

CHARACTERIZATION OF DIFFERENT METAL OXIDE PROMOTED ALUMINA CATALYST

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ABSTRACT. *In this study, different metal oxide alumina promoted catalysts were prepared and characterized. All the catalysts (CaO/Al₂O₃, CuO/Al₂O₃, FeO/Al₂O₃, MnO/Al₂O₃, NiO/Al₂O₃ and ZnO/Al₂O₃) were prepared using the incipient wetness impregnation method followed by drying and calcination. The characterization of all six samples of catalysts was done to determine the surface morphology, porosity, functional group, thermal stability, metal content and particle size distribution. Scanning electron microscope (SEM) analysis of samples showed that there were pores on the surface of the alumina. Mercury intrusion porosimetry (MIP) showed that copper oxide alumina promoted (CuO/Al₂O₃) had the high porosity which is 36.77 m²/g followed by zinc oxide (ZnO/Al₂O₃), calcium oxide (CaO/Al₂O₃) nickel oxide (NiO/Al₂O₃) manganese oxide (MnO/Al₂O₃) and ferric oxide alumina promoted (FeO/Al₂O₃) catalysts. Fourier transform infrared spectroscopy (FTIR) analysis showed the presence of by-product existed in all catalysts. Atomic absorption spectroscopy (AAS) analysis showed the presence of Cu, Fe and Zn in the CuO/Al₂O₃, FeO/Al₂O₃ and ZnO/Al₂O₃, while Ca was absent in CaO/Al₂O₃. Besides, through thermo-gravimetric analyzer (TGA) and differential thermal analysis (DTA), all the catalysts showed a slight decrease in weight which can be considered as a stable catalyst. The particle size distribution analysis using the Zetasizer showed the particle size mean based on the intensity of CaO/Al₂O₃, CuO/Al₂O₃, FeO/Al₂O₃, MnO/Al₂O₃, NiO/Al₂O₃ and ZnO/Al₂O₃ were 2305 nm, 5560 nm, 5560 nm, 1281 nm, 1281 nm and 3580 nm, respectively.*

KEYWORDS. Biofuel, metal oxide promoted alumina catalyst, wet incipient impregnation method

INTRODUCTION

Fossil fuels are the main source of energy worldwide. The nature of fossil fuels is unsustainable and their cost is rapidly increasing. Besides that, fossil fuels have huge environmental impact including greenhouse effect which cause global warming and climate change (Aliyu *et al.*, 2014; Dorado *et al.*, 2003). An alternative and renewable energy source such as biomass has been developed in order to decrease the dependence on fossil fuels and reduce the carbon dioxide (CO₂) emissions (Gan and Li, 2008; Hashim and Ho, 2011). Even though the generation of energy out of this fuel releases CO₂, it is in fact much lower compared to the CO₂ emissions from fossil fuels. Besides, the CO₂ release from the biomass is available to produce a new biomass via photosynthesis process where the CO₂ in the air react with water and sunlight to produce carbohydrates that form the building blocks of biomass (McKendry, 2002).

In order to make use of the biomass energy potential, several conversion methods can be applied including biochemical and thermochemical conversion. In biochemical conversion processes, basically the biomass or biomass-derived compounds will be converted into desirable products with the presence of enzymes and microorganisms as the biocatalysts. This process produces a small number of discrete products in high yield using biological catalysts (Bridgwater, 2011). In thermochemical conversion, there are three main thermal processes available including pyrolysis, gasification and combustion.

Like biochemical conversion, thermochemical conversion can also be done with and without the presence of catalyst. Catalyst accelerates a chemical reaction without affecting the position of the equilibrium (Hagen, 2006). It increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction. A variety of metal oxide promoted alumina catalyst was synthesized using the incipient wetness impregnation method. Impregnation is contacting a solid with a liquid containing the components to be deposited on the surface (Haber *et al.*, 1995).

In this study, six types of metal oxide alumina promoted catalysts were prepared and characterized accordingly. All of these catalysts were characterized using scanning electron microscope (SEM), mercury intrusion porosimetry (MIP), fourier transform infrared spectroscopy (FTIR), atomic adsorption spectrophotometer (AAS), thermal gravimetric analysis (TGA) and Zetasizer. Impregnation method which was chosen in this study was contacted with a certain amount of solution of the metal precursor followed by drying and calcination. Table 1 summarized the previous studies of different metal oxide catalysts preparation

Table 1: Previous studies of different metal oxide catalysts preparation

Reference	Impregnation method	Drying method	Calcination method
Huang <i>et al.</i> , 2005	γ -Al ₂ O ₃ was ground to 150-250 μ m particles. The appropriate amount of metal nitrate, (Zn(NO ₃) ₂ ·6H ₂ O), dissolved in distilled water to form an aqueous solution. The solution was added dropwise to γ -Al ₂ O ₃ particles and the solid was shaken for 10 min to ensure uniform distribution of the solution.	The wet solid was dried in air (90°C, 16 hours)	The catalyst precursors were calcined at 500°C for 3 hours in static air, at the temperature ramp rate of 10°C/min
Bakar <i>et al.</i> , 2009	Ni(NO ₃) ₂ ·6H ₂ O was dissolved with minimum amount of distilled water. Mixed catalysts solution was prepared by mixing appropriate amount of metal nitrate salts. Wet impregnation method was used to prepare Al ₂ O ₃ supported catalyst by impregnating the catalyst solution on Al ₂ O ₃ beads support for 15 min.	Dried at 80°C for 24 hours	Calcined in air at 400°C for 5 hours
Kiss <i>et al.</i> , 2012	Spinel of Zn, Mg and Cu were synthesized by impregnation of alumina or their precursors, with the corresponding metal salts, Zn(NO ₃) ₂ ·6H ₂ O and Cu(NO ₃) ₂ ·3H ₂ O in a aqueous solution.	The impregnation sample precursors were dried at 105 °C overnight.	Calcined at 350°C for 4 hours in air
Buitrago-Sierra <i>et al.</i> , 2012	The alumina was calcined at 500°C for 5 hours. The ZnO-modified alumina support were prepared by impregnating the γ -Al ₂ O ₃ with an aqueous solution of Zn(NO ₃) ₂ ·6H ₂ O. The slurry formed was stirred at room temperature for 12 hours and the excess solvent was removed by heating at 80°C under vacuum in a rotary evaporator.	The solids were dried overnight at 100°C	Calcined at 700°C for 4 hours at a heating rate of 2 K min ⁻¹
Rosal <i>et al.</i> , 2010	The MnO ₂ /Al ₂ O ₃ catalyst was prepared by incipient wetness impregnation dried γ -Al ₂ O ₃ using an aqueous solution of Mn(CH ₃ COO) ₂ ·4H ₂ O.	Dried in air at 150°C	Calcined at 500°C for 3 hours
Zabeti <i>et al.</i> , 2009	8 g of γ -alumina in powder form was preheated at 600°C for 1 hour to remove physisorbed water. For each catalyst, a desired amount of precursor was dissolved in 50 mL of distilled water and introduced onto the alumina in a glass flask; the mixture was stirred for 4 hours at room temperature.	The obtained precipitation was heated overnight in an oven in order to remove water through evaporation.	All catalysts were calcined in air at desired temperature for 5 hours.
Zabeti <i>et al.</i> , 2010	The CaO/Al ₂ O ₃ catalyst was prepared using optimum condition, calcium acetate with a mass ratio of 1:1 to the support was dissolved in 50 mL of distilled water and stirred with 40 g alumina at room temperature for 4 hr.	The obtained slurry was heated up at 100°C in an oven overnight in order to remove the water.	Catalyst was calcined in air at 718°C for 5 hours using a muffle furnace.

MATERIALS & METHODS

Materials

The activated alumina was obtained from Edwards High Vacuum Int. In this study, a total of six metal nitrate were used, one of the metal nitrate was calcium nitrate tetrahydrate $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$, in crystalline form, and it was obtained from R & M Marketing, Essex, U.K, while the rest, copper (II) nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; ferric (III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; nickel (II) nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; manganese (II) nitrate tetrahydrate, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; zinc nitrate hexahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were in liquid form, and all of these metal nitrates were obtained from Scharlab S.L. The mass for each metal solution varied from one another since each metal have their own properties that affect the molarity of solution formed. By following Hongmei method, molarity of 0.2M is fixed for each solution. By using this molarity, the mass and volume for each metal used was calculated accordingly.

Incipient wetness impregnation

All the metal oxide promoted alumina catalysts were prepared using the incipient wetness impregnation method followed by drying and calcination. The alumina was first calcined for 1 hour at 600°C before used so that the physisorbed water can be removed. An appropriate amount of metal nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, were dissolved in distilled water (0.9 mL) to form an aqueous solution. Then, the aqueous solution was introduced into 1 g of the alumina and stirred at room temperature for 4 hours. The obtained slurry was dried at 120°C for 18 hours and calcined in nitrogen gas by using tube furnace as shown in Figure 1 at 500°C for 5 hours. Catalyst was then kept in desiccator with the presence of silica and KOH pellets in order to avoid water and CO_2 contact with the catalyst (Zabeti *et al.*, 2009; Zabeti *et al.*, 2010; Buitrago-Sierra *et al.*, 2012). Figure 1 showed the experimental set up for the metal oxide catalysts preparation.

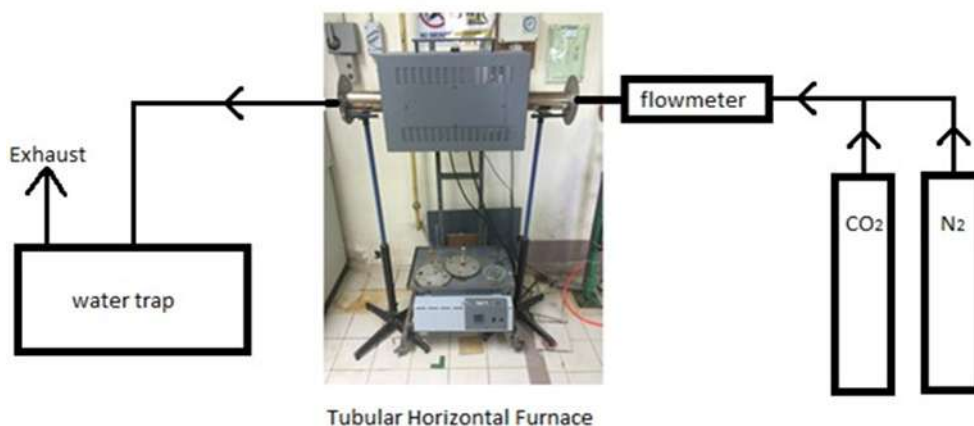


Figure 1: Experimental set up for the metal oxide catalysts preparation

Characterization of metal oxide promoted alumina catalyst

The characterization of all six samples was carried out in order to determine the functional group present in the catalyst, thermal stability of the catalyst, surface morphology, surface area and porosity, metal content and particle size distribution of the catalysts.

Surface morphology

The surface morphology of metal oxide promoted alumina catalyst was done by using scanning electron microscope (SEM) Carl Zeiss Model MA10. The instrument set up were as follow; vacuum mode = variable pressure, magnifications = 1000x, and signal VPSE G3 was chosen for non-conductive sample.

Surface area and porosity

The analysis in determining the surface area and total porosity of the metal oxide promoted alumina catalyst was done by using mercury intrusion porosimetry (MIP) of Thermo Electron Corporation (Pascal 440 Series). Mercury porosimetry technique is useful method to investigate the porous structure by giving reliable information such as pore size/volume distribution, particle size distribution, bulk density and specific surface area. About 0.80 g \pm 0.05 of sample was prepared and inserted into a dilatometer. Dilatometer was then placed into the mercury preparation machine. Before the mercury was purged into the dilatometer, vacuum was applied for 5 minutes. After that, mercury was filled slowly until it reached the half of the dilatometer. Then, the air was purged slowly to prevent any bubbles in the dilatometer. After that, the air was stopped and the vacuum was applied again for 5 minutes. Next, the mercury was filled until it reached the line mark at the tube that was attached to the dilatometer. The dilatometer was brought out and some oil was put after the line mark. The mercury was weighed using a mass balance. Finally, the dilatometer was placed in the porosimetry machine for analysis.

Functional group

The analysis of functional group was done using Cary 630 FTIR, Agilent Technologies and the name of method used was Betullin ATR 030714. Initially, the sample holder was cleaned by using propan-2-ol and kimwipes tissue to prevent the new samples that were analyzed from being contaminated. A small amount of sample (~1 g) was placed on the sample holder. The FTIR was set to scan in the range of 650 cm^{-1} to 4000 cm^{-1} . After obtaining the results, the data was saved as ASCII file and then used to plot a graph in Microsoft Excel.

Metal element

The analysis of metal element contained in the catalysts samples were done by using Z-5000 Polarized Zeeman atomic absorbance spectrophotometer (AAS). To analyze the sample, it must be in liquid form. In order to convert the powder catalyst to liquid, the digest method was followed and standard solution for each sample was prepared.

Thermal stability

The thermal stability of catalysts samples were analyzed by using TGA 6 Thermo-Gravimetric Analyzer (Perkin Almer). There are two analyses done which was thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). TGA was used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, and the weight is recorded as a function of increasing temperature, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, DTA). About 15.0 mg \pm 0.5 of samples were measured and placed in the sample holder in the instrument. The operating condition of the analysis was done at 50 to 1000°C, ramped at 30°C/min under the presence of nitrogen gas which flow was set at 100 mL/min. The collection of information on the decomposition of the sample was then interpreted based on the data obtained for TGA and DTA.

Particle size

The particle size distribution of the samples was done by using Malvern Zetasizer Nano Series Instrument with water as a dispersant with refractive index of 1.330. Initially, 0.5 g of each sample was prepared and placed in the beaker. After that, 20 mL of distilled water was poured into the beaker and mixed with the sample. The mixture was left to sediment for 24 hours before it can be pipetted. After the solution was pipetted, it was inserted to a specific cuvette of the instrument with minimum sample volume of 15 μ m.

RESULTS & DISCUSSION

SEM analysis

The SEM images of the alumina were shown in Figure 2 with the magnification of 1000x which operated at 15 kV. Based on the Figure 2, it showed that the alumina support showed uniform roughness at the surface with granular structure and had pores on the surface. Pores on the surface of the alumina were important because the pores would be introduced to the metal oxide catalyst by using impregnation method.

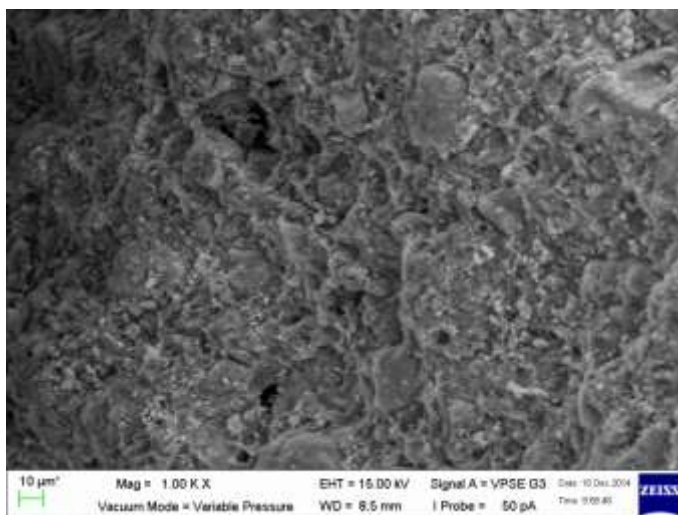


Figure 2: SEM micrographs (x1000 magnification) of alumina

Surface area and porosity

The activity of the catalytic system usually related to its textural properties, particularly, the specific surface area and the crystallite size. On account of this, the surface area and porosity of the alumina and metal oxide catalysts promoted alumina was done by using MIP. The results were shown in Table 2.

Table 2: Data of porosimetry for alumina and metal oxide promoted alumina catalyst

Samples	Total specific surface area, m ² /g	Total porosity (%)	Average pore diameter (nm)	Total cumulative volume (mm ³ /g)
Alumina	17.59	14.21	25.83	173.33
ZnO/Al ₂ O ₃	22.07	36.14	37.81	246.81
CaO/Al ₂ O ₃	23.84	32.60	20.88	242.63
MnO/Al ₂ O ₃	24.78	18.08	59.37	262.22
CuO/Al ₂ O ₃	26.14	36.77	34.82	271.08
FeO/Al ₂ O ₃	26.72	16.01	53.67	290.00
NiO/Al ₂ O ₃	28.55	23.18	29.53	308.54

Based on Table 2, all the metal oxide promoted alumina catalysts exhibited low specific surface areas ranging from 22.07 to 28.55 m²/g. NiO/Al₂O₃ had the highest surface area within the catalysts. While ZnO/Al₂O₃ showed the smallest surface area. However, it could be observed that the specific surface area of the metal oxide promoted alumina catalysts were bigger than the area of the alumina support. It could be assumed that the impregnation method used did not cause any blockage of the support pores.

According to Nascimento *et al.*, (2011), blockage will only occur when there was too long contact time between the support and the solution used for the impregnation in order to perform the ion exchange. High total porosity was shown by CuO/Al₂O₃ and ZnO/Al₂O₃ which were 36.77% and 36.14% respectively, while FeO/Al₂O₃ had the lowest total porosity of 16.01%. Large surface area and high porosity would increase the rate of reaction. Large surface area allowed the penetration through the catalyst and therefore making it became easier, meanwhile high porosity allowed more molecule to molecule collision occur which also known as molecular diffusion. The largest pore diameter was recorded by MnO/Al₂O₃ followed by FeO/Al₂O₃ which were about 59.37 nm and 53.67 nm respectively. CaO/Al₂O₃ showed the smallest pore diameter of 20.88 nm and it was even smaller than the alumina support which was 25.83 nm. The total cumulative volumes for all metal oxide catalysts were recorded higher than the cumulative volume of the alumina support where NiO/Al₂O₃ stated the highest value of 308.54 mm³/g. The increasing cumulative volume of the alumina support might be due to its non-affected structure which meant that there was no shrinkage or broken bonds within the alumina structure during the impregnation process (Pua *et al.*, 2011).

FTIR analysis

The results of the analysis functional group of metal oxide promoted alumina catalyst were as shown in Figure 3.

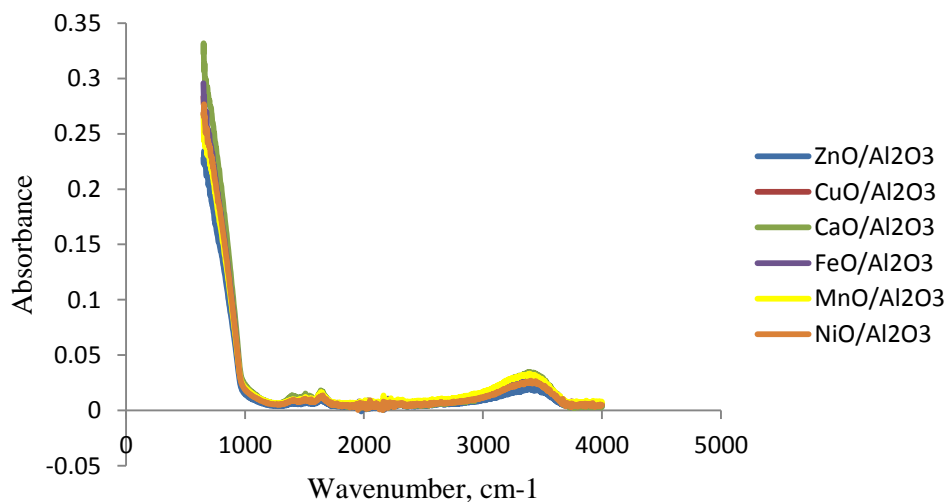


Figure 3: FTIR Spectra for CuO/Al₂O₃, CaO/Al₂O₃, FeO/Al₂O₃, MnO/Al₂O₃, NiO/Al₂O₃, ZnO/Al₂O₃

Based on Figure 3, it could be observed that all metal oxide promoted alumina catalysts had similar wavenumber. Based on Li (2005), the absorption bands at 1350 to 1500 cm⁻¹ associated with the CH₃ deformation mode and the CH₂ scissor mode. While, absorption

band at 1635 cm^{-1} assigned to the C=C stretching mode. Absorption due to C-H stretching modes between 3100 to 3000 cm^{-1} were also observed even the peak could occur in a very small range. Plus, absorption bands at 1688 and 1709 cm^{-1} were assigned to C=O stretching mode of the COOH group. However, all of these were possibly due to the by-products, since all the metal oxide promoted alumina catalyst were heavy metals and may not contain any functional group.

Elemental compositions

The metal oxide promoted alumina catalysts had been analyzed by using atomic absorption spectrophotometer to determine the selected elements that might exist in the samples. The results were shown in Table 3.

Table 3: Concentration (ppm) of metal elements in catalyst samples

Samples	Concentration (ppm)			
	Ca	Cu	Fe	Zn
CaO/Al ₂ O ₃	-0.037	-	-	-
CuO/Al ₂ O ₃	-	1.577	-	-
FeO/Al ₂ O ₃	-	-	1.922	-
ZnO/Al ₂ O ₃	-	-	-	1.491

From Table 3, it could be seen that only CaO/Al₂O₃ obtained a negative value for the concentration which meant that there was no calcium element present in the catalyst. This might be due to the time taken for the impregnation method for CaO/Al₂O₃. The Ca(NO₃)₂·4H₂O was in crystalline form and when it dissolved in 0.9 mL of distilled water, the solution that was formed was very little quantity in which it only can be stirred manually with the alumina instead of using the hot plate. It took 10 minutes for the impregnation of CaO/Al₂O₃ which was really short compared to the impregnation time for other catalysts which was approximately 4 hours. This was mainly because there was no ion exchange occurrence between the Ca(NO₃)₂·4H₂O and alumina due to the very short time taken for impregnation.

Thermal gravimetric analysis

Based on the TGA, there were two analyses done in the same time which are TGA and DTA. TGA provided information about the percentage weight loss of the sample and DTA analyzed the decomposition of the functional group in the sample per unit time. Figure 4 and Figure 5 showed the sample results of CaO/Al₂O₃ for TGA and DTA respectively.

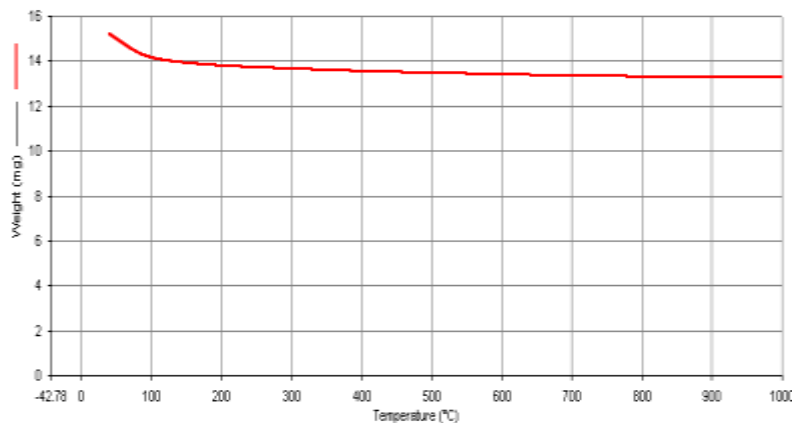


Figure 4: Thermal gravimetric analysis (TGA) of CaO/Al₂O₃

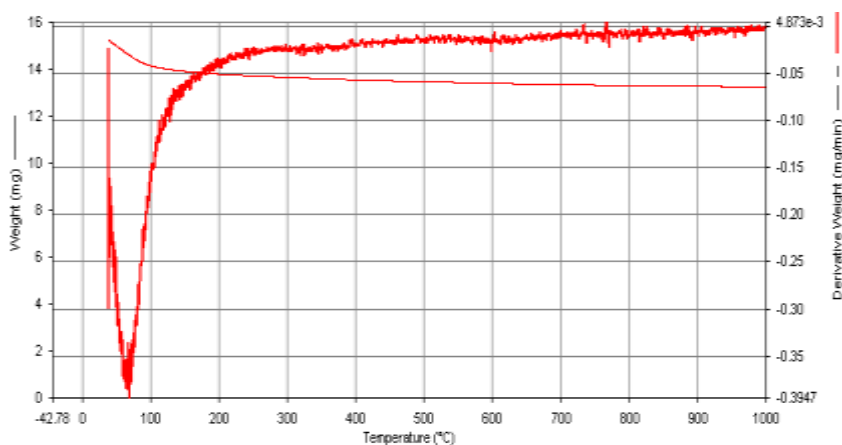


Figure 5: Derivative thermal analysis (DTA) of CaO/Al₂O₃

Based on the result of TGA, it could be observed that the CaO/Al₂O₃ showed only a slight decrease in weight up to 100°C. Generally, all the metal oxide promoted alumina catalyst had shown the same results, it could be observed that there was no change except for the weight loss that corresponded to liberation of adsorbed moisture between room temperature and 100°C (Ookawa 2012). Besides that, no other losses were recorded in the temperature range of 150 to 1000°C. It was because the temperature from 0 to 800°C was basically to measure the organic burning. Since all of the samples were in metal oxide state, not organic, it would be burnt at the temperature of 1500°C and above. However, the available analyzer could only reach the burning temperature of a maximum of 1000°C. The final weights (mg) of CaO/ Al₂O₃, CuO/ Al₂O₃, FeO/ Al₂O₃, MnO/ Al₂O₃, NiO/ Al₂O₃ and ZnO/ Al₂O₃ up to 1000°C were 13.26 mg, 14.50 mg, 13.30 mg, 14.08 mg, 13.56 mg and 13.96 mg, respectively. On the other hand, the decomposition of moisture could be seen clearly in DTA (in mg/min) as shown in Figure 5, which was interconnected with TGA analysis, between 30 to 100°C.

Particle size distribution

The particle size distribution was analyzed by using the Zetasizer in determining the size of the particle of metal oxide promoted alumina catalysts. The result of particle size distribution by intensity of metal oxide promoted alumina catalyst was shown in Figure 6.

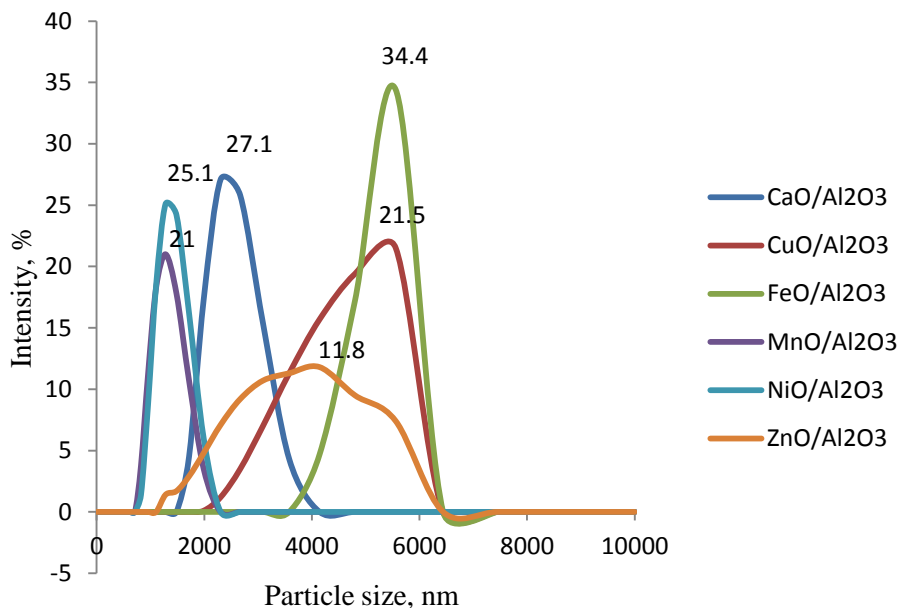


Figure 6: Particle size distribution based on intensity for metal oxide promoted alumina catalyst

Based on Figure 4, the particle size distribution by intensity of Cu/Al₂O₃ and FeO/Al₂O₃ stated the larger particle size of 5560 nm. Whereas NiO/Al₂O₃ and MnO/Al₂O₃ recorded the smallest particle size which was 1281 nm. It could be observed that NiO/Al₂O₃, CaO/Al₂O₃, MnO/Al₂O₃ and FeO/Al₂O₃ showed a normal continuous distribution graph which was a bell shaped graph. However, for CuO/Al₂O₃ and ZnO/Al₂O₃, the shape of the graph was slightly different. This might be due to the inconsistent data values obtained during the analysis. The particle size distribution analysis showed the particle size mean based on intensity of CaO/Al₂O₃, CuO/Al₂O₃, FeO/Al₂O₃, MnO/Al₂O₃, NiO/Al₂O₃ and ZnO/Al₂O₃ were 2305 nm, 5560 nm, 5560 nm, 1281 nm, 1281 nm and 3580 nm, respectively.

CONCLUSION

Based on the AAS analysis, from four metal oxides promoted alumina catalysts that were analyzed, only metal content of Cu, Fe and Zn were present in CuO/Al₂O₃, FeO/Al₂O₃ and ZnO/Al₂O₃ meanwhile Ca element was absent in CaO/Al₂O₃. Throughout the TGA and DTA analysis, above the temperature of 100°C all catalyst samples showed a stable result. Furthermore, alumina support that was analyzed by using SEM was observed to have pores on the surface which could be introduced to the metal solution for impregnation method. On the other hand, the automated mercury porosimetry analysis showed that CaO/Al₂O₃, CuO/Al₂O₃ and ZnO/Al₂O₃ had high total porosity (%). Based on results from Zetasizer, all the catalyst samples demonstrated different particle sizes in the range of 800-6500 nm based on their intensity.

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