

CaO Nanocatalyst for Transesterification Reaction of Palm Oil to Biodiesel: Effect of Precursor's Concentration on the Catalyst Behavior

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Abstract. Depletion of fossil fuel sources in a few decades due to industrialization and motorization has led to a keen interest in the production of alternative fuels like biodiesel. Research on the development and improvement of more efficient transesterification process for biodiesel production has attained great attention in the last decade. The using of low cost catalyst is one of the main focuses on the biodiesel production. As a basic heterogeneous catalyst, CaO has been examined in the transesterification of vegetable oils for biodiesel production. In this research, calcium oxide (CaO-X) catalysts were prepared by sol-gel method at different Ca^{2+} precursor concentration ($X = 1.0, 1.5, 2.0 \text{ M}$). The crystalline structure and morphology of the synthesized catalysts were characterized by means of x-ray diffraction (XRD) and N_2 adsorption-desorption analysis. All the synthesized catalysts were then applied to transesterification reaction of palm oil to produce biodiesel. The characterization by x-ray diffraction demonstrate CaO-1.0 was partially hydrated due to the incomplete reaction during synthesis. As a matter of fact, formation of H_2O on the surface of CaO causes lower basic strength of the catalysts, thus responsible in lowering the catalytic activity. It is demonstrated that CaO-2.0 exhibits mesoporous structure with least chemisorb amount of H_2O on the catalysts surface has a very active catalytic activity. It was found that 2.0M of calcium precursor has high catalytic activity and 81% FAME yield was obtained within 3h reaction.

1. Introduction

Biodiesel, a clean renewable fuel, has as of late been considered as the best possibility for a diesel fuel substitution on the grounds that it can be utilized as a part of any pressure ignition motor without the requirement for adjustment. There are four primary ways to produce biodiesel which are direct use and blending of raw oils, micro-emulsions, thermal cracking and transesterification [1]. Transesterification is a process in which fat or oil reacts with an alcohol to form esters and glycerol. It can be catalyzed by both homogeneous catalysts and heterogeneous catalysts [2], [3]. Biodiesel catalyzed by heterogeneous catalysts has advantages over homogeneous catalysts from both economic and environmental standpoints. Using heterogeneous catalysts can reduce the cost of biodiesel production because they more readily separate from the liquid and have a long lifetime



[4], [5]. Solid base catalysts, calcium oxide has been extensively investigated due to its high basicity, low solubility in the organic solvents, and low cost [6].

Commonly calcium oxide, CaO are produced via thermal treatment (decomposition) or could be synthesized by the sol – gel method without using any surfactants and complicated tools. The sol-gel method is based on inorganic polymerization reactions and has a cutting age over the common solid-state routes because it allows molecular mixing of constituents leading to chemical homogeneity, and that shorter diffusion distances for reactants lead to lower sintered temperature for crystallization [7], [8]. In a sol – gel process, the precursor solution is converted into an inorganic solid by dispersion of colloidal particles in a liquid (sol) and conversion of sol into rigid phase (gel) by hydrolysis and condensation reactions. The method is well applicable for the synthesis of nanoparticles of oxides of different metals like Sn, Ti, V, Zr, Ta, Nb, Hf, In, Fe, Cr, Ni, Mn, Sm, W, Li, Al, in aqueous, non – aqueous (organic), mediums with or without surfactants. The method allows better control on the properties of nanoparticles such as volatilization, contamination, phase separation, etc. The advantage of being able to control these properties lead to the formation of highly pure and homogenous multi component compounds [9].

Despite its low cost and easy preparation, there is a problem that related to CaO catalyst employed in the reaction of producing biodiesel which is the low catalytic activity of CaO in transesterification of biodiesel [10]–[12]. This problem could affected the yield of biodiesel. Therefore, this research addresses the method that can be used to increase the catalytic activity in biodiesel production. In this research, the study was focused on the synthesized heterogeneous catalysts of calcium oxide, CaO via sol – gel method with different concentration which are 0.5M, 1.0M, 1.5M and 2.0M. Besides that, this study was also focused on the study of the physical properties of CaO, the characterization of CaO and also the production of biodiesel from palm oil and methanol catalyzed by prepared CaO in laboratory scale. The crystallinity, phase structure and crystallography of CaO were characterized using X-ray diffraction analysis (XRD). Whereas, the surface area, pore volume, pore sizes and isotherm profile of the catalyst were characterized by N₂ adsorption-desorption analysis.

2. Experimental

2.1 Materials and Catalyst Preparation

The sol-gel sample of calcium oxides (CaO) were prepared using a modified Pechini procedure reported elsewhere [10], [11], [13]. Briefly, equimolar of an aqueous solution (1.0M) containing calcium nitrate tetrahydrate and citric acid was prepared. For this purpose, approximate weight of Ca(NO₃)₂·4H₂O (Merck, Malaysia) was completely dissolved in approximately 80mL of deionized water and added slowly to thus prepared citric acid/deionized water solution. The mixture was heated at 80±2°C under vigorous stirring until a viscous gel (translucent pale yellow) was formed. The gel was dried overnight at 130±5°C. The sample was then crushed in porcelain mortar before calcined in a muffle furnace at 850°C for 5h with a step of 5°C/min heating rate. Other samples were prepared accordingly to the same procedure with different molarity of 1.5M and 2.0M

2.2 Catalysts Characterization

The crystallinity behavior of the catalysts was recorded using Rigaku Ultima IV diffractometer with Cu K α (0.15418nm) radiation source over 2 θ range from 20° to 70° with a 1.2°/min operating at 40kV and 30mA. The textural properties were obtained using N₂ adsorption-desorption (Autosorb-1 Quanta Chrome Instrument TUSA).

2.3 Transesterification of palm oil with methanol over CaO

The catalytic activity of transesterification of palm oil was carried out under reaction condition of 60°C reaction temperature, 3h reaction time, 9:1 methanol to oil molar ratio, and 4 wt% catalyst under 600 rpm stirring. First mixture was prepared by dissolving methanol and catalysts for 30min. Then, 25g of oil was heated up to the reaction temperature in 50mL conical flask using hot plate

equipped with temperature probe sensor. The mixture of methanol/catalyst was added into heated oil and heated up to the reaction temperature in a specified reaction time. The catalyst was separated from the product by centrifuging at 10 000 rpm for 5 min and finally separated by separation funnel. The biodiesel yields were calculated from the equation below:

$$\text{Yield (\%)} = \frac{\text{weight of biodiesel produced}}{\text{weight of palm oil}} \times 100 \quad (1)$$

3. Result and Discussion

3.1 Crystallinity behavior of CaO-X Catalysts

The phase and purity of the synthesized catalysts were characterized by powder x-ray diffraction (XRD) analysis. Figure. 1 shows the x-ray diffraction patterns of the samples CaO-1.0, CaO-1.5 and CaO-2.0 respectively.

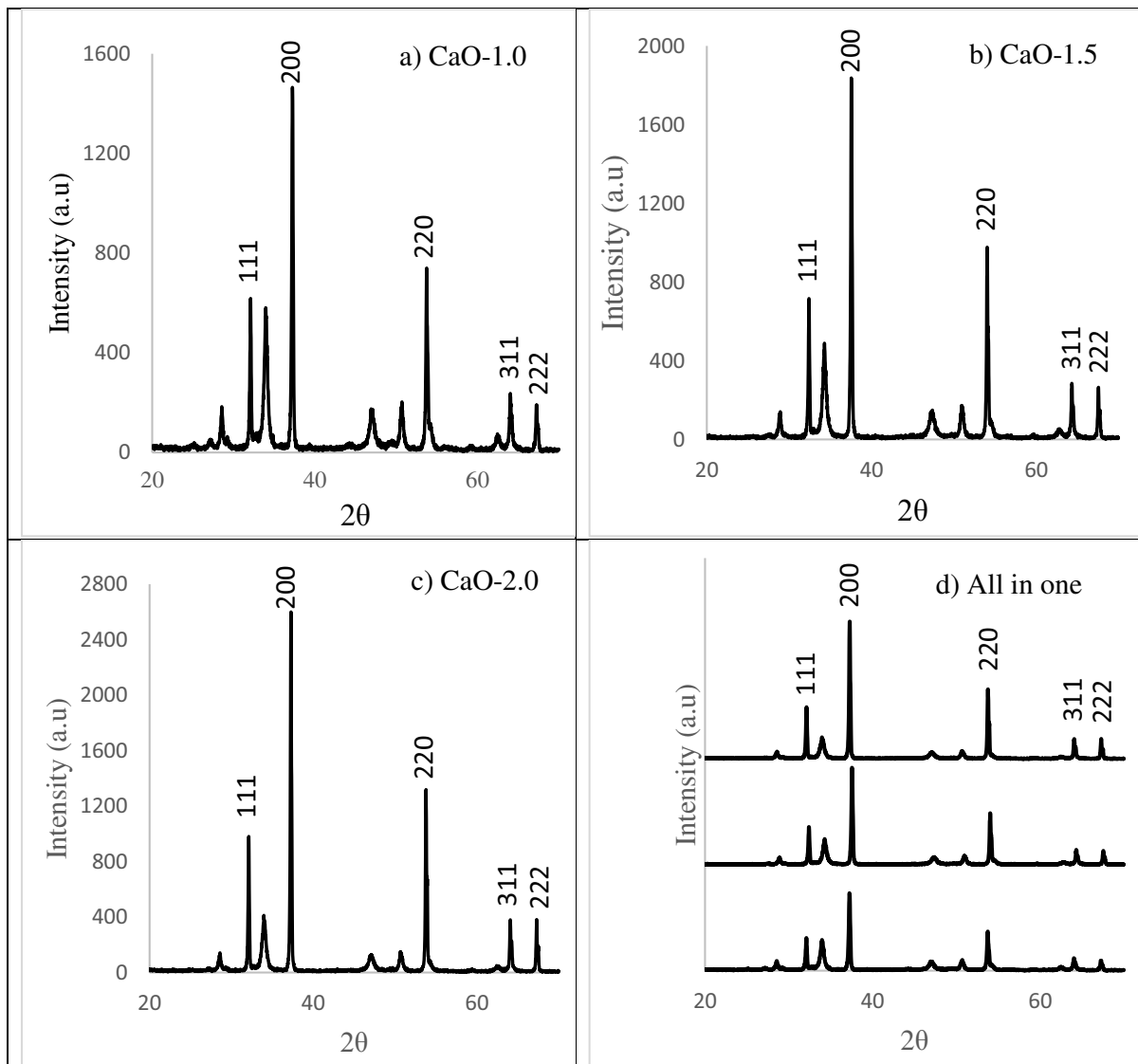


Figure 1. XRD patterns for CaO catalysts with different precursor concentrations: a) CaO-1.0, b) CaO-1.5, c) CaO-2.0, and d) All in one.

It can be seen that they are nearly identical patterns with traces of impurities are observed. All the diffraction peaks of the catalysts can be indexed to a cubic structure of CaO at $2\theta = 32.41^\circ$, 37.60° , 54.23° , 64.18° , and 67.86° (PDF 00-001-1160, $a = 4.7970\text{\AA}$ and $c = 4.7970\text{\AA}$) with high crystallinity. For all the catalysts, traces of the impurities are also identified at peaks corresponding to portlandite, Ca(OH)_2 at $2\theta = 28.78^\circ$, 34.20° , 47.31° , 50.98° , and 62.73° (PDF 00-002-0968, $a = 3.5790\text{\AA}$ and $c = 4.9060\text{\AA}$) are present at relatively high intensity ($>30\%$). It is clear that CaO sample are not pure. It seems that chemisorption of H_2O on CaO surface is very significant due to the reaction with moisture in the exposed environment during cooling process after calcination, storage and handling of the catalysts. This explains that sample CaO-1.0 is possibly damaged since the diffractogram of CaO-1.0 exhibits strong peaks corresponding to Ca(OH)_2 ($I = 69.1\%$) compared to sample CaO-2.0 which almost pure CaO was obtained. Diffractogram of all catalysts exhibits a strong orientation along c -axis (200). The intensity of plane (200) increases with the increase of the precursor concentration. The crystallite size is calculated based on Scherrer's formula corresponding to full width of half maximum (FWHM) of the most intense peak (200). Table 1 shows the crystallite size of the catalysts at different concentration. It is clear that the average crystallite size of the catalysts increases in the order of $\text{CaO-1.0} < \text{CaO-1.5} < \text{CaO-2.0}$ according to the intensity of the most intense peak (200).

Table 1. The crystalline size for CaO catalysts.

Sample Code	[Precursor] (M)	Crystallite size (nm)
CaO-1.0	1.0	46
CaO-1.5	1.5	51
CaO-2.0	2.0	61

3.2 Morphologies of CaO-X catalysts

Figure. 2 (a) shows the nitrogen adsorption-desorption isotherms of CaO-X.

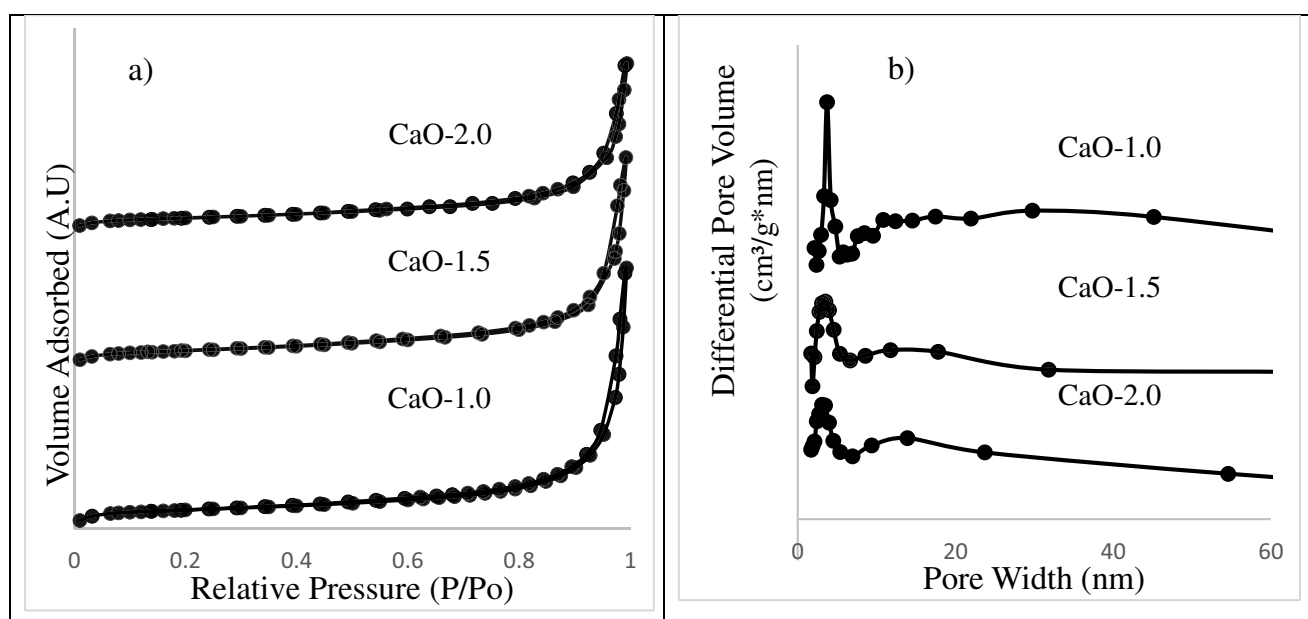


Figure 2. (a) Nitrogen adsorption-desorption isotherms of CaO-X catalysts, and (b) Pore size distribution curve of CaO-X.

According to the International Union of Pure and Applied Chemistry classification, all the CaO-X catalysts exhibit the type-IV isotherm with type-H4 hysteresis loop, which means that the prepared catalysts possess mesoporous structure [14]. The pore-size distribution shown in Figure. 2(b) of all catalysts is calculated using BJH model. The pore size distribution of all catalysts display nearly identical pattern and exhibit average pore size in the range of 21.78-28.48 nm. Textural properties of CaO-X catalysts are summarized in Table 2. The surface area and the average pore volume of CaO-X catalysts decreases with increasing precursor concentration. This result is well consistent with XRD result, where at higher concentration of precursor solution, larger crystallite size is obtained with reduced in surface area.

Table 2. Textural properties of CaO-X catalysts

Sample	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Dpore (nm)
CaO-1.0	11.19	0.058	28.48
CaO-1.5	9.19	0.049	23.56
CaO-2.0	7.74	0.037	21.78

3.3. Transesterification of Palm Oil over CaO

Figure. 3 shows the FAME yield obtained in the transesterification reaction of palm oil over CaO-X samples. It is observed that the yield of biodiesel increases with the increase of the concentration of the precursor. The yield increases in the order of 64% < 75% < 81% with respect of the concentration of the precursor.

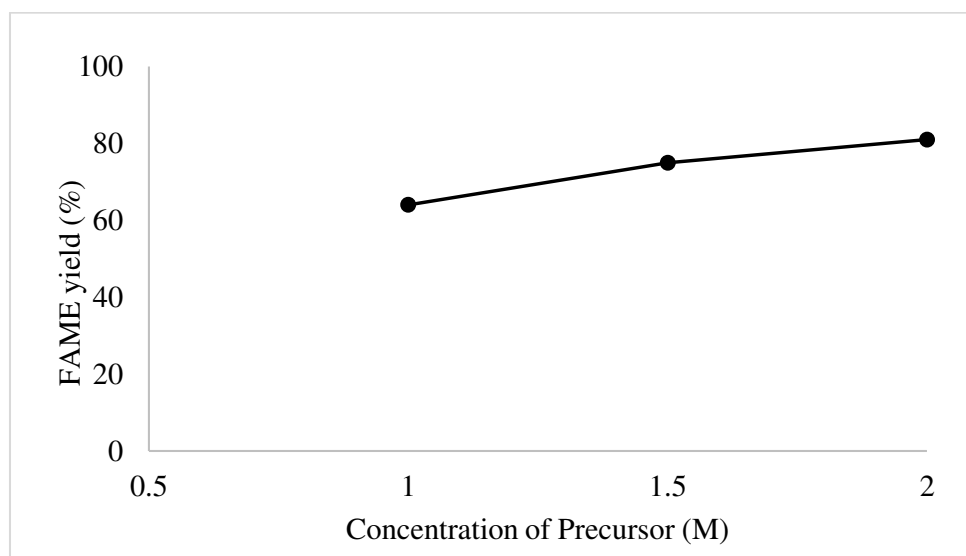


Figure 3. FAME yield of CaO-X catalyzed palm oil.

The trend can be explained by the relation with the XRD and N₂ adsorption-desorption results. From previous characterization, XRD results indicate that the fresh catalysts CaO-X is partially hydrated and sample CaO-1.0 has high possibility of damaged. This observation elucidate CaO is rapidly undergoes hydration processes during cooling event from calcination process, storage and handling. There was expectation that catalysts with higher surface area, smaller particle size could promote the catalytic activity in the conversion of product. Of note, all catalysts exhibit mesopores which are suitable for the accessibility or large molecules of free fatty acid. However, in this case of study, CaO-1.0 which exhibit good physical properties unable to promote the rate of reaction due to the poisoned active surface sites by hydration of H₂O on CaO core surfaces [15]. Besides, Alonso et al. also pointed out that low basic strength of Ca(OH)₂ is not strong enough to promote the

transesterification reaction of fatty acids, thus suggesting that CaO-1.0 is practically has lower catalytic activity (lowest FAME yield of 64%) [16]. By increasing the precursor concentration, lower hydroxyl was formed on the catalysts surface. Catalysts CaO-2.0 emerge as a very active catalysts with least traces of hydroxyl, in 3h of reaction time a yield of 81% is obtained.

3. Conclusion

Metal oxides of calcium, CaO-X catalysts were prepared by sol-gel method at different calcium precursor concentrations ($X = 1.0, 1.5, 2.0$ M) to modify the morphology and physical properties of CaO-X catalysts. They were then applied in the transesterification of palm oil to biodiesel. Among the CaO-X ($X = 1.0, 1.5$, and 2.0 M) catalysts, CaO-1.0 catalyst showed the smallest crystallite size with larger surface area. However, the catalytic activity of CaO-1.0 was deteriorated by the poisoned active surface sites by hydroxyl due to the incomplete reaction during synthesis of the catalyst. In the transesterification of palm oil, yield of the biodiesel increased with respect to the concentration of the reactant. With respect to the sample of high concentration of reactant (CaO-2.0), a very intense peaks from CaO are visible indicates small amount of hydroxyl was formed on the CaO surface. It was found that 2.0 M of calcium precursor has high catalytic activity as a heterogeneous catalyst and it was obtained 81% FAME yield within 3h reaction. This results demonstrate strong basic sites present at the surface of CaO causes significant activation of the catalytic activity in transesterification reaction. Thus, it is very reasonable to assume that hydroxylation of CaO is detrimental for the catalytic activity.

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