like structure particles ( $530.41 \pm 21.69$  nm in diameter and  $157.38 \pm 5.69$  nm in thickness) and large aggregated round particles ( $302.30 \pm 46.93$  nm in diameter). The higher crystallinity of CM10 was confirmed by FESEM (Fig. 7(k) and (l)). The crystallites of the CM10 catalyst were larger than those observed for the CM8 catalyst, which presented aggregates of variable morphology. The micrograph of FESEM endorsed the crystallinity result of XRD.

The TEM micrographs of the CM12 catalyst gave an irregular shape of Ca(OCH<sub>3</sub>)<sub>2</sub>, for which the synthesis time was 12 hours. The particle sizes were measured from the TEM image and the average particle sizes were  $366.52 \pm 24.82$  nm in diameter, as shown in Fig. 6(m) and (n). The FESEM micrographs of the CM12 catalyst gave irregular bulky round-shape on the external surface of the catalyst, as shown in Fig. 7(m) and (n). The CM12 catalyst with compact agglomeration was in agreement with the TEM images.



Fig. 5 FTIR spectra of the calcium methoxide catalysts.

The results demonstrated that the synthesis time is the key for controlling the morphology evolution of the cluster thin plate-like calcium methoxide architectures. The collapsing of the plate-like structure of calcium methoxide catalysts led to the reduction of the total surface area of the catalysts. Notice that, from Table 2, the particle sizes measured between XRD and TEM show dissimilarity. The sizes obtained from TEM were greater than those obtained from the XRD measurement. This deviation is known to depend on the aspect ratio for nonplated shaped crystallites, apart from the contributions to the FWHM by the microstrain in the crystallite.<sup>22</sup> Despite this limitation, the agreement that is seen between the sizes measured by these two techniques may be taken to be good in terms of the conclusion drawn as to the shape and, to a limited extent, as to the approximate true size of these crystallites.

### Transesterification reaction: correlation between biodiesel yield and synthesis time, surface area and morphology of catalysts

The transesterification reaction involved the cleavage of the ester group RCOO<sup>-</sup>, from triglycerides (TG), by an alcohol moiety of methanol to produce new esters with the original alcohol moiety exchanged with the reacting alcohol. Since there are three ester groups in a TG molecule, the three fatty acid moieties attached to a single alcohol moiety yielded intermediate formation of diglycerides (DG), monoglycerides (MG) and glyceride (Gly). The consecutive-competitive steps of the transesterification reaction between TG and methanol are shown in Scheme 4.

Different synthesis times of bulk  $Ca(OCH_3)_2$  catalysts on transesterification of crude JCO are presented in Table 3. It is

noteworthy that the catalytic activity of synthesized Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts showed high transesterification activity in the range of 74–87% under conditions of: 2 wt% of catalyst, molar ratio of methanol/oil (12 : 1) and reaction time 2 h at 65 °C. The FAME yield was increased from CM2 to CM8, while the further increment of synthesis time from CM10 to CM12 resulted in small decreases in catalytic performance.

The BET surface area of a catalyst is believed to be an important factor which affects the catalytic activity.<sup>12,20,23</sup> The correlation between surface area of catalysts and FAME yield is demonstrated in Fig. 8. The enhancement in FAME content from 74% to 87% while shifting from CM2 to CM8 might be due to the increase in the catalysts' surface area from 16.2 to  $30.5 \text{ m}^2 \text{ g}^{-1}$ . The further increment of synthesis time for CM10 and CM12 led to a slight drop in surface area, giving areas of 28.8 and 26.0 m<sup>2</sup> g<sup>-1</sup>, respectively. The collapsing plate-like structures in CM10 and CM12 tend to reduce the catalyst's surface area. The lower catalyst surface with synthesis times above 8 h is the reason for the decrease in catalyst activity. This might be due to the diffusion limitation between the reactant and the active sites which were located inside the pores of the catalyst.

As shown in Fig. 8, the morphology of the CM2 and CM4 catalysts was revealed to be an irregular round shape, with a surface area lower than that of the CM8 catalyst. However, their catalytic activity was comparable. This was probably due to the synergistic effect of the presence of CaO and Ca(OCH<sub>3</sub>)<sub>2</sub> phases in the CM2 and CM4 catalysts, which were observed from the XRD profile (Fig. 2). The lower surface area of the CM2 and CM4 catalysts was contributed to by the CaO phases. Excessive CaO phases caused lesser porosity on the catalyst surface, which contributed to the reduction in surface area. On the other hand,



Fig. 6 TEM micrographs of calcium oxide and calcium methoxide catalysts: (a) & (b) CaO; (c) & (d) CM2; (e) & (f) CM4; (g) & (h) CM6; (i) & (j) CM8; (k) & (l) CM10; (m) & (n) CM12.



Fig. 7 SEM micrographs of calcium oxide and calcium methoxide catalysts: (a) & (b) CaO; (c) & (d) CM2; (e) & (f) CM4; (g) & (h) CM6, the insets are close-up views focused on one bunch of plate-like structure particles; (i) & (j) CM8, the insert of (i) is an enlarged image focused on a cluster of tiny plate and the inset of (j) is a magnified FESEM image of a few cluster plates; (k) & (l) CM10; (m) & (n) CM12.



Scheme 4 Stepwise consecutive transesterification reaction and formation of DG, MG and Gly.

the BET surface area of CM6 was 20.5 m<sup>2</sup> g<sup>-1</sup>, which raised the FAME yield to 81.2%. The presence of well arranged irregular plate-like shape particles in the catalyst provided more active surfaces for the transesterification reaction.

The CM8 catalyst exhibited much higher biodiesel production than that of the other catalysts, and a biodiesel yield of 87.1% was achieved at 2 h. There was only a pure Ca(OCH<sub>3</sub>)<sub>2</sub> phase found at CM8 catalyst to be the highest surface area which provide strong basic property toward the transesterification reaction. The cluster thin plate-like architectures of the CM8 catalyst showed mesoporous and macroporous

Table 3Transesterification activities of bulk CM2, CM4, CM6, CM8,CM10 and CM12 catalysts with different synthesis times for biodieselproduction $^{a}$ 

Catalysts	Yield of FAME (%)		
CM2	74		
CM4	78		
CM6	81		
CM8	87		
CM10	79		
CM12	80		

<sup>*a*</sup> Transesterification conditions: catalyst dosage 2%, n(methanol) : n(JCO) = 12 : 1, reaction time 2 h, reaction temperature 65 °C.

properties, as shown in Fig. 4. Mesoporous and macroporous materials can serve as effective catalysts in transesterification reactions for adsorbing large organic molecules, due to uniform structure and extremely high surface area.<sup>12,20</sup> Therefore, the reactivity of a catalyst is directly correlated with the external surface area of the catalyst.

#### Recyclability study

Fig. 9 summarizes the experimental results of reusability between  $Ca(OCH_3)_2$  and CaO catalysts. Unlike the CaO catalyst,



Fig. 8 Correlation between biodiesel yield with surface area of CM2, CM4, CM6, CM8, CM10 and CM12 catalysts. Reaction conditions: oil = 10 g, catalyst dosage = 2%, n(methanol) : n(oil) = 12 : 1, reaction time = 1.5 h, reaction temperature = 65 °C.

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Fig. 9 Recyclability study of CM8 and CaO catalysts. Reaction conditions: oil = 10 g, catalyst dosage = 2%, n(methanol) : n(oil) = 15 : 1, reaction time = 1.5 h, reaction temperature = 65  $^{\circ}$ C.

the transesterification operation of Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst was successively repeated 5 times and maintained sustained activity to produce yields in excess of 86% biodiesel at 65 °C. The only slightly reduced in biodiesel yield was found during successive cycles of use. Due to the lesser porosity and fewer active surface basic sites of the CaO catalyst, the CaO catalyst was not suitable for transesterification of crude JCO at short reaction times in the presence of only low concentrations of catalyst.23

The proposed mechanism of the transesterification reaction by the  $Ca(OCH_3)_2$  catalyst with methanol and triglyceride process is demonstrated in Scheme 5.

Firstly, when calcium methoxide is used as a solid base catalyst, the catalysis mechanism could be assumed on the basis that the catalytic reactions take place on the surface of the catalyst, with  $Ca^{\delta^+}$  and  $O^{\delta^-}$  being the two catalytically

active sites participating in the reaction. Methanol and triglyceride are adsorbed on the two neighboring free catalytic sites, as indicated by step (a) and step (b). In step (a), the surface  $O^{\delta-}$  extracts  $H^{\delta+}$  and  $Ca^{\delta+}$  adsorbs  $CH_3O^{\delta-}$  from methanol. Meanwhile, the adsorbed triglyceride forms a surface intermediate between  $O^{\delta-}$  with the  $Ca^{\delta+}$  on the surface of the catalyst, as shown in step (b). The two neighboring adsorbed species react with each other, in step (c), which results in the formation of a fatty acid methyl ester and a diglyceride. Using the stepwise consecutive and reversible reaction, the diglyceride and monoglyceride react with methanol on the surface of the catalyst to produce methyl esters and glycerol in a similar fashion.

## Conclusions

 $Ca(OCH_3)_2$  is a powerful heterogeneous catalyst for the transesterification reaction of non-edible Jatropha curcas oil for biodiesel production. Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts have three types of morphologies: irregular round shape particles, a well arrangement of plate-like structures with a rough surface and a cluster of tiny plate-like architectures with smooth surfaces. Under optimum conditions of 65 °C, 12:1 methanol to oil molar ratio and 2% catalyst concentration, a greater than 87% yield was achieved in 2 h. Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst can be separated easily from the reaction mixture and reused to give consistent transesterification activity (five times reuse). This hydrothermal method is simple and the steps to fabricate the Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst are easily performed. The  $Ca(OCH_3)_2$  catalyst produced can be used for various application *i.e.* (i) transesterification of trimethylolpropane for bio-lubricant production, (ii) ring-opening polymerization of lactone and (iii) as an effective consolidants precursor material for polymerization.



Scheme 5 Reaction mechanism for the transesterification of triglyceride with methanol over the calcium methoxide catalyst, where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> represent the long-chain alkyl groups.

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