

Synthesis and characterization of metal oxide promoted alumina catalyst for biofuel production

S M Anisuzzaman¹, D Krishnaiah, A Bono, S Abang, M Sundang, E Suali, F A Lahin, A Shaik Alawodeen

Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

E-mail: ¹anis_zaman@ums.edu.my, ¹dr.anis.ums@gmail.com

Abstract. Alumina has been widely used as a support in catalysis process which owing to its extremely thermal and mechanical stability, high surface area, large pore size and pore volume. The aim of this study was to synthesize calcium oxide-supported basic alumina catalysts ($\text{CaO}/\text{Al}_2\text{O}_3$) by impregnation method and to characterize the properties of the catalyst based on its surface area and porosity, functional group, surface morphology and particle size. Impregnation method was chosen for the synthesis of catalyst which involved contacting the support with the impregnating solution for a particular period of time, drying the support to remove the imbibed liquid and calcination process. In the preparation of catalyst, catalytic performance of $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst was measured at different calcined temperatures (650°C, 750°C and 800°C). Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Mercury intrusion porosimetry (MIP), and particle size analyzer (Zetasizer) was used to characterize the catalyst. The highest total specific area and the total porosity of the catalyst was obtained at 750°C. FTIR analysis basically studied on the functional groups present in each catalyst synthesized, while SEM analysis was observed to have pores on its surface. Moreover, $\text{CaO}/\text{Al}_2\text{O}_3$ catalysts at 650°C produced the smallest particle size (396.1 nm), while at 750°C produced the largest particle size (712.4 nm). Thus it can be concluded that $\text{CaO}/\text{Al}_2\text{O}_3$ catalysts has great potential commercialization since CaO has attracted many attentions compared to other alkali earth metal oxides especially on the transesterification reaction.

1. Introduction

The most common preparation of catalyst methods are impregnation, ion-exchange, adsorption and desorption-precipitation. Even though the preparation procedures considerably differ from one catalyst to another, three broad categories can be introduced to classify the catalysts with respect to the preparation procedure which includes bulk catalyst and supports, impregnated catalysts and mixed-agglomerated catalysts [1].

¹ To whom any correspondence should be addressed.



Calcium oxide (CaO) has attracted many attentions compared to others alkali earth metal oxides especially on the transesterification reaction since it possess relatively high basic strength and less environmental impacts due to its low solubility in methanol [2-4]. Besides that, it can be synthesized from cheap sources such as limestone and calcium hydroxide. In addition, CaO has been widely used as a catalyst for reactions involved in organic compounds isomerization such as 5-vinylbicyclo hept-2-ene to 5-ethylidenebicyclo hept-2-ene which showed high activity for organic reactions [5].

The impregnation method involves contacting the support with the impregnating solution for a particular or certain period of time and drying the support to remove the imbibed liquid. Besides that, it helps by activating the catalyst by calcination, reduction or other appropriate treatment. Lithium impregnated CaO is expected to show higher activity towards the transesterification reaction in comparison to pure CaO. Previous studies have indicated that nickel supported alumina (Ni/Al₂O₃) is not completely reduced to the metallic state because of the strong oxide-support interaction between them [6,7]. The major interest in Ni/Al₂O₃ catalyst has centered on interactions between the metal and the support where the metal-support interactions appreciably affect the surface properties of these catalysts and their catalytic properties. Apart from that, Mattisson et al. [8] investigated on the reactivity of some metal oxides supported on alumina with alternating methane and oxygen (application for chemical-looping combustion). Basically in this study, the researchers found that some metal oxides of the transition state metals such as Fe, Cu, Co, Mn, and Ni were feasible candidates to be used as oxygen carriers in a chemical-looping combustion system based on interconnected fluidized beds.

This study was mainly focused on the preparation of calcium oxide-supported basic alumina catalysts (CaO/Al₂O₃) which involved impregnation method. Alumina has been used as a support in catalysis processes due to its extremely thermal and mechanical stability, high specific surface area, large pore size and pore volume. The catalytic performance of CaO/Al₂O₃ catalysts was measured at different calcination temperatures (650, 750 and 800°C). The characterization of the catalyst was done by determining the functional groups by fourier transform infrared spectroscopy (FTIR), observing the surface morphology by scanning electron microscopy (SEM), determination of surface area and porosity by mercury intrusion porosimetry (MIP) and determination of particle size distribution analysis by Zetasizer.

2. Materials and methods

2.1 Preparation of catalysts

CaO/Al₂O₃ were prepared by impregnation method where a calculated amount of calcium acetate (Ca(CH₃COO)₂ · H₂O) were dissolved in a certain amount of deionized water, that was stirred at room temperature for 30 min. Then the solution was added drop wise to the basic alumina, and impregnation for 24 h. The solid was filtered and collected by washing thoroughly with deionized water and ethanol, and subsequently dried at temperature of 110°C for 3 h to ensure the residual solvent was removed. The dried catalyst was calcined in the absence of air at required temperature for 2 h.

2.2 Characterization of catalysts

2.2.1 Functional groups determination

FTIR was used to analyse and determine the functional present in the each of the catalysts. In other words, it offers quantitative and qualitative analysis for organic and inorganic samples where it identifies chemical bonds in a molecule by producing an infrared absorption spectrum, where some of the infrared radiation is absorbed by the sample, while some of it is passed through (transmitted).

2.2.2 Morphological characterization

SEM analysis was done to examine the surface morphology of the catalysts. The setting was chosen as follows; working distance (WD) was 6.0mm, 6.5mm and 7.0mm and Electron High Tension (EHT) was 10 kV.

2.2.3 Surface area and porosity

The analysis in determining the surface area and porosity of the catalyst was analysed by using MIP of Thermo Electron Corporation (Pascal Series 440). The mercury porosimetry technique is one of the most highly or recommended methods in terms of investigating the porous structure of solid samples in a quantitative way. Basically, it provides reliable information about pore size/volume distribution, bulk or envelope density, particle size distribution and specific surface for most porous solids.

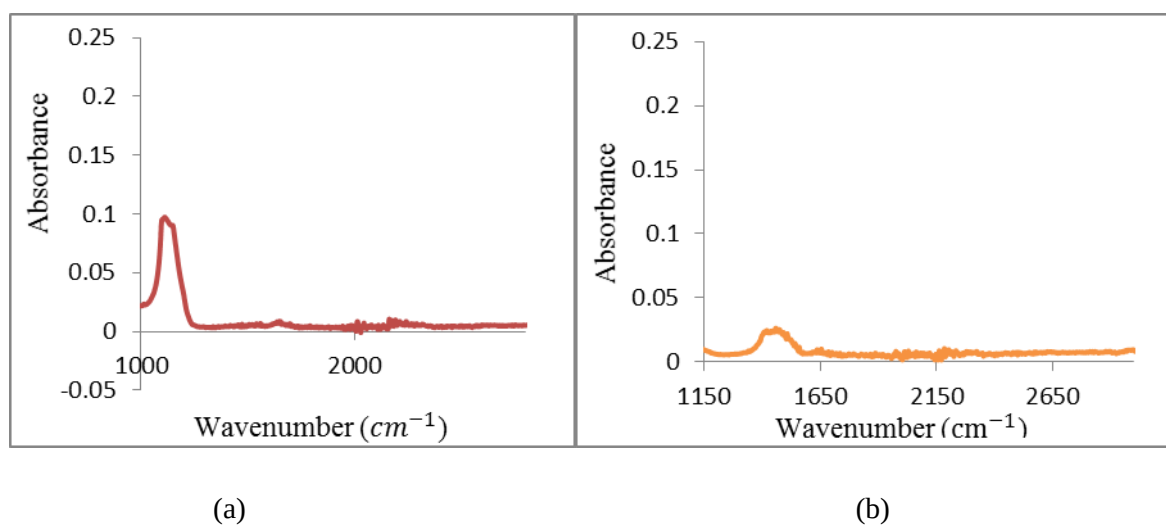
2.2.4 Particle size distribution

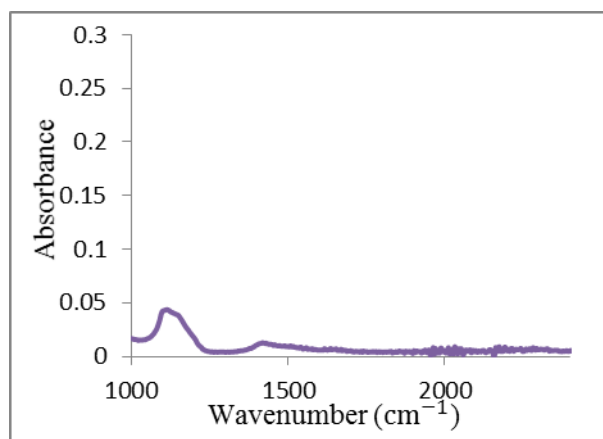
In this study, to determining the particle size of the catalysts used Malvern Zetasizer Nano Series Instrument with laser diffraction technique in the operation. Laser diffraction measures particle size distribution and the particle was reported as a volume equivalent sphere diameter at refractive index of 1.330.

3. Results and discussions

3.1 FTIR analysis

Functional groups of the synthesized catalysts were analysed using FTIR. The results are shown in Figure 1 (a,b and c).





(c)

Figure 1. FTIR Spectra for CaO/ Al_2O_3 (a) 650°C, (b) 750°C (c) 800°C

Figure 1 (a) shows that there was presence of broad band at 1236 cm^{-1} can be assigned to C-O bond and carboxylic acid stretching, while the weak strength of peak at 1680 cm^{-1} indicates the functional group of alkenes C=C. In the range between 2220 to 2260 cm^{-1} , those peaks which are small but exposed, indicates the presence of CN triple bond (nitriles), absorptions. As in figure 1 (b), bands at around $\sim 1600\text{ cm}^{-1}$ which can be assigned as C=C stretching. Besides that, it is observed that it is weak band at around $\sim 1700\text{ cm}^{-1}$, where this can be related to the presence of C=O bonds in carboxylic acids. The CC triple bond (alkynes) and CN triple bond (nitriles) absorptions at around $\sim 2100\text{ cm}^{-1}$ are small but exposed. The structure of aromatic compounds may also be confirmed from the pattern of the weak overtone and combination tone bands found from 1650 to 2000 cm^{-1} . While as in Figure 1 (c), which is under calcined temperature of 800°C , it showed C-O absorption between 1080 and 1200 cm^{-1} where these peaks are normally rounded like the O-H and N-H peak where carboxylic acids, esters, ethers, alcohols and anhydrides all containing this peak. Furthermore, it showed the CC triple bond (alkynes) and CN triple bond (nitriles) absorptions that was around 2100 - 2260 cm^{-1} are small but exposed.

3.2 SEM analysis

The analysis of the surface morphology of CaO/ Al_2O_3 catalyst with different calcination temperatures were done by SEM S-3400N Hitachi. In this surface morphology analysis, the SEM used a focused beam of high-energy electrons to generate variety of signals at the surface of solid specimens where the signals that derive from electron-sample interactions reveal information about the particular sample such as its crystalline structure, external morphology (texture), chemical composition and orientation of materials making up the sample [9,10]. The SEM images of the CaO/ Al_2O_3 with different calcination temperatures are shown in Figure 2 (a, b and c).

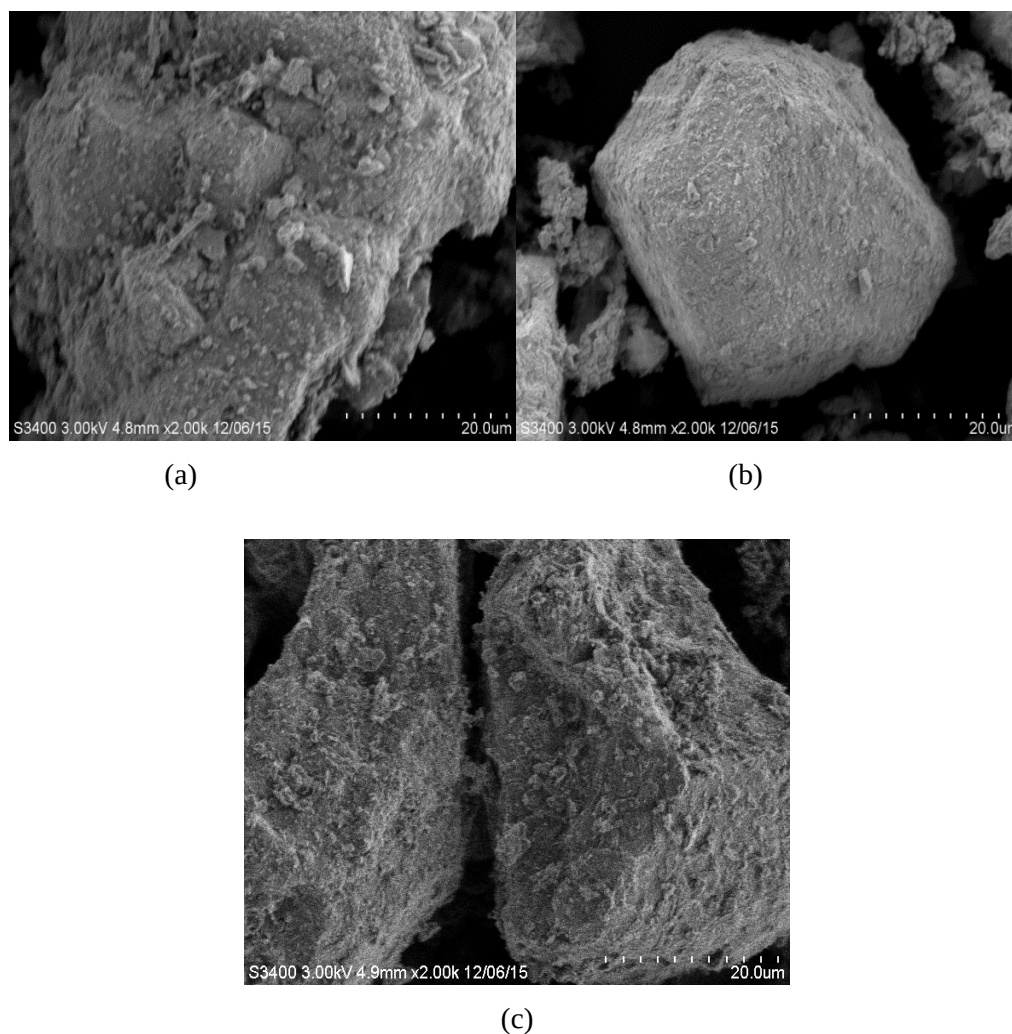


Figure 2. SEM images of $\text{CaO}/\text{Al}_2\text{O}_3$ (a) 650 °C, (b) 750 °C (c) 800 °C

3.3 MIP analysis

Table 1 shows the results of porosimetry data for $\text{CaO}/\text{Al}_2\text{O}_3$ with different calcination temperatures

Table 1. Porosimetry data for $\text{CaO}/\text{Al}_2\text{O}_3$ with calcination temperature of 650°C, 750°C, 800°C

Samples	650°C	750°C	800°C
Total specific area (m^2/g)	8.12	22.97	21.12
Total porosity (%)	20.50	69.31	67.97
Average pore diameter (nm)	3587.80	2640.67	3427.17
Total cumulative volume (mm^3/g)	165.30	400.00	407.63

The catalyst of $\text{CaO}/\text{Al}_2\text{O}_3$ with temperature of 750°C has surface area of 22.97 m^2/g and decreases at the temperature of 800°C which reduced to 21.12 m^2/g . As for total porosity, it represents 20.50% for

temperature of 650°C, and increased dramatically to 69.31 % at 750°C and slightly decreases at 800°C with 67.97%. The reduction of pores and surface area at higher temperature, perhaps, due to the penetration of metal oxide onto the surface of alumina [11]. Basically, this indicated that impregnation process under calcined temperature of 750°C caused the internal pores to collapse, thus, reduced the porosity of 800°C calcined temperature. Apart from that, the total cumulative volume seems increased from calcined temperature of 650°C, 750°C and 800°C with 165.30 mm³/g, 400 mm³/g and 407.63 mm³/g respectively. Most probably, the increase in the cumulative volume is due to the strong bond and structure of the catalysts (calcium oxide promoted alumina). As for calcined temperature of 650°C, it has the largest average pore diameter that is 3587.80 nm compared to calcined temperature of 750 °C and 800 °C, that is 2640.673 nm and 3427.168 respectively.

3.4 Zetasizer analysis

Particle size distribution by intensity (%) of CaO/Al₂O₃ for different calcination temperature is shown in Figure 3.

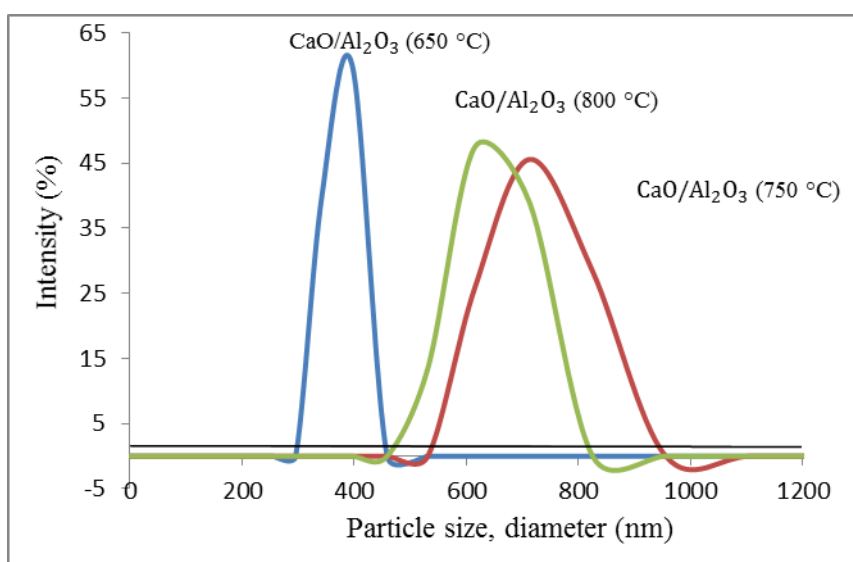


Figure 3. Particle size distribution based on intensity for CaO/Al₂O₃ with calcination temperature of 650°C, 750°C and 800°C.

The particle size distribution was analysed at different calcination temperatures. Based on the Figure 3, the result shows that the particle size distribution by intensity of CaO/Al₂O₃ (650°C), CaO/Al₂O₃ (750°C) and CaO/Al₂O₃ (800°C) are 396.1 nm, 712.4 nm and 615.1 nm respectively. In this analysis, three measurement data were taken for each calcination temperature, and the highest percentage of intensity were taken since it represent the peak of the graph. As for calcined temperature of 650 °C, the intensity results produced were 60.1%, 39.9% and 46.5%. While for calcined temperature of 750 °C, the percentage of intensity obtained were 45.6%, 25.9% and 28.4 %. Intensity percentage achieved by calcined temperature of 800°C were 47.5%, 13.5% and 39.0%. Hence, it can be observed that the peak, which represents particle size, of each calcined temperature was based on the highest percentage of its intensity. Most probably, the difference of particle size of the catalyst is due or affected by the way of grinding the powder form of catalyst [9]. For instance, if the size of a catalyst metal particle is reduced into the nanoscale, its properties initially remain the same as a larger particle. But when the size is smaller than about 10 nm, the movements of electrons in the metal are confined, so their inherent energies are increased. Hence, a finely powdered solid has a larger surface area than an equal mass of a coarsely powdered solid where a larger surface area is a much easier target for colliding

molecules. The bigger the target, the easier it is to hit and this shows that fine powders therefore react faster than coarse powders.

4. Conclusion

The $\text{CaO}/\text{Al}_2\text{O}_3$ was prepared by impregnation method with calcined temperature of 650°C, 750°C and 800°C. As in FTIR analysis, it showed the functional groups present in each catalyst produced, $\text{CaO}/\text{Al}_2\text{O}_3$. Furthermore, all the catalysts were observed to have pores on the surface by using SEM analysis. Besides that, based on the analysis of MIP method, it can be concluded that $\text{CaO}/\text{Al}_2\text{O}_3$ at 750 °C produced highest total specific area with the total porosity of the catalyst. In terms of particle size, each of the catalyst produced different particle based on its intensity where $\text{CaO}/\text{Al}_2\text{O}_3$ (650°C) produce the smallest particle size, while $\text{CaO}/\text{Al}_2\text{O}_3$ (750°C) produce the largest particle size. Hence, $\text{CaO}/\text{Al}_2\text{O}_3$ has great potential commercialization since CaO has attracted many attentions compared to others alkali earth metal oxides especially on the transesterification reaction.

References

- [1] Perego C and Villa P 1997 *Catal Today* **34** 281-305
- [2] Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S and Hidaka J 2008 *Fuel* **87** 2798-806
- [3] Kiss A A, Dimian A C and Rothenberg G 2006 *Adv. Synth. Catal.* **348** 75-81
- [4] Chai F, Cao F, Zhai F, Chen Y, Wang X and Su Z 2007 *Adv. Synth. Catal.* **349** 1057-65
- [5] Baba T, Endou T, Handa H and Ono Y 1993 *Appl. Catal. A-Gen.* **97** L19-L23
- [6] Derouane E G, Simoens A, Colin C, Martin G A, Dalmon J A, Védérine J C 1973 *J.Catal.* **70** 50-8
- [7] Li C and Chen Y W 1995 *Thermochim. Acta*, **256** 457-65
- [8] Mattisson T, Jardnas A., Lyngfelt A. 2003 *Energ. Fuel*, **17** 643-51
- [9] Anisuzzaman S. M., Joseph C G., Taufiq-Yap Y H, Krishnaiah D and Tay V V 2015 *J. King Saud Univ.- Sci.* **27** 318-30
- [10] Anisuzzaman S M, Joseph C G, Daud W M A W, Krishnaiah D and Ho S , 2015 *Int. J. Ind. Chem.* **6** 9-21
- [11] Pua F L, Fang Z, Zakaria S, Guo F, Chia C H 2011 *Biotechnol. Biofuels* **4** 56

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