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# Solid Metal Oxide Catalysts: Synthesis and Characterisation

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#### ABSTRACT

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Metal oxide particles have been studied by many researchers as potential catalysts for the production of biofuel. However, better understanding of catalysts preparation and characterisation are essential. A series of solid metal oxide catalysts were synthesised by chemical precipitation method using metal salt precursor such as magnesium nitrate hexahydrate,  $(Mg(NO_3)_2.6H_2O)$ , copper (II) nitrate tryhidrate  $(Cu(NO_3)_2.3H_2O)$  and nickel nitrate hexahydrate,  $(Ni(NO_3)_2.6H_2O)$ . The synthesised catalysts before and after calcination were further characterised using Thermal Gravity Analysis (TGA), Fourier Transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), N<sub>2</sub> physisorption and Scanning Electron Microscope (SEM) analysis. Higher catalytic activity and higher production of biofuel may benefits from this higher surface area metal oxide catalysts synthesis by precipitation method in this work.

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# Introduction

Metal oxide is a class of inorganic compound that have been used widely in various application such as catalysis, sensors, fuel technology, water treatment and etc (Védrine, 2017). In the context of catalysis, metal oxide catalysts play a major role in industrial chemical process. There are two types of heterogeneous catalyst; acid catalysts and base catalysts. It was reported that acid catalysts usually show low activity and require high reaction temperature and longer reaction time as compared to base heterogeneous catalysts (Lam et al., 2010). Single component of metal oxides are further categorised into alkaline earth metal oxides, alkali metal oxides, rare earth oxides and some solid basic materials which those oxides behave differently in the transesterification reaction. Nowadays, there has been an increasing demand in the synthesis of nanosized crystalline metal oxides because of their large surface areas, unusual adsorptive properties, surface defects, and fast diffusivities (Liu et al., 2011). Many methods have been used to synthesise crystalline metal oxides such as precipitation, sol-gels, hydrothermal, impregnation and sol-immobilised methods. Precipitation method is widely used not only in lab scale but also in large industrial scale. Therefore, in this present work, our aim is to synthesise high

surface area of metal oxide catalysts using precipitation method. The thermal stability, surface chemistry, textural properties and morphology were further investigated using Thermal Gravity Analysis (TGA), Fourier Transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), N<sub>2</sub> physisorption and Scanning Electron Microscope (SEM).

#### **Materials and Methods**

MO (M=Mg,Ni,Cu) nanostructures were synthesised by precipitation method using magnesium nitrate hexahydrate (Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) (R&M chemical, 99.5%), copper (II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O) (R&M chemical, 99.0%) and nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) (Emsure,99%). First, each metal salts solution was dissolved in 500 ml deionised water to form 0.2 M of concentration. Then, 0.4 M of NaOH solution (precipitant) was filled in burette and slowly dripped into each metal salt solution under continuous stirring (250 rpm) until the solution reached pH=12. The precipitation method was performed at room temperature. White, black and green precipitates were form from different precursors. The precipitates obtained was filtered and washed with deionised water and absolute ethanol for several times until it reach pH=7. Then, the washed precipitates were dried at 354 K for 16 hours in conventional oven. In order to form metal oxide, precipitates powder was calcined at different temperature range from 574 K to 774 K in furnace for 4 hours under atmospheric condition.

# **Catalyst Characterization**

Thermogravimetric analysis (TGA) was performed to study the thermal and oxidative stabilities of solid fresh M(OH)<sub>2</sub> properties using thermo-gravimetric analyser (TGA, Perkin Elmer Model STA 8000) at a heating rate of 283 K/min under oxygen environment from 289 K to 1273 K. Optimum calcination temperature to form solid MO catalyst was determined from the TGA profile. The morphology was monitored by scanning electron microscope (VPSEM, Model LEO1455). The catalyst samples were dispersed on the sticky carbon tape and then coated with gold to protect the induction of electric current and to generate second electron using a BIO-Ras Sputter Coater. The functional groups of the catalyst were carried by using Fourier Transmission Infrared Spectra (FTIR) analysis. KBr pellets that contained 1 wt.% of the sample in KBr were used. The spectrum was recorded in the wavelength range from 600-4000 cm<sup>-1</sup> using Perkin Elmer 400 Spectrometer. Nitrogen adsorption measurements were performed at 77 K by means of a Nova 1200 (Quantachrome) analyser. The surface area was calculated using Brunauer Emmett-Teller (BET) calculations. Pore-size distributions were calculated by the BIH (Barrett, Joyner and Halender) method using the desorption branch of the isotherm. Prior to measurement, the samples were degassed under vacuum for 390 K for 5 hours prior to analysis. The crystalline phases and diffraction peaks of calcined catalyst were determined by X-Ray Diffraction (XRD, Bruker Model D8 Advance) with theta-two measurement ranging from 10° to 80°.

#### **Results and Discussion**

#### i. Precipitation process.

Precipitation process of mixed M (M=Mg,Cu,Ni) salts solution with Sodium hydroxide (NaOH) as precipitant was performed using increasing pH titration experiment. The titration curve was plotted in order to monitor the hydrolysis chemistry in the solution. The hydrolysis product or so-called precipitates that were formed from the metal ion solution was metal hydroxides, M(OH)<sub>2</sub> according to equation 1;

$$M^{2+} + 2OH \rightarrow M(OH)_2$$
 (1)

Fig. 1 shows the titration curve of three different metal salts solution during precipitation process. For Mg salt solution, the starting pH is at 5.18. Adding 0.2 mol/L NaOH into the solution leads to drastically pH shifted to higher value to pH = 9.37. At this pH, a buffering sets in the solution, which is followed by the pH increases gradually to pH=12 to reached it supersaturation state. The total NaOH volume for each set is fixed to 100 ml. From the first derivatives curve (not shown here), heterogeneous nucleation process takes place at around pH 10.2 when cloudy suspension was observed, but no obvious precipitate was noticed. Spontaneous white precipitated can be observed when the pH reached 10.52. It is

noteworthy large amount of base is needed to obtained precipitate from Mg salt solution. Similar trend can be observed in Ni salt solution. The starting pH of the salt solution was 4.95. The pH slightly shifted to 7.06 and buffering start to occur. However, less amount of NaOH needed to initiate the nucleation process which starts at around pH=7.95. After white precipitates were observed, the pH was gradually increases but less steeper to reach it final pH. Copper salt solution shows typically an initial pH at around 4. Addition of NaOH did not gives much changes on the pH value and buffering immediately start in the solution (Meulenkamp, 1998). However, after heterogeneous nucleation process took place at around pH 5.38, then the pH drastically jumped to pH = 9.92 was observed. Above this region, again the pH increased gradually and less steeper to reach its final pH. In overall, precipitates occur at lower pH values of copper followed by nickel and magnesium with the addition of alkali solution (Chang et al., 2010). Even though copper solution is much more acidic compared to the other metals salt solution, the amount of alkali needed to initiate the nucleation process is lesser. This is due to the different metal ion species that are dominant in the solution at certain pH value. In the case of copper solution, the dominant species are Cu(OH)<sub>2</sub> at pH value above 7.



Fig. 1: Titration curve of 0.2 M metal nitrate salt solution (M=Mg,Cu,Ni) with an addition of 0.4 M NaOH at room temperature.

# ii. Catalyst characterization

Thermal gravimetry analysis was performed in order to determine the calcination required for the chemical and physical changes of our metal hydroxide. Fig. 2 (a)-(b) shows the thermogravimetric analysis (TGA) curves and the differential thermogravimetric (DTG) curve of the decomposition and transformation of  $Mg(OH)_2$ ,  $Cu(OH)_2$  and  $Ni(OH)_2$  particles into MgO, CuO and NiO particles. The TG profile for Mg(OH)<sub>2</sub> gave two steps of weight loss accompanied by exothermic DTG peak. The first weight loss in the region between the temperature 300 K and 415 K was related to the loss of physically adsorbed or unbound water molecules (Rowsell & Yaghi, 2004). The measured mass loss was about 4% at this stage. The second weight loss (25%) was in the range of 611 K to 675 K accompanied by DTG peak at 635 K coinciding with the evolution of chemisorbed water and NO<sub>X</sub> molecules. Third weight loss (4%) occurred in the TG profiles with no observation of DTG event was due to the transformation of the hydroxide to oxide and was associated with the phase transformation of amorphous MgO into its cubic ordered phase (Zhang et al., 2009). At temperature above 1054 K, it showed that the molecules were stable and the weight of molecule was nearly constant without further weight loss. TGA profiles of  $Ni(OH)_2$  gives similar behaviour as above with two temperature regions. However, first weight loss (8%) between 304 K to 399 K is accompanied by broad DTG peak. The second weight loss (10%) appeared at early temperature region between 479 K and 598 K with DTG peak centred at 549 K. The occurrence of the first endothermic peak centred at 335 K is linked with the evolution of OH and  $H_2O$ , which has band structure with nickel and oxygen atoms inside the molecule, will be eliminated in this region. Whereas for the second endothermic is due to evolution of NOx (Assowe et al., 2012). A Significant weight loss occurs before the sample reached it stability state, this event may lead to transformation to pure oxide particles.

This event may lead to pure NiO particles. At last regions it show that the molecule stable and the weight of molecule is nearly constant without any other weight loss.



Different TGA behaviour are observed for Cu(OH)<sub>2</sub> sample. The thermal decomposition of the molecule can be divided to four separated regions. The first region is related to the loss or evaporation of the absorbed water between 304 K and 374 K, corresponding to 2% weight loss, was attributed to the removal of weakly bond water molecules. The second region with weight loss of 6%, occurring in the 419 K to 496 K, was assigned to the loss of water molecules adsorbed in the surface and in the interlayer space. De-hydroxylation and decomposition of the anion in the interlayer space should take place in the second step, leading to the destruction of the layered structure. The third region with small shoulder in DTG peak was assigned to thermal decomposition and destruction of the layered structure through dehydroxylation reactions to transformation of nitrate ions (present in the interlayer space) to nitrogen oxides (Aguirre et al., 2011; Rojas et al., 2008). Lower thermal stability of copper hydroxide was found as compared to magnesium hydroxide and nickel hydroxide. It can be concluded that Mg(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> were fully combusted at temperature  $\geq$ 770 K while Cu(OH)<sub>2</sub> was fully combusted at temperature 570 K in order to transform from hydroxide to active oxide phase. Thus, the suitable calcination temperature of Mg(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> were calcined at 770 K and 570 K under N<sub>2</sub> atmosphere for 2 h to synthesise the for biodiesel production.



Fig. 3: FTIR spectra of fresh solid metal hydroxides (a) and metal oxide catalysts (b).

The IR spectrum of the fresh solid  $Mg(OH)_2$  and MgO are shown in Fig. 3 (a-b). A sharp and intense peak centred at wavenumber of 3700 cm<sup>-1</sup> with an addition of broad shoulder at around 3421 cm<sup>-1</sup> can be seen clearly for Mg(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> solid sample. These absorption bands between 3700 cm<sup>-1</sup> and 3200 cm<sup>-1</sup> indicated the stretching mode of vibration in hydroxyl group (O-H) group in crystal water (De Rosa et al., 2011). Both samples gave slight absorption peaks in range of 1380 to 1640 cm<sup>-1</sup> that may be assigned to OH bending vibrations combined with magnesium, and nickel atoms (Tan et al., 2011). Whereas for Cu(OH)<sub>2</sub> sharp peak at 3544 cm-1 and broad peak can be seen at wavenumber 3490 cm<sup>-1</sup> which is slightly shifter can be assigned to structural OH- groups and to water molecules in the interlamellar space (Rajamathi et al., 2005). Furthermore, the frequency vibrational mode attributed to Cu-O-H bonds can also be found in below wavenumber 1000 cm<sup>-1</sup>. The peak in the lower region between 1500 cm<sup>-1</sup> to 1000 cm<sup>-1</sup> can be assigned to vibrational mode of nitrates (NO<sub>3</sub>-) ions interact with metal hydroxides layers (Rajamathi et al., 2005). The absorption peak almost disappeared in the calcined samples as seen in Fig. 3(b) suggesting that the conversion of  $M(OH)_2$  to MO during calcination was almost completed and indicated phase transformation in the samples as pointed out from X-ray diffraction results (Yang et al., 2010; Xie & Zhao, 2014). NiO still have a broad peak at range 3445 cm<sup>-1</sup> due to the fact that the calcined powder tends to physically absorb water still present even after calcination. The same observation was also obtained by Abolanle (Adekunle et al., 2014). The frequency of the vibrational modes attributed to Mg–O–H, Cu–O–H and Ni–O–H bonds depended on the degree of hydrogen bonding and were found at 819, 673 and 674 cm<sup>-1</sup>, in good agreement with those reported by Henrist et al., 2003.



The X-ray diffractograms of calcined samples are shown in Fig. 4. For MgO sample, the phase identification revealed that all curve belonged to MgO phase of face-centred cubic (JCPDS 01-078-0430) with the diffraction peaks at 37°, 43°, 62°, 75° and 79° are assigned to 111, 200, 220, 311 and 222 planes. This clearly indicated that Mg(OH)<sub>2</sub> was completely transformed to crystalline MgO (Vatsha et al., 2013). This result shows that calcining at temperature 723 K is adequate to produce pure MgO. X-ray diffractograms patterns of CuO indicates similarity of sharp peak as in Fig. 4. The diffraction lines are sharp and no any impurity peak was observed, indicating the high crystallinity and purity of the two samples. The peak located at 32°, 35°, 39° and 49° are assign to 110, 111, 200 and 202 planes orientation. After calcination process at temperature of 723 K, the peak intensity at 111 and 200 planes increases in CuO catalysts. This result indicates that the crystallinity of CuO was enhanced by sufficient nucleation energy from thermal treatment (Wang et al., 2011). XRD peaks confirm that the final product (after calcination) CuO was base centred monoclinic (JCPDS 48-1548) (Sharma & Ghose, 2014). No characteristic peaks of impurities or other precursor compounds were observed. Whereas, the XRD pattern of NiO catalysts gave well defined and resolved broad peaks indicating the crystalline nature of the nanoparticles, and also confirming the transformation of Ni(OH)<sub>2</sub> to NiO after calcination process at 523 K. XRD peaks confirmed that the formation of NiO catalysts was rhombohedral structure by comparison with JCPDS card no. 44-1159.

Sample notation	Specific surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)	Average Pore diameter (Å)
Mg(OH) <sub>2</sub>	42.77	0.0730	68
MgO	194.2	0.4000	82
Cu(OH) <sub>2</sub>	21.75	0.0987	181.6
CuO	125.4	0.4069	129.8
Ni(OH) <sub>2</sub>	17.37	0.0779	179.5
NiO	173.9	0.4274	93.4

Table 1: Surface properties of metal hydroxide and its calcined products



Fig. 5: N<sub>2</sub> adsorption-desorption isotherm plot of metal hydroxides (a) and metal oxide catalysts samples (b).

Nitrogen sorption at 77 K was used to evaluate the pore texture of the solid catalysts. Table 1 show the textural properties of our solid hydroxides and oxide sample, whereas Fig. 5 shows the nitrogen sorption isotherms plot. Based on the nitrogen absorption isotherm plot, all samples exhibit Type IV characteristic of mesopore solids (Shahbazi et al., 2011). The existence of a hysterisis loop at relative pressure  $(P/P_0)$  of 0.4 to 1.0 indicates the porosity shape arising from the non-crystalline intra-aggregate voids and spaces formed by interparticle contacts and also correspond to a capillary condensation phenomena. Samples  $Mg(OH)_2$  gives hysterisis of type I (HI) while the rest of the samples exhibited type 3 (H3). Hysteresis of H1 is usually associated to different size of pore mouth and pore body (this is the case of ink-bottle shaped pores) or to a different behaviour in adsorption and desorption in near cylindrical through pore (Sanz et al., 2010). For types 3 hysterisis loop are usually found on solids consisting of aggregates or agglomerates of particles forming slit shaped pores (plates or edged particles like cubes)(Wu et al., 2012) The porous textural properties such as specific surface area (BET) and pore volume ( $V_{total}$ ) for all samples are listed in Table 1. It can be seen that all calcined sample resulted in a higher specific surface area and total pore volume as compares to the hydroxides samples. This is due the calcination process at temperature above 574 K results in fast removal of hydroxyl species and the pore walls collapse, which causes the surface area and pore volume to increase dramatically. The average pore size also enlarged. Specific surface area and total pore volume are two significant factors which can affect the catalytic performance. It was well known that the catalyst that can produce higher specific surface area and total volume could be resulted in the good performance for catalytic activity.



Fig. 6: The SEM images for a) Mg(OH)<sub>2</sub>, b) MgO, c) Cu(OH)<sub>2</sub>, d) CuO, e) Ni(OH)<sub>2</sub> and f) NiO (1000 Magnification)

The morphology of the particles obtained after precipitation and calcined were observed by SEM as displayed in Figure 6. The SEM images of  $Mg(OH)_2$  showed morphology flakes like structure and has a good dispersion. While for MgO catalysts showed some clustered form were clearly occurred. For  $Cu(OH)_2$  precipitates possess some cracks on the surfaces with some dispersion of fluffy-like particles. Whereas for CuO catalyts possess nearly the same morphology as before calcined (Dubal et al., 2010) (Phiwdang et al., 2013). However, Ni(OH)<sub>2</sub> and NiO have same morphologies which are rock like structure.

## Conclusion

The solid metal oxide catalyst was successfully synthesised by precipitation method using three metal included magnesium, iron, nitrate salt solution and sodium hydroxide solution under mild condition. The choice of calcination temperature is crucial in order to produce high crystallinity and high surface area catalysts. From the above findings, it will enable us to understand the correlation of catalysts and their catalytic properties during the production of biofuel from microalgae.

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