

Effect of Calcination Temperatures of CaO/Nb₂O₅ Mixed Oxides Catalysts on Biodiesel Production

(Kesan Suhu Pengkalsinan Oksida Campuran CaO/Nb₂O₅ ke atas Penghasilan Biodiesel)

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ABSTRACT

Calcination temperature greatly influences the total basicity and surface area of catalysts. Investigations were conducted on calcium and niobium (CaO-Nb₂O₅) mixed oxides catalysts prepared via conventional solid state method (oxides were mixed and ground in agate mortar) and calcined at different temperatures ranging from 300-800°C for 5 h. The catalysts were then characterized by using X-ray diffraction (XRD), CO₂ temperature-programmed desorption (TPD-CO₂), Brunauer-Emmett-Teller (BET) surface area analyzer and scanning electron microscope (SEM). The formation of Ca(OH)₂ and CaCO₃ at lower calcination temperatures (< 600°C) reduced the surface area of the catalyst and masked the basic active sites, hence lowered the total basicity of the catalyst. Besides, low surface area and total basicity were observed at higher calcination temperatures (> 600°C), due to sintering of the fine crystals, which promotes cluster agglomeration. Thus, the optimum calcination temperature for CaO/Nb₂O₅ mixed oxides was 600°C, which produced the largest surface area (7 m²/g) and total basicity (1301 μmol/g). The biodiesel was produced via transesterification of palm oil, methanol and the catalysts calcined at various temperatures. CaO/Nb₂O₅ mixed oxide calcined at 600°C showed the highest biodiesel conversion (98%) with methanol/oil molar ratio of 12, 3 wt.% of catalyst, a reaction temperature of 65°C and reaction time of 2 h.

Keywords: Biodiesel; calcium oxide; niobium oxide; palm oil; transesterification

ABSTRAK

Suhu pengkalsinan mempengaruhi jumlah luas permukaan dan jumlah kebesan pemangkin. Kajian ini telah dilakukan ke atas campuran oksida CaO/Nb₂O₅ yang disediakan dengan menggunakan kaedah konvensional keadaan pepejal (oksida dicampur dan dikisar dalam mortar batu akik) dan dikalsin pada julat suhu daripada 300-800°C selama 5 jam. Pencirian pemangkin telah dilakukan dengan menggunakan kaedah pembelauan sinar-X (XRD), mikroskop imbasan elektron (SEM), TPD-CO₂ dan analisis Brunauer-Emmett-Teller (BET). Pada suhu pengkalsinan yang lebih rendah (< 600°C), pembentukan Ca(OH)₂ dan CaCO₃ akan menyebabkan jumlah luas permukaan pemangkin berkurang. Selain itu, suhu pengkalsinan yang lebih tinggi (> 600°C) menyebabkan kekurangan dalam jumlah luas permukaan dan jumlah kebesan pemangkin kerana suhu pengkalsinan yang tinggi akan menyebabkan taburan pemangkin halus menjadi kelompok. Suhu pengkalsinan optimum bagi campuran oksida CaO/Nb₂O₅ adalah 600°C dengan jumlah luas permukaan (7 m²/g) dan jumlah kebesan (1301 μmol/g). Biodiesel dihasilkan melalui transesterifikasi minyak sawit, metanol dan pemangkin yang dikalsin pada pelbagai suhu. Campuran oksida CaO/Nb₂O₅ yang dikalsin pada suhu 600°C menunjukkan hasil biodiesel yang paling tinggi, 98% dengan nisbah metanol/ minyak kelapa sawit 12, pemangkin 3 %bt, suhu tindak balas 65°C dan masa tindak balas selama 2 jam.

Kata kunci: Biodiesel; kalsium oksida; minyak sawit; niobium oksida; transesterifikasi

INTRODUCTION

Recently, the emergent of biodiesel has drawn most attention from researchers as the potential substitute for current petroleum-based fossil fuel. Biodiesel is a methyl esters derived from vegetable oil or animal fats via transesterification process. This qualifies biodiesel as renewable energy, readily and continuously obtainable as long as the supplies of biomass are available. Biodiesel possesses many advantages such as a high flash point, high cetane number, high lubricity, lower carbon monoxide emission profile and biodegradable. Thus it is considered

as green fuel from the environmental viewpoint (Dorado et al. 2003). Transesterification process is a reaction between hydroxyl group of alcohol and carboxylic group of triglycerides to form ester. Currently, biodiesel is industrially produced via homogeneously catalyzed transesterification process by using sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Alamu et al. 2008; Dmytryshyn et al. 2004). However, this process has limitations. The catalysts cannot be regenerated and reused. The recovery of catalyst is complex and require expensive step where the product needs to be neutralized

with an acid and wash with a lot of water to separate the catalyst from the methyl ester. This will generate a lot of waste water which lead to environmental issues as well as addition in the production cost (Vicente et al. 2007).

The emerging of heterogeneous catalysts seems to be a solution for the problems faced. Various heterogeneous catalysts such as metal oxides (Jitputti et al. 2006; Patil & Deng 2009; Zabeti et al. 2009), hydrotalcites (Silva et al. 2010) and zeolites (Brito et al. 2007; Chung et al. 2008; Sasidharan & Kumar 2004) have been applied in transesterification process. Many studies showed that calcium oxide, CaO is a potential catalyst in transesterification process. It has shown the promising results with 94% yield at reaction temperature of 60°C and 1:13 methanol: oil molar ratio in the transesterification of sunflower oil (Granados et al. 2007). The other study done by Lim et al. (2009) who compared the application of heterogeneous catalysts (CaO) and conventional catalysts (NaOH and KOH) in transesterification of adsorbed waste palm oil on spent bleaching clay, showed the CaO-catalyzed reaction yielded much higher (about 90%) biodiesel compared to only 46 and 61% yield using NaOH and KOH, respectively. However, calcium oxide is not stable and tend to leach out into the reaction medium. This eventually reduces the activity of the catalyst (Kouzu et al. 2009; Sharma et al. 2011).

The researchers are now focusing on improving the stability and performance of calcium oxide and one of the ways is by mixing calcium oxide with other metal oxides. Ngamcharussrivichai et al. (2008) mixed calcium oxide, CaO with zinc oxide and ZnO, found that Ca/Zn ratio of 0.25 gave palm kernel methyl esters above 94% in 3 h reaction time and can be reused up to three times with a methyl esters content of more than 90%. In another study (Albuquerque et al. 2009), a series of Ca/Mg mixed oxides were prepared and evaluated by transesterifying ethyl butyrate with methanol. Conversion of 60% can be obtained by mixing Ca/Mg with a molar ratio of 3 and no leached active species was detected during the course of reaction. This again proves the stability of the heterogeneous state of the mixed catalysts.

In this study, calcium oxide was mixed with niobium oxide and its catalytic activity was evaluated by transesterifying palm oil and methanol in a batch type reaction. Physicochemical properties of the catalyst were determined by using various characterization techniques. The effect of catalysts' calcination temperature on biodiesel yield was investigated where the calcination temperature varies from 300 to 800°C.

EXPERIMENTAL DETAILS

CHEMICALS AND CATALYST PREPARATION

Palm oil was provided by IOI Group, Malaysia and was used without further purification. Before using, the palm oil was pre-melted at 50-60°C and thoroughly homogenized.

Fatty acid methyl esters (Sigma-Aldrich) were used as the standards and methanol (Merck) was used as reaction reagent. High purity calcium oxide (99.9 %, Aldrich) and niobium oxide (99.9 %, Alfa Aesar) were used for samples preparation. All the metal oxides were preheated at 300°C for 2 h before use.

Calcium and niobium mixed oxides were prepared by using conventional solid state method. About 1.500 g of calcium oxide and 3.500 g of niobium oxide, respectively, were measured. Then, the oxides were mixed and ground in agate mortar by using acetone as grinding medium. The mixed samples were then calcined in air at temperature range 300 – 800°C for 5 h and denoted as CaO/Nb₂O₅ x00°C, where *x* is the respective calcination temperatures.

CATALYSTS CHARACTERIZATION

The phase identity of the samples were determined by x-ray diffraction (XRD) analysis (Shimadzu diffractometer XRD-6000) which was equipped with a diffracted-beam graphite monochromator using CuK α , radiation (1.5406 Å) over a scanning range of 10 to 60°. The scanning electron microscopy (JEOL JSM-6400 SEM) was used to study the morphology of the samples. The samples were coated with gold using a Sputter Coater.

Fourier-transform infrared (FT-IR) spectrometer (Perkin-Elmer model 1725x) with the wavenumber range in the region of 4000 and 400 cm⁻¹ was used for structural analysis. Attenuated total reflection (ATR) technique has been employed for measurement of infrared spectra of sample. The BET surface area of the catalysts was determined by N₂ adsorption-desorption at -196°C using Quantachrome Autosorb 1. Prior to each measurement, the sample has to be degassed at 300°C for 9 h. The basicity of the catalyst was evaluated by temperature-programmed desorption (Thermo Finnigan TPDRO 1100) equipped with a thermal conductivity detector and using CO₂ as probe molecules (TPD-CO₂).

TRANSESTERIFICATION REACTION

The catalytic activities of the prepared catalysts were evaluated by transesterifying palm oil and methanol in a batch-type reaction. About 10 g of palm oil, 3.75 g of methanol and 0.3 g of catalyst were mixed in a 100 mL two-necked flask equipped with reflux condenser and the mixture was stirred with magnetic stirrer. The mixture was heated at 65°C in water bath for 2 h. The collected reaction mixture was then centrifuged at 3000 rpm for 3 min to separate catalyst, glycerol and methyl esters phases. The glycerol and methyl esters phases were loaded into a rotary evaporator to recover the excess methanol in mixture. The mixture was then poured into the separating funnel to separate glycerol and methyl ester phase.

The biodiesel yield was analyzed by using a gas chromatograph GC-14B (model Shimadzu) equipped with a flame ionization detector and a capillary column (RTX-65, 30 m × id 0.25 mm). Helium was used as the carrier gas throughout the whole experiment. Methyl heptadecanoate

was added as internal standard for biodiesel during measurement.

RESULTS AND DISCUSSION

CHARACTERIZATION OF CATALYSTS

Phase identities of the calcined $\text{CaO}/\text{Nb}_2\text{O}_5$ samples were determined by X-ray diffraction (XRD) and their XRD patterns were shown in the Figure 1. No CaO peaks were observed in the catalysts with calcination temperature 300°C . CaO peaks were only appeared after the catalyst calcined at 400°C . Meanwhile, $\text{CaO}/\text{Nb}_2\text{O}_5$ with calcination temperatures of 400 , 500 and 600°C showed similar XRD patterns, where calcium oxide and niobium oxide were identified in the samples. The CaO peaks occurred at 2θ around 32.2° , 37.3° and 53.8° were indexed in the cubic structure with space group of Fm-3m (JCPDS file 37-1497). Besides, Nb_2O_5 (JCPDS file 37-1468) was co-existed with its polymorph, $\text{Nb}_{16.8}\text{O}_{42}$ (JCPDS file 71-336) in the 2θ range of $10 - 60^\circ$. It can be observed that the intensity of the CaO increased with the increasing calcination temperature from 400 to 600°C . However, the intensity of CaO dropped with further heat treatment at 700°C . At this temperature, CaO started to react with Nb_2O_5 , thus, not only calcium oxide and niobium oxide were identified, but binary oxide, CaNb_2O_6 was also observed in the sample. CaNb_2O_6 became a dominant phase when the catalyst was further calcined at 800°C . Meanwhile, Nb_2O_5 no longer co-existed with its polymorph, $\text{Nb}_{16.8}\text{O}_{42}$, it rather presented as orthorhombic phase (Ristic et al. 2004).

Figure 2 shows the FT-IR spectra of $\text{CaO}/\text{Nb}_2\text{O}_5$ mixed oxides calcined at various temperatures ranging from 300 to 800°C . A weak and sharp absorption band observed in the wavenumber of 3639 cm^{-1} , was assigned to the

OH groups bonded to the CaO. It became less intense with increasing calcinations temperature where more OH groups were removed as water molecules. At lower calcination temperature, the band at $1425\text{--}1471\text{ cm}^{-1}$ which due to carbonate vibrations was appeared to be broad and intense. The intensity of this band decreased with increasing calcination temperature. The band around 870 cm^{-1} is due to the highly distorted octahedral NbO_6 containing Nb=O bond (Paulis et al. 1999). This band was observed to transform from a broad band to a sharp band when calcined at higher temperature. After calcined at 600°C , the bands splitting was observed between 500 and 700 cm^{-1} , probably due to the greater asymmetry in the slightly distorted octahedral NbO_6 structures and the possible interaction between the Nb=O groups (Paulis et al. 1999).

Calcination temperature is greatly influence the crystallite size and surface area of the catalysts. Crystallite size of the catalysts was calculated using Debye-Scherrer's equation (Patterson 1939) while BET surface area was determined from Brunauer-Emmett-Teller (BET) isotherm. The crystallite size and BET surface area was shown in Table 1 and Figure 3. It was shown that the calculated average crystallite size for CaO reduced from 80 to 54 nm with increasing calcination temperature from $400\text{--}600^\circ\text{C}$, which was due to the decomposition of larger CaCO_3 and $\text{Ca}(\text{OH})_2$ into smaller CaO, CO_2 and H_2O . Further heat treatment at 700°C leads to an increment in crystallite size, about 67 nm . Meanwhile, crystallite sizes of Nb_2O_5 in the mixed oxides increased linearly with calcination temperature. At 800°C , instead of separated phase CaO and Nb_2O_5 , CaNb_2O_6 was present and its crystallite size was 53 nm . The BET surface area of $\text{CaO}/\text{Nb}_2\text{O}_5$ catalysts calcined at 300 , 400 , 500 , 600 , 700 and 800°C were 2.4 , 4.6 , 4.9 , 7.5 , 5.9 , $1.3\text{ m}^2/\text{g}$, respectively. Increment and reduction

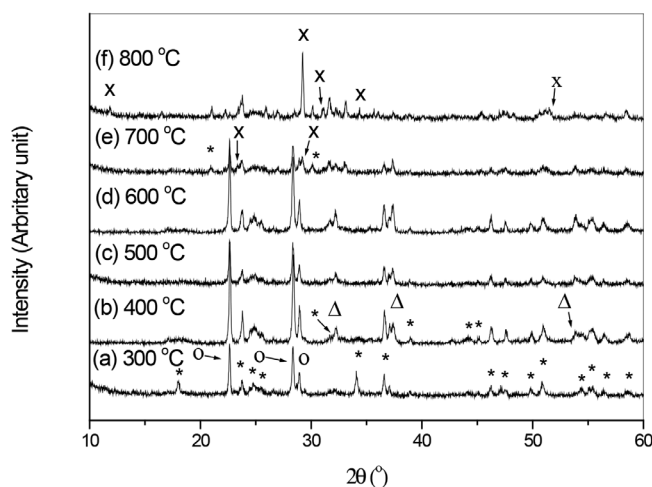


FIGURE 1. XRD patterns of $\text{CaO}/\text{Nb}_2\text{O}_5$ mixed oxides catalysts calcined at various temperatures: (a) 300°C , (b) 400°C , (c) 500°C , (d) 600°C , (e) 700°C and (f) 800°C . (peaks labeled as (Δ) CaO, ($*$) Nb_2O_5 , (o) $\text{Nb}_{16.8}\text{O}_{42}$ and (x) CaNb_2O_6)

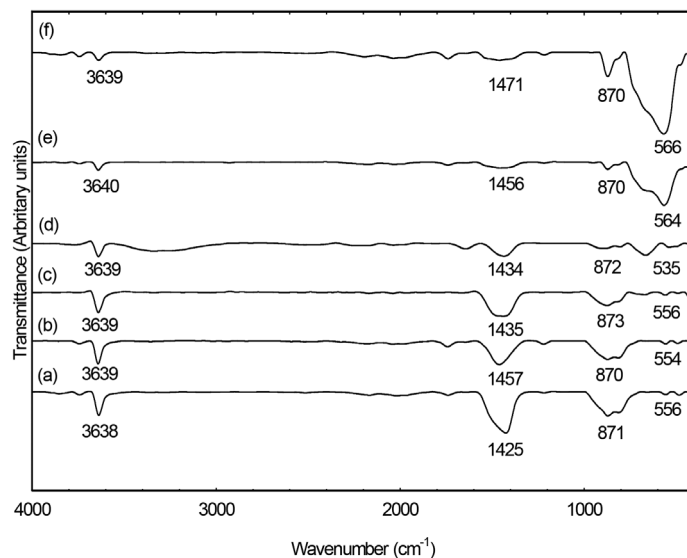


FIGURE 2. FT-IR spectra of CaO/Nb₂O₅ mixed oxides catalysts calcined at various temperatures: (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C and (f) 800°C

TABLE 1. Physical properties and catalytic activities of CaO/Nb₂O₅ mixed oxides catalysts calcined at different temperatures

Samples	Surface area (m ² /g) ^a	Crystallite size ^b (nm)			Yield (%) ^c
		CaO	Nb ₂ O ₅	CaNb ₂ O ₆	
CaO/ Nb ₂ O ₅ 300°C	2.4	-	47.6	-	0
CaO/ Nb ₂ O ₅ 400°C	4.6	80.3	45.3	-	82
CaO/ Nb ₂ O ₅ 500°C	4.9	61.2	47.9	-	92
CaO/ Nb ₂ O ₅ 600°C	7.5	53.9	48.2	-	98
CaO/ Nb ₂ O ₅ 700°C	5.9	66.5	51.8	-	89
CaO/ Nb ₂ O ₅ 800°C	1.3	-	-	53.1	0

^aDetermined from BET isotherm; ^bCalculated from Debye-Scherrer's equation and ^cReaction condition: methanol/oil molar ratio of 12, catalysts amount of 3 wt.%, reaction temperature of 65°C and reaction time of 2 h

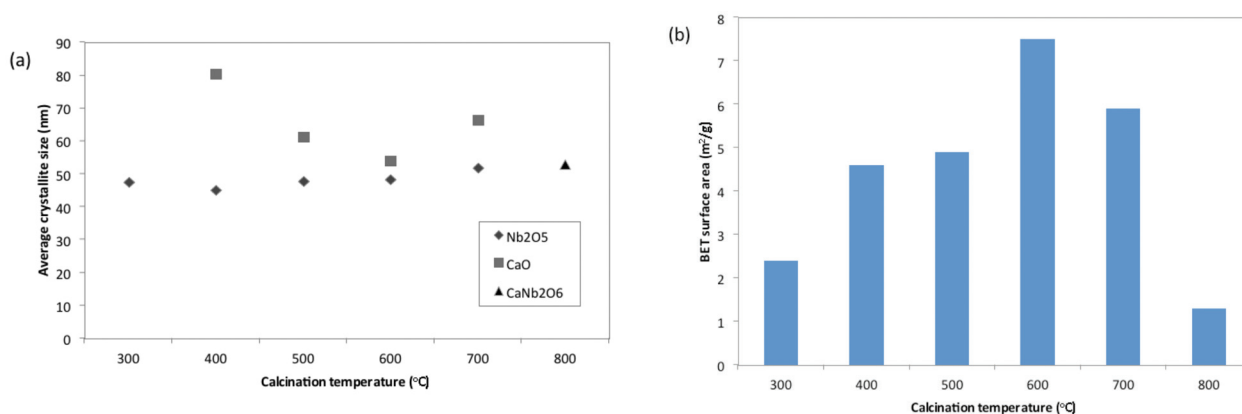


FIGURE 3. (a) Crystallite sizes and (b) BET surface area of CaO/Nb₂O₅ mixed oxides catalysts calcined at various temperatures ranging from 300-800°C

of surface area was closely related to the calcination temperature. Owing to continuously decomposition of CaCO_3 and Ca(OH)_2 to CaO , CO_2 , and H_2O from 300 to 600°C, the crystallite size of CaO decreased which in turn increased the surface area of the catalysts. However, further increasing calcination temperature at 700 and 800°C lead to sintering of fine crystals, promote cluster agglomeration (Boynton 1980) and resulted in reduction of surface area. This fact indicated that the relationship of BET surface area and crystallite size was inversely proportional, in which large crystallite size reduced surface area and vice versa (Rownaghi et al. 2009).

The TPD- CO_2 profiles of $\text{CaO/Nb}_2\text{O}_5$ mixed oxides catalysts are depicted in Figure 4 and the total amount of CO_2 desorbed is listed in Table 2. All TPD- CO_2 showed a similar pattern with one desorption peak at temperature range of 500 to 750°C, corresponded to the association of $\text{Ca}^{2+}\text{-O}^{2-}$ pairs which have a very strong basic strength. The amount of CO_2 desorbed increased with calcination temperature from 300 to 600°C. This could be due to the increase in surface area, making more surface area

available for CO_2 desorption. Meanwhile, the formation of binary phase, CaNb_2O_5 and reduction of surface area lead to lower desorption amount of CO_2 at high calcination temperature (700 and 800°C). Among these catalysts, Ca/Nb 600°C with the largest surface area showed the highest total basicity (showed the most intense desorption peak) with total amount of CO_2 desorbed of 1301 $\mu\text{mol/g}$.

CATALYTIC ACTIVITY

Calcination temperature affects largely on the structural and catalytic properties of the catalysts. Therefore, the effect of calcination temperature of $\text{CaO/Nb}_2\text{O}_5$ mixed oxides catalysts on biodiesel conversion was investigated and was presented in Figure 5. At 300°C, no biodiesel conversion was observed. This is mainly due to CaO present as CaCO_3 and Ca(OH)_2 at low calcination temperature (< 600°C). CaO requires a thermal activation to remove the adsorbed CO_2 and moisture (Boey et al. 2011). The biodiesel conversion increased with increasing calcination temperature. This is due to the increase in the

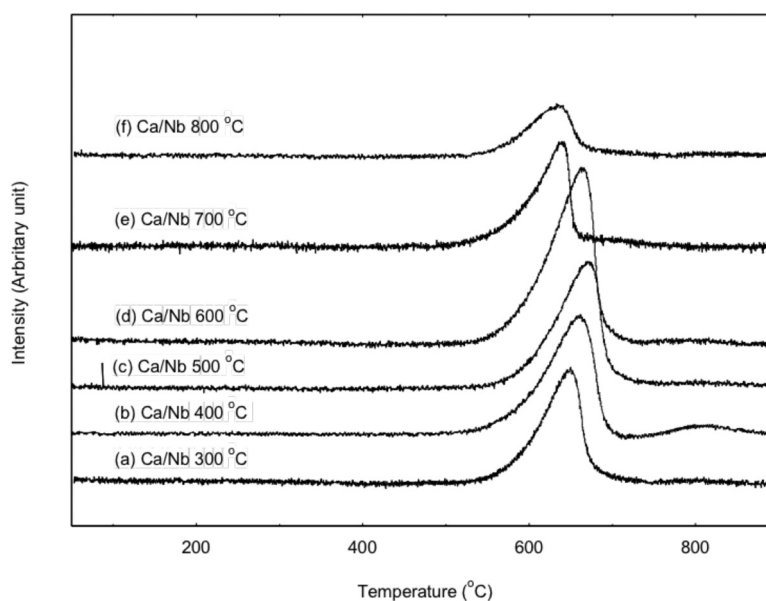


FIGURE 4. TPD- CO_2 profile of $\text{CaO/Nb}_2\text{O}_5$ mixed oxides catalysts calcined at various temperatures

TABLE 2. Total basicity of $\text{CaO/Nb}_2\text{O}_5$ mixed oxides at different calcination temperature, expressed in $\mu\text{mol CO}_2/\text{g}$ desorbed

Catalyst	CO_2 desorbed ($\mu\text{mol/g}$)	Temperature range ($^{\circ}\text{C}$)	Peak temperature ($^{\circ}\text{C}$)
$\text{CaO/Nb}_2\text{O}_5$ 300 $^{\circ}\text{C}$	576.49	550-750	662
$\text{CaO/Nb}_2\text{O}_5$ 400 $^{\circ}\text{C}$	982.14	550-750	673
$\text{CaO/Nb}_2\text{O}_5$ 500 $^{\circ}\text{C}$	1281.13	550-750	638
$\text{CaO/Nb}_2\text{O}_5$ 600 $^{\circ}\text{C}$	1301.23	550-750	672
$\text{CaO/Nb}_2\text{O}_5$ 700 $^{\circ}\text{C}$	1139.02	500-700	663
$\text{CaO/Nb}_2\text{O}_5$ 800 $^{\circ}\text{C}$	113.67	500-700	633

amount of CaO (decomposition of CaCO_3 and Ca(OH)_2) with increasing calcination temperature which provides important active sites for the transesterification process. However, with the formation of binary oxide, CaNb_2O_6 at 700°C , the biodiesel conversion started to drop and drastically dropped to null when the CaNb_2O_6 became a dominant phase at 800°C . The formation of CaNb_2O_6 greatly reduced the amount of free CaO active sites in which play an important roles in the transesterification process.

The correlation between the basicity of the catalysts and biodiesel conversion is shown in Figure 6. The highest biodiesel conversion (98%) was observed for the catalyst $\text{CaO/Nb}_2\text{O}_5$ 600°C with the highest total basicity

(with total amount of CO_2 desorbed of $1301 \mu\text{mol/g}$). It shows good agreement with the results reported by other researchers (Kouzu et al. 2008; Verziu et al. 2009; Xie et al. 2006) which claimed that transesterification is greatly relied on the basicity of the catalysts. In our study, transesterification is also highly depended on the surface area of the catalysts and the relationship between the surface area and biodiesel conversion is shown in Figure 7. The reduction in biodiesel conversion when shifting from 600 to 800°C is due to the decrease of catalyst's surface area from 7 to $1 \text{ m}^2/\text{g}$. Low catalyst's surface area may limit the diffusion between the reactant and the basic active sites which were located inside the pores of the catalyst (Wang et al. 2008).

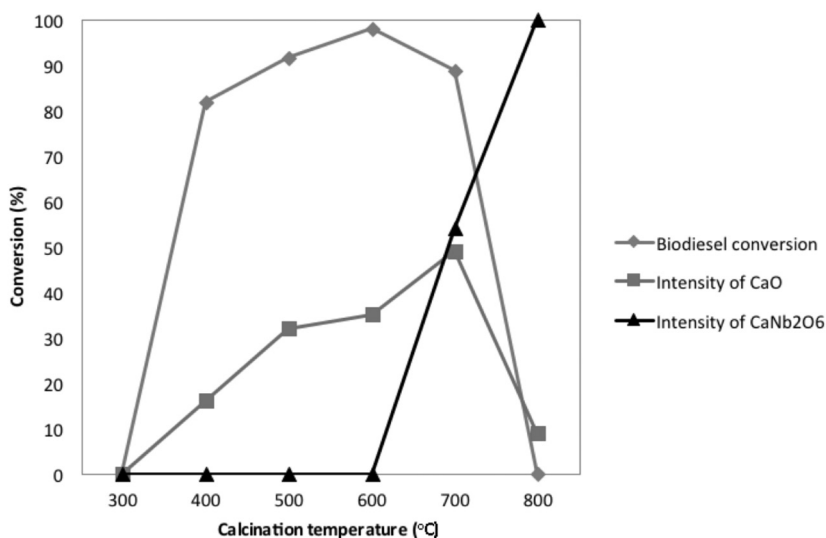


FIGURE 5. Effect of calcination temperatures of $\text{CaO/Nb}_2\text{O}_5$ mixed oxides catalysts on the biodiesel conversion. Reaction conditions: methanol/oil ratio, 12; catalyst amount, 3 wt.%; reaction temperature, 65°C and reaction time, 2 h

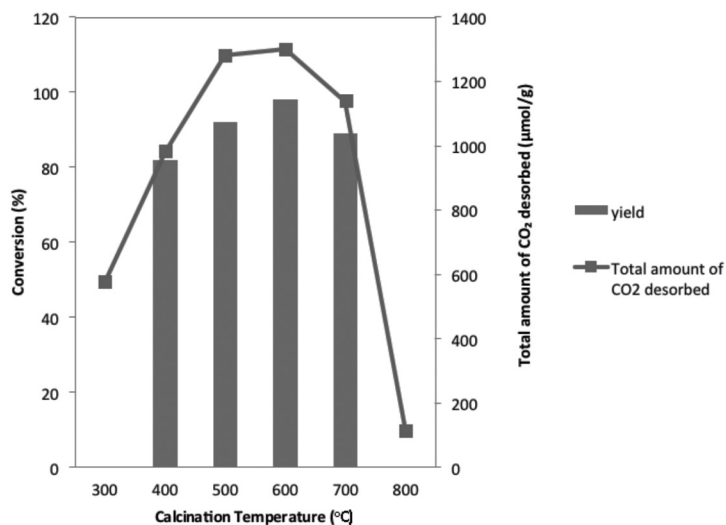


FIGURE 6. Correlation between calcination temperatures and total basicity on biodiesel conversion

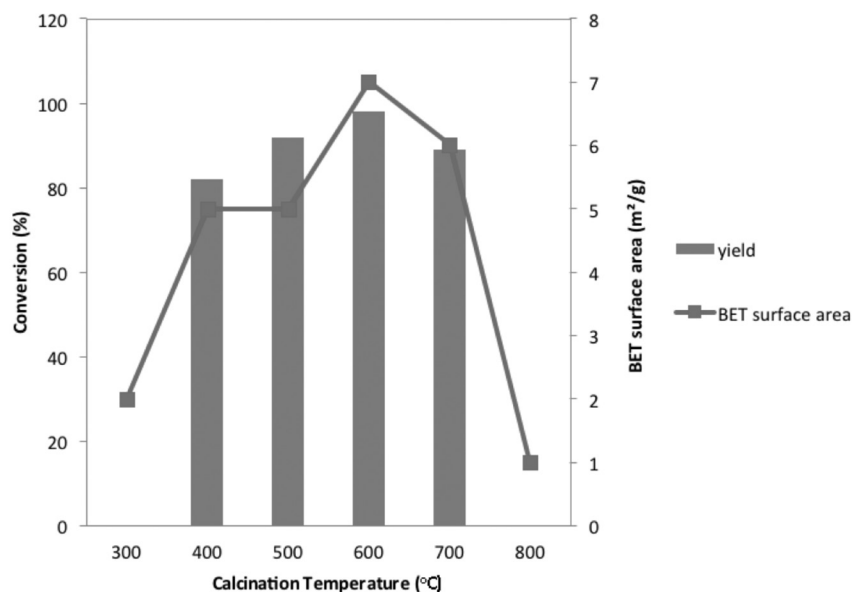


FIGURE 7. Correlation between calcination temperatures and BET surface area on biodiesel conversion

CONCLUSION

CaO and Nb₂O₅ mixed oxides prepared by conventional solid state method have been successfully applied in biodiesel production. Transesterification process is greatly depended on the total basicity and surface area of the catalysts. These two properties are mainly relied on calcination temperature. The optimum calcination temperature for CaO/Nb₂O₅ mixed oxides catalyst was 600°C. The presence of moisture and CO₂ at lower calcination temperatures (< 600°C) are responsible for the low catalytic activities of catalyst. The formation of Ca(OH)₂ and CaCO₃ reduced the surface area of the catalysts and masks the active sites of the CaO, resulted in low total basicity. Low catalytic activities in low catalyst's surface area might be due to diffusion limitation between the reactants and the basic active sites. However, high calcination temperature (> 600°C) will sinter fine crystal, promote cluster agglomeration which resulted in low catalysts' surface area and total basicity. High biodiesel conversion (98%) is obtained for catalyst calcined at 600°C and reflux in the optimum conditions: methanol/oil molar ratio of 12, catalysts amount of 3 wt.%, reaction temperature of 65°C and reaction time of 2 h.

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REFERENCES

- Alamu, O.J., Waheed, M.A. & Jekayinfa, S.O. 2008. Effect of ethanol-palm kernel oil ratio on alkali-catalyzed biodiesel yields. *Fuel* 87: 1529-1533.
- Albuquerque, M.C.G., Azevedo, D.C.S., Cavalcante Jr., C.L., Santamaría-González, J., Mérida-Robles, J.M., Moreno-Tost, R., Rodríguez-Castellón, E., Jiménez-López, A. & Maireles-Torres, P. 2009. Transesterification of ethyl butyrate with methanol using MgO/CaO catalysts. *Journal of Molecular Catalysis A: Chemical* 300: 19-24.
- Boey, P.L., Maniam, G.P. & Abd Hamid, S. 2011. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chemical Engineering Journal* 168: 15-22.
- Boynton, R.S. 1980. *Chemistry and Technology of Lime and Limestone*. 2nd ed. New York: John Wiley & Sons.
- Brito, A., Borges, M.E. & Otero, N. 2007. Zeolite Y as a heterogeneous catalyst in biodiesel production from used vegetable oil. *Energy Fuel* 21: 3280-3283.
- Chung, K.H., Chang, D.R. & Park, B.G. 2008. Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. *Bioresource Technology* 99: 123-130.
- Dmytryshyn, S.L., Dalai, A.K. & Chaudhari, S.T. 2004. Synthesis and characterization of vegetable oil derived esters: Evaluation for their diesel additive properties. *Bioresource Technology* 98: 1724-1733.
- Dorado, M.P., Ballesteros, E., Arnal, J.M., Gómez, J. & López, F.J. 2003. Exhaust emissions from a diesel engine fueled with transesterified waste olive oil. *Fuel* 82: 1311-1315.
- Granados, M.L., Poves, M.D.Z., Alonso, D.M., Mariscal, R., Galisteo, F.C., Moreno-Tost, R., Santamaria, J. & Fierro, J.L.G. 2007. Biodiesel from sunflower oil by using activated calcium oxide. *Applied Catalysis B: Environmental* 73: 317-326.
- Jitputti, J., Kitiyanan, B., Rangsuwigit, P., Bunyakiat, K., Attanatho, L. & Jenvanitpanjakul, P. 2006. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. *Chemical Engineering Journal* 116: 61-66.

- Kouzu, M., Yamasaka, S., Hidaka, J. & Tsunomori, M. 2009. Heterogeneous catalysis of calcium oxide used for transesterification of soybean oil with refluxing methanol. *Applied Catalysis A: General* 355: 94-99.
- Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, M., Yamanaka, S. & Hidaka, J. 2008. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel* 87: 2798-2806.
- Lim, B.P., Maniam, G.P. & Hamid, S.A. 2009. Biodiesel from adsorbed waste oil on spent bleaching clay using CaO as a heterogeneous catalyst. *European Journal of Scientific Research* 33: 347-357.
- Ngamcharussrivichai, C., Totarat, P. & Bunyakiat, K. 2008. Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. *Applied Catalysis A: General* 341: 77-85.
- Patil, P.D. & Deng, S. 2009. Transesterification of camelina sativa oil using heterogeneous metal oxide catalysts. *Energy Fuels* 23: 4619-4624.
- Patterson, A.L. 1939. The Scherrer formula for X-ray particle size determination. *Physical Review* 56: 978-982.
- Paulis, M., Martin, M., Soria, D.B., Diaz, A., Odriozola, J.A. & Montes, M. 1999. Preparation and characterization of niobium oxide for the catalytic aldol condensation of acetone. *Applied Catalysis A: General* 180: 411-420.
- Ristic, M., Popovic, S. & Music, S. 2004. Sol-gel synthesis and characterization of Nb₂O₅ powders. *Materials Letters* 58: 2658-2663.
- Rownaghi, A.A., Taufiq-Yap, Y.H. & Rezaei, F. 2009. Solvothermal synthesis of vanadium phosphate catalysts for n-butane oxidation. *Chemical Engineering Journal* 155: 514-522.
- Sasidharan, M. & Kumar, R. 2004. Transesterification over various zeolites under liquid-phase conditions. *Journal of Molecular Catalysis A: Chemical* 210: 93-98.
- Sharma, Y.C., Singh, B. & Korstad, J. 2011. Latest development on application of heterogeneous basic catalysts for an efficient and eco-friendly synthesis of biodiesel: A review. *Fuel* 90: 1309-1324.
- Silva, C.C.C.M., Ribeiro, N.F.P., Souza, M.M.V.M. & Aranda, D.A.G. 2010. Biodiesel production from soybean oil and methanol using hydrotalcites as catalyst. *Fuel Processing Technology* 91: 205-210.
- Verziu, M., Florea, M., Simon, S., Simon, V., Filip, P., Parvulescu, V.I. & Hardacre, C. 2009. Transesterification of vegetable oils on basic large mesoporous alumina supported alkaline fluorides-evidences of the nature of the active site and catalytic performances. *Journal of Catalysis* 263: 56-66.
- Vicente, G., Martínez, M. & Aracil, J. 2007. Optimization of integrated biodiesel production, part I. a study of the biodiesel purity and yields. *Bioresource Technology* 98: 1724-1733.
- Wang, G., Liu, G., Xu, M., Yang, Z., Liu, Z., Liu, Y., Chen, S. & Wang, L. 2008. Ti-MCM-41 supported phosphotungstic acid: An effective and environmentally benign catalyst for epoxidation of styrene. *Applied Surface Science* 255: 2632-2640.
- Xie, W., Peng, H. & Chen, L. 2006. Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. *Applied Catalysis A: General* 300: 67-74.
- Zabeti, M., Daud, W.M.A.W. & Aroua, M.K. 2009. Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology* 90: 770-777.

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