

Research Article

Synthesis of Ca-Doped Three-Dimensionally Ordered Macroporous Catalysts for Transesterification

Tanat Chokpanyarat,¹ Vittaya Punsuvon ^{1,2} and Supakit Achiwawanich ¹

¹Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok, Thailand

²Center of Excellence-Oil Palm, Faculty of Science, Kasetsart University, Bangkok, Thailand

Correspondence should be addressed to Supakit Achiwawanich; fsciska@ku.ac.th

Received 27 October 2017; Revised 27 December 2017; Accepted 8 January 2018; Published 13 March 2018

Academic Editor: Joon-Hyung Lee

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The novel three-dimensionally ordered macroporous (3DOM) CaO/SiO₂, 3DOM CaO/Al₂O₃, and 3DOM Ca₁₂Al₁₄O₃₂Cl₂ catalysts for biodiesel transesterification were prepared by sol-gel method. The 3DOM catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The hierarchical porous structure was achieved; however, only 3DOM CaO/Al₂O₃ and 3DOM Ca₁₂Al₁₄O₃₂Cl₂ catalysts were used for transesterification due to high amount of active CaO. Various parameters such as methanol to oil molar ratio, catalyst concentration, reaction time, and their influence on the biodiesel production were studied. The result showed that 99.0% RPO conversion was achieved using the 3DOM Ca₁₂Al₁₄O₃₂Cl₂ as a catalyst under the optimal condition of 12 : 1 methanol to oil molar ratio and 6 wt.% catalyst with reaction time of 3 hours at 65°C.

1. Introduction

In recent years, the demand of fossil energy is increasing by a rapid growth of global transportation and industrial evolution, thus driving world economic. In addition, the fossil energy becomes expensive due to limited resources. It is predicted that the fossil energy would be exhausted by 20 centuries [1]. Hence, more researchers are focusing on new alternative energy resources. Biodiesel is one of the alternative energies consisting of monoalkyl ester that was derived from recycled cooking oil, vegetable oil, and animal fats. In addition, it is renewable, clean-combustion diesel replacement. Biodiesel is produced by transesterification from either vegetable oil or animal fat with methanol in the presence of a catalyst, resulting in glycerol and biodiesel. This clean diesel provides low carbon monoxide emission, low greenhouse gases emission, noncombustion of hydrocarbon, and nonsulfur dioxide content compared to those of fossil fuel. The physical properties and energy content of biodiesel are similar to fossil fuel; therefore, it can be used to function conventional diesel engines efficiently without modification [2].

The catalysts for transesterification are categorized into two groups: homogeneous and heterogeneous. The homogeneous catalysts such as sodium hydroxide or potassium hydroxide are most often used commercially because of their high catalytic activity and high productivity. However, the product must be neutralized, preventing corrosion in engine. The solid catalysts or heterogeneous catalysts, on the other hand, are easily separated from the produced biodiesel. For example, KNO₃/Al₂O₃, La₂O₃/ZrO₂, and K₂CO₃ on alumina/silica support are highly active for transesterification of vegetable oils [3–5].

Recently, a new hierarchical material named three-dimensionally ordered macroporous (3DOM) has been extensively studied because of its unique ordered structure with the interconnected wall. Owing to this structure, the refined palm oil (RPO) may not only enter the 3DOM catalyst pores easily but also transfer into the inner area of the catalyst. This may enhance biodiesel production. In this work, the three-dimensionally ordered macroporous (3DOM) CaO/SiO₂, 3DOM CaO/Al₂O₃, and 3DOM Ca₁₂Al₁₄O₃₂Cl₂ were synthesized by the sol-gel method (SG). The obtained 3DOM catalysts were characterized by various techniques such as X-ray diffraction (XRD), scanning electron microscopy

(SEM), and Fourier transform infrared spectroscopy (FTIR). The catalytic efficiency of the 3DOM catalysts for transesterification was investigated. Optimal conditions for transesterification using the obtained 3DOM catalysts were studied. The property of the produced biodiesel using the 3DOM catalysts was reported herein.

2. Experimental Procedures

2.1. Synthesis of PMMA Colloidal Crystal. The monodispersed poly(methyl methacrylate) (PMMA) spheres were synthesized by emulsifier-free emulsion polymerization as previously described by Phumthiean [6]. A mixture of water and methyl methacrylate was stirred at 75°C under nitrogen (N₂) atmosphere. Then, 1.2 g of 2,2'-azobis(2-amidinopropane) dihydrochloride, an initiator, was added into the mixture and stirred for 2 h until reaction was completed. After reaction, the mixture was cooled down to room temperature and filtrated through glass wool to remove large particles. The PMMA spheres were self-assembled by gravitation until a clear solution and a colloidal crystal arrays were observed. The obtained PMMA arrays were dried at 60°C for 24 h.

2.2. Preparation of 3DOM Catalysts by Sol-Gel Method. The Ca-doped 3DOM catalysts were synthesized by the sol-gel method using calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) and tetraethoxysilane (TEOS) for 3DOM CaO/SiO₂, calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) and aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O) for 3DOM CaO/Al₂O₃, and aluminium isopropoxide (AIP) and calcium chloride dihydrate (CaCl₂·2H₂O) for 3DOM Ca₁₂Al₁₄O₃₂Cl₂. The precursor of each catalyst was mixed in ethanol and was stirred for 30 min at room temperature. Subsequently, each precursor solution was added on the PMMA arrays until the PMMA template was saturated with the precursor solution. The materials were dried at 80°C for 24 h and calcined at 700 and 800°C. The heating rate was set at 2°C/min. The atomic mol percentage is shown in Table 1.

2.3. Characterization of the 3DOM Catalysts. All 3DOM catalysts were characterized by XRD, FTIR, and SEM techniques in order to investigate the crystal structure, functional group, and morphology of the synthesized materials, respectively. X-ray diffraction measurements were performed by a Bruker D8 advance diffractometer using Cu K α radiation ($\lambda = 0.154$ nm) with current of 40 mA and voltage of 40 kV. Data were collected in range of 10–70° 2 θ with step size of 0.02°.

The infrared spectra were recorded at room temperature in the range of 400–4000 cm⁻¹ with 32 scans and 4 cm⁻¹ resolution using a Bruker Equinox 55 FTIR spectrometer. The surface morphology of the catalysts was observed by a FEI Quanta 450 scanning electron microscope (SEM) using an acceleration voltage of 20 kV.

2.4. Transesterification: Catalytic Study of the Synthesized 3DOM Catalysts. The transesterification condition, adapted from Suwanthai [7], was employed to study catalytic efficiency

TABLE 1: Atomic mol percentage used for Ca-doped 3DOM material synthesis.

Material	Atomic mol percentage
3DOM CaO/SiO ₂	2:1 (mol Ca: mol Si)
3DOM CaO/Al ₂ O ₃	2:1 (mol Ca: mol Al)
3DOM Ca ₁₂ Al ₁₄ O ₃₂ Cl ₂	2:1 (mol Ca: mol Al)

of two Ca-doped 3DOM materials, 3DOM CaO/Al₂O₃ and 3DOM Ca₁₂Al₁₄O₃₂Cl₂. The reaction was carried out in a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer. A 10 g of palm oil was added into the flask, and then the temperature of oil was raised to the designated temperature. The 3DOM catalyst and methanol were added into the flask using 8 wt.% of catalyst amount and 12:1 of molar ratio of methanol to oil. The reaction was then stirred under 750 rpm at the temperature of 65°C for 3 h. After the reaction was completed, the 3DOM catalyst was separated by centrifugation.

An optimal condition for transesterification using the 3DOM catalyst was achieved by varying the amount of the 3DOM catalyst (6–12 wt.%), molar ratio of methanol to oil (9:1–24:1), and reaction time (3–5 h), respectively. The reaction temperature was fixed at 65°C.

2.5. Refined Palm Oil (RPO) Conversion Analysis and Biodiesel Analysis. Nuclear magnetic resonance (NMR) spectra were recorded on a VARIAN NMR spectrometer. The spectrum was obtained at 400 MHz for ¹H, using CDCl₃ as a solvent. The conversion of fatty acid methyl ester was measured using peak areas of the ¹H NMR signals from methyl ester at 3.6 ppm and that of glycerol at 2.3 ppm [8]. The percentage of the fatty acid methyl ester conversion was calculated as follows:

$$C = \left(\frac{2A_1}{3A_2} \right) \times 100, \quad (1)$$

where C is the percentage of fatty acid methyl ester conversion, A_1 is peak of the methyl esters, and A_2 is peak of the methylene in glycerol.

The biodiesel product from transesterification has been purified and used to study its properties using the following standard condition: acid value (ASTM D664), kinematic viscosity at 40°C (ASTM D445), density (ASTM D1298), and flash point (ASTM D93).

3. Results and Discussions

3.1. Characterization of the 3DOM Materials. The morphology of the synthesized PMMA templates revealed monodispersed PMMA spheres with face-centered cubic (FCC) arrangement [9] (Figure 1(a)). The average diameter was approximately 338 ± 38 nm. These PMMA colloidal crystals were used as templates for syntheses of 3DOM CaO/SiO₂, 3DOM CaO/Al₂O₃, and 3DOM Ca₁₂Al₁₄O₃₂Cl₂ catalysts for transesterification reaction.

The morphology of the 3DOM CaO/SiO₂ calcined at 600, 700, and 800°C was exhibited in Figures 1(b)–1(d). It can be seen that a highly ordered porosity was achieved at the temperature of 600 and 700°C (Figures 1(b) and 1(c)),

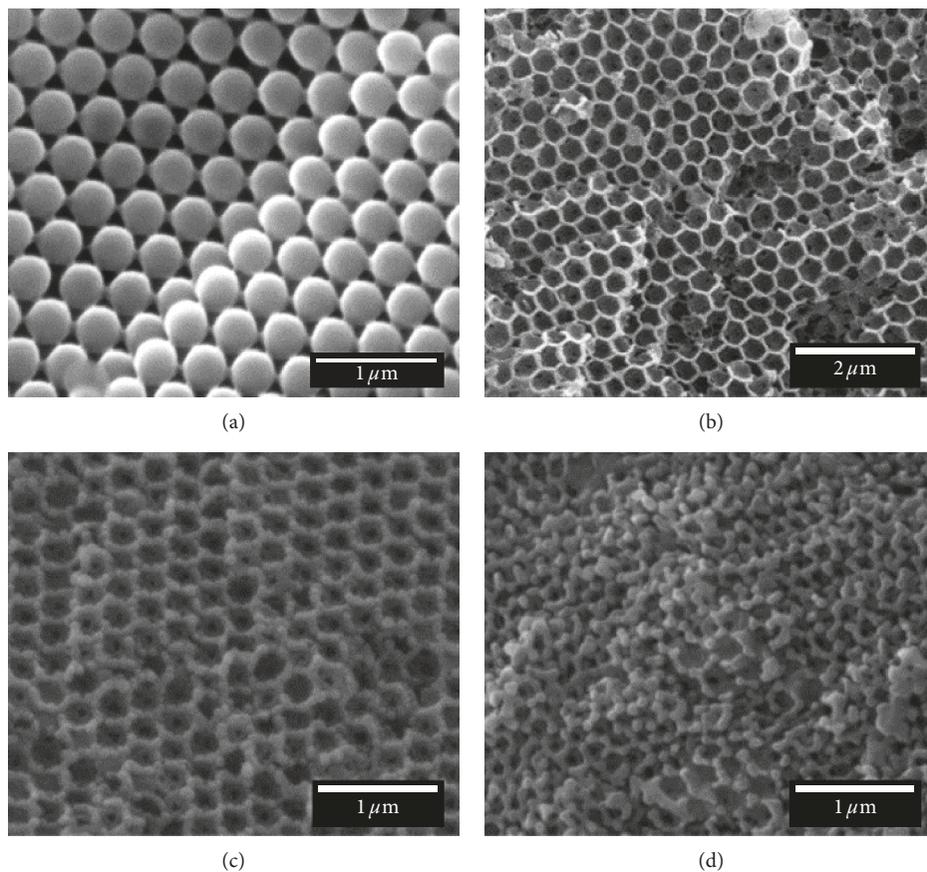


FIGURE 1: SEM images of (a) PMMA colloid crystals and (b-d) 3DOM CaO/SiO₂ at 600, 700, and 800°C, respectively.

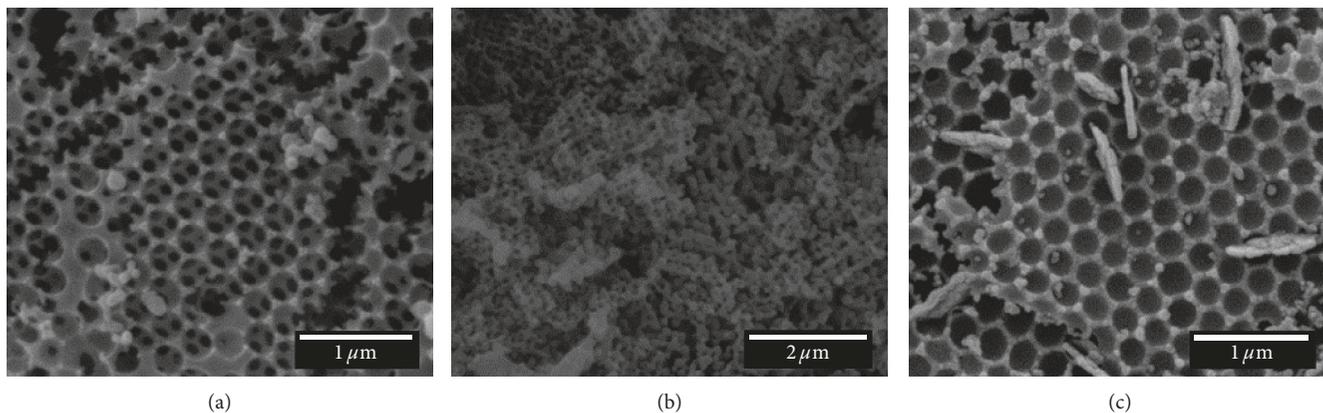


FIGURE 2: SEM images of 3DOM CaO/Al₂O₃ (a) at 700°C (×40000) and (b) at 800°C (×20000) and (c) 3DOM Ca₁₂Al₁₄O₃₂Cl₂ at 700°C (×40000).

respectively. However, the 3DOM CaO/SiO₂ at 800°C was a nonordered structure due to high calcination temperature (Figure 1(d)). Increasing the calcination temperature may result in accumulation and sintering of Ca, resulting in bigger particles and decreasing in surface area [10, 11].

The SEM images of the synthesized 3DOM CaO/Al₂O₃ at 700 and 800°C were shown in Figures 2(a) and 2(b). The 3DOM structures were obtained after calcination at 700°C with average

porous diameter of 231 ± 17 nm. At 800°C, the failures of the hierarchical structures of the 3DOM CaO/Al₂O₃ were similar to the 3DOM CaO/SiO₂ at 800°C. The morphology of 3DOM Ca₁₂Al₁₄O₃₂Cl₂ at 700°C was also achieved with a pore diameter of 165 ± 9 nm with irregular particles on the surface (Figure 2(c)).

The XRD patterns of the 3DOM CaO/SiO₂ catalysts at 600–800°C are shown in Figure 3. At 600°C, an amorphous SiO₂ band centered at 30° and CaCO₃ at 29° (104) were

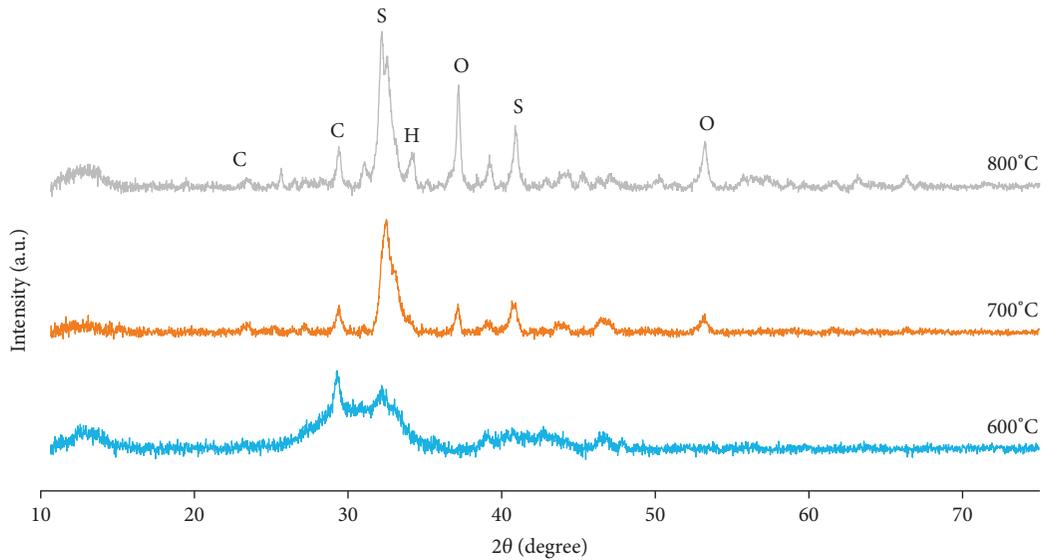


FIGURE 3: XRD patterns of the 3DOM CaO/SiO₂. H = Ca(OH)₂, O = CaO, S = Ca₂SiO₄, and C = CaCO₃.

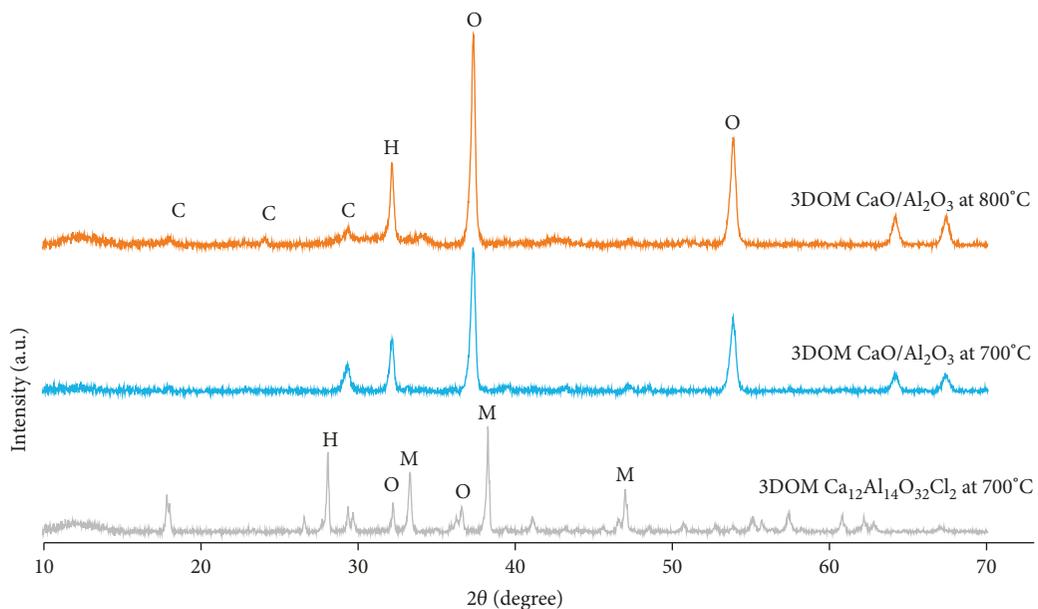


FIGURE 4: XRD patterns of the 3DOM CaO/Al₂O₃ at 700–800°C and the 3DOM Ca₁₂Al₁₄O₃₂Cl₂. H = Ca(OH)₂, O = CaO, M = Ca₁₂Al₁₄O₃₂Cl₂, and C = CaCO₃.

presented. No calcium oxide was observed because a decomposition of CaCO₃ to CaO occurs at temperature higher than 600°C [12]. The diffraction peaks at 32° (222), 41° (081), and 44° (281) corresponded to calcium silicate (Ca₂SiO₄) (JPCDS 33-303) and CaCO₃ at 23° (012), 29° (104), and 47° (018) (JPCDS. 5-586) were observed after calcination at 700 and 800°C. The 3DOM CaO/SiO₂ at 800°C exhibited similar XRD patterns with Ca₂SiO₄ as a major phase and CaO, CaCO₃, and Ca(OH)₂ as minor phases (Figure 3).

The XRD patterns of the 3DOM CaO/Al₂O₃ after calcination at 700 and 800°C are shown in Figure 4. Both samples exhibited diffraction peaks at 32° (111), 37° (200), 54° (220), 64° (311), and 67° (222) corresponding to CaO and weak diffractions peaks

of Ca(OH)₂ and CaCO₃. The XRD pattern of the 3DOM Ca₁₂Al₁₄O₃₂Cl₂ at 700°C exhibited mixed phase of Cl-bearing mayenite (JCPDS 1-77-4045) [13] with CaO and Ca(OH)₂.

The FTIR spectra of all 3DOM CaO/SiO₂ exhibited characteristic bands at 1000 cm⁻¹ and 480 cm⁻¹, corresponding to stretching and bending vibration of Si–O bond, respectively [14] (Figure 5). The band at approximately 3600 cm⁻¹ was associated with the OH stretching vibrations of surface hydroxyl groups (Ca–OH) due to moisture absorption [15]. The band at 1460 cm⁻¹ was a C=O vibration of the carbonate group. It is noted that different calcination temperatures did not significantly alter the FTIR pattern of the 3DOM CaO/SiO₂. FTIR spectra of both 3DOM CaO/Al₂O₃ and 3DOM

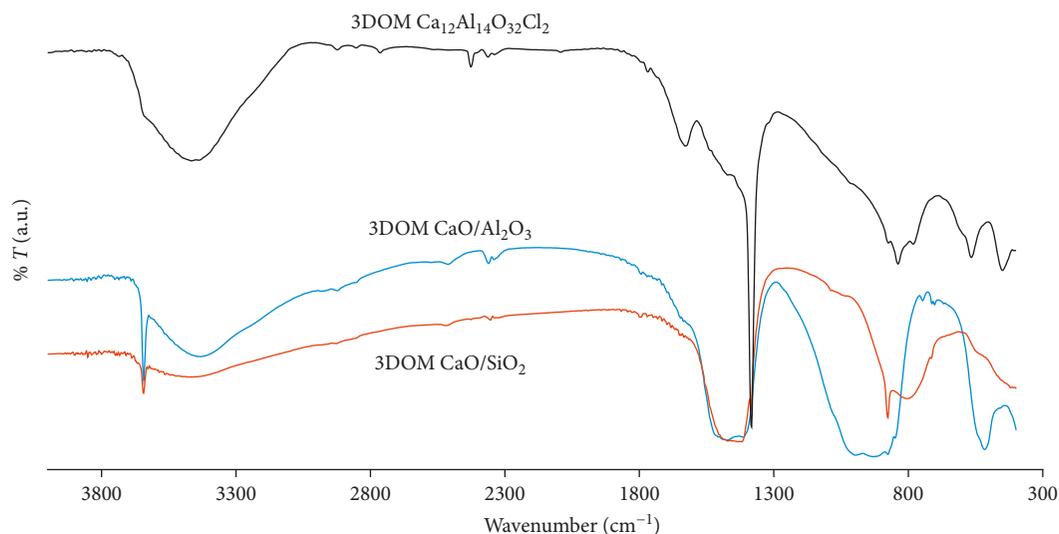


FIGURE 5: FTIR spectra of the 3DOM CaO/Al₂O₃ at 700–800°C and the 3DOM Ca₁₂Al₁₄O₃₂Cl₂.

Ca₁₂Al₁₄O₃₂Cl₂ exhibited characteristic bands at 500–700 cm⁻¹ and 700–900 cm⁻¹ which corresponded to Al–O vibration of octahedral and tetrahedral Al₂O₃, respectively [3]. The strong band centered at 1460 cm⁻¹ was attributed to C=O vibration of the carbonate group. The band at 3645 cm⁻¹ indicated OH stretching vibration of the adsorbed water molecules onto CaO giving rise to Ca(OH)₂ [16].

3.2. Transesterification. Numerous 3DOM catalysts were prepared. However, not all 3DOM catalysts were suitable for transesterification; for example, the 3DOM CaO/SiO₂ calcined at 600°C was achieved but no active CaO was found. At 700–800°C, CaO was produced in the 3DOM CaO/SiO₂, but preliminary transesterification studied showed no RPO conversion. Therefore, all 3DOM CaO/SiO₂ catalyst were not used for transesterification.

Both 3DOM CaO/Al₂O₃ and 3DOM Ca₁₂Al₁₄O₃₂Cl₂ were used as a solid catalyst for transesterification of palm oil with methanol at 65°C and stirring rate at 750 rpm. The basicity of the catalysts was previously studied using the Hammett indicator [16–18]. The basicity of 3DOM CaO/Al₂O₃ was in the range of 10.0 < H₋ < 12.2, whereas that of 3DOM Ca₁₂Al₁₄O₃₂Cl₂ is 11 < H₋ < 15.

For 3DOM CaO/Al₂O₃, the effect of catalyst amount was investigated ranging from 6 to 12 wt.% with molar ratio of methanol to oil of 12 : 1 at 65°C for 3 h. It was found that the refined palm oil (RPO) conversion increased with the increase of the catalyst amount (Figure 6(a)). The 12 wt.% of catalyst gave the highest RPO conversion of 58%. Although the stoichiometric ratio of methanol to palm oil for transesterification is 3 : 1, additional of methanol makes equilibrium moving forward to produce more biodiesel. In this study, it was found that the reaction using 3DOM CaO/Al₂O₃ catalyst at 12 : 1 MeOH : oil ratio resulted in 47% RPO conversion. However, the higher MeOH : oil ratio at 18 : 1 and 24 : 1 only produced 40% and 17% RPO conversion, respectively (Figure 6(b)). The decreasing of RPO

conversion may be due to an alternation of the reaction equilibrium. Excess methanol may increase the solubility of glycerol; therefore, the equilibrium of the reaction shifted backward, resulting in a reduction of biodiesel [16, 19]. The effect of reaction time is shown in Figure 6(c). The reaction time of 3 h gave the lowest RPO conversion of 47% because reaction was incomplete. When the reaction time was increased, the RPO conversion increased to the highest value of 94% at 5 h. The optimal conditions using the 3DOM CaO/Al₂O₃ catalyst were as follows: 12 wt.% catalyst, methanol to oil molar ratio of 12 : 1, and reaction time 5 h under the temperature of 65°C.

For the 3DOM Ca₁₂Al₁₄O₃₂Cl₂ catalyst, the effects of the catalyst amounts varied from 3 to 12 wt.%. It can be seen that increasing catalyst amount gives higher RPO conversion (Figure 6(a)). However, a high catalyst amount (12 wt.%) was not suitable for transesterification because the high catalyst amount led to high viscosity in mixture. The optimum catalyst amount is 6 wt.% by weight. At MeOH : oil molar ratio of 9 : 1, the RPO conversion of 96% was observed (Figure 6(b)). The increasing methanol to oil molar ratio of 12 : 1 and 18 : 1 gave the maximum highest RPO conversion of 99%. The effects of reaction time are shown in Figure 6(c). It obtained the highest RPO conversion at 3 h. The optimal conditions for transesterification were obtained as follows: by the catalyst amount 6 wt.%, methanol to oil molar ratio 12 : 1, and reaction time of 3 h. The RPO conversion was obtained at 99% under the optimal condition.

3.3. Biodiesel Properties. The properties of biodiesel obtained from transesterification using 3DOM CaO/Al₂O₃ and 3DOM Ca₁₂Al₁₄O₃₂Cl₂ were studied following the biodiesel standard of USA (ASTM) and Europe (EN) as shown in Table 2. The density of the produced biodiesel was acceptable, but the acid value and viscosity did not meet the standard value. This may be due to the high acid value (3.02) of raw material. Therefore, the raw material should be esterified to reduce free fatty acid

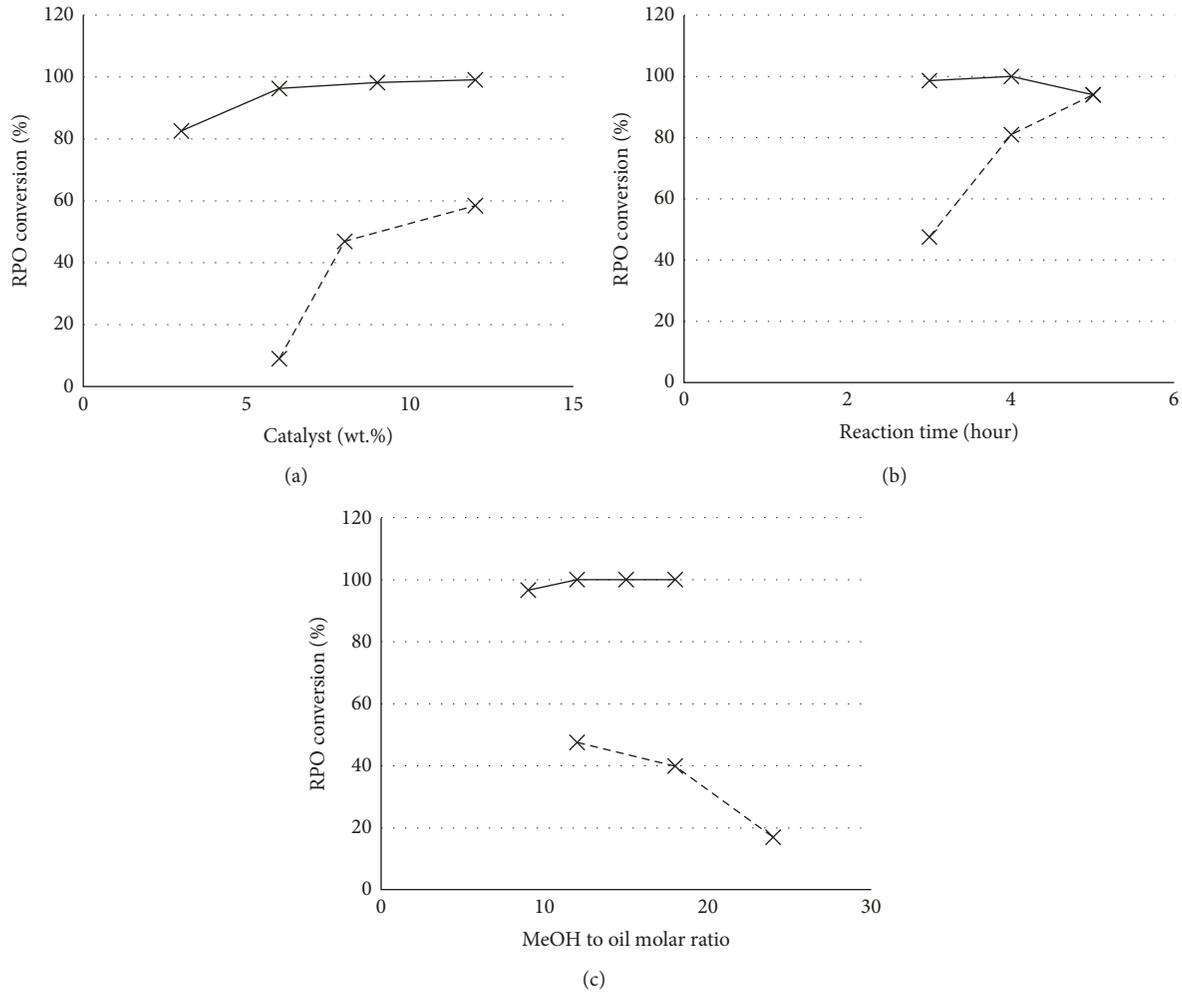


FIGURE 6: RPO conversion: (a) effect of % wt. catalyst, (b) effect of MeOH:oil molar ratio, and (c) effect of reaction time.

TABLE 2: Properties of RPO biodiesel.

Parameters	Testing method (standard value)	Limitation of Thai community	Biodiesel in this study
Viscosity at 40°C (cSt)	ASTM D445 (1.9–6.0)	1.9–6.0	7.1
Density at 15°C (g/cm ³)	EN 14214 (0.86–0.90)	0.86–0.90	0.86
Acid value (mg KOH/g)	ASTM D664 (0.50 max)	0.80 max	1.64

[7]. The high viscosity may be due to the Ca contaminant which causes side reaction (saponification) producing soap which then increases the viscosity of the biodiesel.

4. Conclusion

The 3DOM CaO/SiO₂, 3DOM CaO/Al₂O₃, and 3DOM Ca₁₂Al₁₄O₃₂Cl₂ were successfully fabricated. The 3DOM CaO/SiO₂ catalysts calcined at 700°C obtained the crystalline phase of CaCO₃, Ca(OH)₂, CaO, and Ca₂SiO₄. The 3DOM CaO/Al₂O₃ catalysts calcined at 700 and 800°C obtained crystalline of CaO and Ca(OH)₂. The results of FTIR spectra were corresponded with functional groups of silica (SiO₂), alumina (Al₂O₃), carbonate (CO₃²⁻), and hydroxyl (OH⁻) groups, depending on the composition of the 3DOM

materials. The 3DOM CaO/SiO₂ was not suitable for the reaction due to no active CaO. In addition, 3DOM materials that calcined at 800°C exhibited collapsed 3DOM structure. Only 3DOM CaO/Al₂O₃ and Ca₁₂Al₁₄O₃₂Cl₂ were used for transesterification, because the ordered structure of both catalysts was maintained with an active CaO phase after calcination.

For 3DOM CaO/Al₂O₃, the optimal condition was 12 wt. % of catalyst, the methanol to oil molar ratio of 12:1, and reaction time of 5 h under stirring rate of 750 rpm and reaction temperature at 65°C, giving rise to 93% of RPO conversion. The optimal condition of the novel 3DOM Ca₁₂Al₁₄O₃₂Cl₂ catalyst was as follows: the catalyst amount 6 wt.%, the methanol to oil molar ratio of 12:1, and reaction time of 3 h under stirring rate of 750 rpm and reaction

temperature at 65°C, giving 99% of RPO conversion. The 3DOM $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$ catalyst had more efficiency than conventional solid and 3DOM $\text{CaO}/\text{Al}_2\text{O}_3$ catalysts. The density of biodiesel was 0.86 g/cm^3 which was in the ASTM specification. The viscosity and acid value of biodiesel product were slightly out of standard range (ASTM D445 and ASTM D664, resp.). This may be due to the Ca contaminant causing saponification. The density of biodiesel, however, was within specification (EN 14214).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors would like to thank the Kasetsart University Research and Development Institute (KURDI) and Faculty of Science, Kasetsart University, for financial supports. The authors also express gratitude to the Center of Excellence-Oil Palm, Kasetsart University, for instrumental assistance.

References

- [1] A. Srivastava and R. Prasad, "Triglycerides-based diesel fuels," *Renewable and Sustainable Energy Reviews*, vol. 4, no. 2, pp. 111–133, 2000.
- [2] S. Al-Zuhair, "Production of biodiesel: possibilities and challenges," *Biofuels, Bioproducts and Biorefining*, vol. 1, no. 1, pp. 57–66, 2007.
- [3] I. Lukić, J. Krstić, D. Jovanović, and D. Skala, "Alumina/silica supported K_2CO_3 as a catalyst for biodiesel synthesis from sunflower oil," *Bioresource Technology*, vol. 100, no. 20, pp. 4690–4696, 2009.
- [4] H. Sun, Y. Ding, J. Duan et al., "Transesterification of sunflower oil to biodiesel on ZrO_2 supported La_2O_3 catalyst," *Bioresource Technology*, vol. 101, no. 3, pp. 953–958, 2010.
- [5] A. P. Vyas, N. Subrahmanyam, and P. A. Patel, "Production of biodiesel through transesterification of Jatropha oil using $\text{KNO}_3/\text{Al}_2\text{O}_3$ solid catalyst," *Fuel*, vol. 88, no. 4, pp. 625–628, 2009.
- [6] N. Phumthian, *Development and Characterization of Three-Dimensionally Ordered Macroporous Hydroxyapatite (3DOM HAp) by Sol-Gel Technique and Its Application as Vancomycin Drug Carrier*, Department of Chemistry, Kasetsart University, Bangkok, Thailand, 2013.
- [7] W. Suwanthai, *Optimization of Refined Bleached and deodorized Palm Oil Biodiesel Production Using Calcium Methoxide Catalyst by Response Surface Methodology*, Department of Chemistry, Kasetsart University, Bangkok, Thailand, 2014.
- [8] M. Tariq, S. Ali, F. Ahmad et al., "Identification, FT-IR, NMR (^1H and ^{13}C) and GC/MS studies of fatty acid methyl esters in biodiesel from rocket seed oil," *Fuel Processing Technology*, vol. 92, no. 3, pp. 336–341, 2011.
- [9] P. N. Pusey and W. van Megen, "Phase behaviour of concentrated suspensions of nearly hard colloidal spheres," *Nature*, vol. 320, no. 6060, pp. 340–342, 1986.
- [10] R.-X. Yang, K.-H. Chuang, and M.-Y. Wey, "Hydrogen production through methanol steam reforming: effect of synthesis parameters on Ni–Cu/CaO– SiO_2 catalysts activity," *International Journal of Hydrogen Energy*, vol. 39, no. 34, pp. 19494–19501, 2014.
- [11] X. Zhang, H. Su, and X. Yang, "Catalytic performance of a three-dimensionally ordered macroporous Co/ZrO₂ catalyst in Fischer–Tropsch synthesis," *Journal of Molecular Catalysis A: Chemical*, vol. 360, pp. 16–25, 2012.
- [12] M. L. Granados, M. D. Zafra Poves, D. MartínAlonso et al., "Biodiesel from sunflower oil by using activated calcium oxide," *Applied Catalysis B: Environmental*, vol. 73, no. 3–4, pp. 317–326, 2007.
- [13] C. Ma, H. C. Connolly, J. R. Beckett et al., "Brearleyite, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$, a new alteration mineral from the NWA 1934 meteorite," *American Mineralogist*, vol. 96, no. 8–9, pp. 1199–1206, 2011.
- [14] H. Yan, K. Zhang, C. F. Blanford, L. F. Francis, and A. Stein, "In vitro hydroxycarbonate apatite mineralization of CaO– SiO_2 sol–gel glasses with a three-dimensionally ordered macroporous structure," *Chemistry of Materials*, vol. 13, no. 4, pp. 1374–1382, 2001.
- [15] B. Wang, S. Li, S. Tian, R. Feng, and Y. Meng, "A new solid base catalyst for the transesterification of rapeseed oil to biodiesel with methanol," *Fuel*, vol. 104, pp. 698–703, 2013.
- [16] N. Pasupulety, K. Gunda, Y. Liu, G. L. Rempel, and F. T. T. Ng, "Production of biodiesel from soybean oil on $\text{CaO}/\text{Al}_2\text{O}_3$ solid base catalysts," *Applied Catalysis A: General*, vol. 452, pp. 189–202, 2013.
- [17] S. Sankaranarayanan, C. A. Antonyraj, and S. Kannan, "Transesterification of edible, non-edible and used cooking oils for biodiesel production using calcined layered double hydroxides as reusable base catalysts," *Bioresource Technology*, vol. 109, pp. 57–62, 2012.
- [18] G. Joshi, D. S. Rawat, B. Y. Lamba et al., "Transesterification of Jatropha and Karanja oils by using waste egg shell derived calcium based mixed metal oxides," *Energy Conversion and Management*, vol. 96, pp. 258–267, 2015.
- [19] G.-Y. Chen, R. Shan, J. F. Shi, and B. B. Yan, "Transesterification of palm oil to biodiesel using rice husk ash-based catalysts," *Fuel Processing Technology*, vol. 133, pp. 8–13, 2015.

