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### Ni<sub>x</sub>Co<sub>y</sub>Fe<sub>1-x-y</sub>O<sub>4</sub> Nanocatalyst: Preparation, Characterization and Catalytic Activity in CO<sub>2</sub>/H<sub>2</sub> Conversion

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#### Abstract

 $Ni_yCo_xFe_{(1-x-y)}O_4$  nanocatalysts (with y = 0,2 and x = 0,1 - 0,3) have been prepared using a simultaneous method of sol – gel and ultra-sonocation. Starting materials used are nitrate salts of iron, nickel and cobalt which are dissolved in white egg solution, respectively before mixing process. After calcining and grinding, the nanocatalysts are characterized by use of X-ray diffraction (XRD) analysis, Infra Red spectroscopy (IR), and Scanning Electron Microscopy (SEM). X-ray diffraction analysis proved that the prepared nanocatalysts consist of various crystalline phases such as  $CoFe_2O_4$  which is superimposed to NiFe<sub>2</sub>O<sub>4</sub> as a major phase,  $Fe_2O_3$ , NiO, and  $Co_3O_4$  as minor phases. Therefore, it is concluded that crystalline phase of NiCoFe<sub>2</sub>O<sub>4</sub> is formed. FTIR Analysis proved that Lewis acid sites is more dominant than BrØnsted – Lowry acid sites for all prepared nanocatalysts. Then, surface morphology analysis showed that  $Ni_yCo_xFe_{(1-x-y)}O_4$  nanocatalysts prepared have not homogeneous form yet. Size of particles is varied and is around 85 nm for  $Ni_{0.2}Co_{0.2}Fe_{0.6}O_4$  catalyst. However, the particle size of other prepared catalysts is between 85 and 110 nm. Catalyst's activity test performance showed that ethanol is produced on a range of temperature reaction with a resulting concentration of 5000 ppm.

**Keywords** : nanocatalyst, sol-gel and ultra-sonocation method, BrØnsted - Lowry and Lewis Acid Sites,  $CO_2/H_2$  conversion, ethanol and propanol formation.

### Introduction

Currently, catalytic conversion of CO<sub>2</sub> into alcohols is growing progressively with the main focuss on design of various catalytic systems. Development and testing of various catalyst systems have been reported in vast numbers of publications, showing that in general the conversion level is still considered as low. The catalytic systems of X/ZrO<sub>2</sub> (where X = Cu, Ni, Ag, Rh, Pd, Pt dan Au) (Wokaun et al., 1999) were investigated under the experimental conditions of temperature range, 490 – 570°C and pressure of 100 bar and found that selectivity for alcohol varied between 30 and 97% but the level of conversion was low (12.5 – 20 mg/g<sub>cat</sub>/h). In another study (Udron, 1997), it was reported that the use of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalyst (where M = Cu and Zn) under the experimental temperatures of 250 – 350°C and pressure 30 – 80 bar resulted in methanol selectivity of 15 – 55%, and CO<sub>2</sub> conversion of 2 – 25%. Furthermore, reaction condition such as temperature and pressure

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will also affect the product distribution. For example, if the reaction goes on at low temperature  $(220 - 250^{\circ}C \text{ and } 25 \text{ bar})$ , the product tends to both wax and diesel fuel selectivities. Otherwise, the product will tends to olefin selectivity (Dry, 2002).

One of nanocatalysts mostly used in many catalytic application is spinel of pyrite, NiMFe<sub>2</sub>O<sub>4</sub>. Preparation of NiMFe<sub>2</sub>O<sub>4</sub> nanocatalysts (where M = Co, Cu, Al, Zn, etc ) has been carried out by using varied methods such as co-precipitation method using surfactant agents leading to particle size of 32 nm (Derakshshi et al., 2012), ceramic method with a particle size of 58 nm (Jin Pak et al., 2008), and sol – gel method with a particle size of 45 nm (Singhal et al., 2005) but calcination temperature used is between 900 and 1200°C. Also, based on its physical and chemical properties, the application of spinel pyrites based materials is huge. Then, preparation method concerning economic point of view, effective due to nanocrystal formation and distribution, and give a good activity, have become a target for many researchers. For example, nano-particles preparation of NiFe<sub>2</sub>O<sub>4</sub> spinel has been successfully obtained by using egg-white solution, with a particle size of NiFe<sub>2</sub>O<sub>4</sub> is a range of 60 – 600 nm (Maensiri et al., 2007).

In our group, the catalyst system that has been explored in several studies for the same purpose is  $Ni_xFe_{2-x}O_4$  (Situmeang et al., 2010). The definite structure of the catalyst is  $NiFe_2O_4$  as spinel and x is ranging from 0.2 to 0.4. The most interesting result obtained was the ability of the catalyst to work at ambient pressure and produced alcohols at concentration of almost 800 ppm in the product. This previous result showed that  $NiFe_2O_4$  catalysts is able to convert  $CO_2$  and  $H_2$  into various alcohols such as methanol, ethanol, propanol, and butanol (Situmeang, et al., 2011). This achievement implies that this catalyst system posseses promising potential to be developed further to improve the performance of the catalyst, both in terms of conversion and the selectivity toward medium and high alcohols. In this respect, modification of the catalyst proposed is introduction of another metal oxide into basic system of  $Ni_xFe_{2-x}O_4$  to produce derivative system of  $NiFe_{2-y}M_yO_4$  (where M = Co) using the combination method of sol – gel and sonocation in an attempt to produce nano-sized catalyst.

In the present work, we would like to report the influence of cobalt ion in NiFe<sub>2</sub>O<sub>4</sub> catalyst's structure and its catalytic behaviour. This result is focused on the preparation of Ni<sub>y</sub>Co<sub>x</sub>Fe<sub>(1-x-y)</sub> O<sub>3± $\delta$ </sub> (y = 0.2 and x = 0.1 – 0.3) catalyst using a mixture method of sol – gel and ultra-sonocation simultaneously and study its catalytic activity performance to convert CO<sub>2</sub>/H<sub>2</sub> at a range of temperature (200 – 500 °C).

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### **Experimental Method**

**Catalysts Preparation**. Solid Ni<sub>y</sub>Co<sub>x</sub>Fe<sub>(1-x-y)</sub>O<sub>3± $\delta$ </sub> were prepared by dissolving Fe(NO<sub>3</sub>)<sub>3</sub>. 9 H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>3</sub>. 6 H<sub>2</sub>O, and Ni(NO<sub>3</sub>)<sub>3</sub>. 6 H<sub>2</sub>O in 100 mL egg - white solution. Then, these solutions (by Fe/Co ratio variation, x = 0.1 to 0.3 and y = 0.2) were mixed, heated, and ultra – sonocated simultaneously until homogenous solution is obtained and evaporated it at 80°C until sol – gel solution formed. Furthermore, the precursor was calcined at 600 °C for 6 hours (increased by 2 °C min<sup>-1</sup>).

**Catalysts Characterization**. A small amount of catalyst's sample (50 – 100 mg) was prepared and put it on sample holder. X-rays power diffraction pattern of  $Ni_yCo_xFe_{(1-x-y)}O_{3\pm\delta}$  were recorded from  $2\theta = 10$  to  $90^\circ$  on a Philips diffractometer Model PW 1710 using Cu K<sub> $\alpha$ </sub> radiation at a step 0.02° per second.

**Catalytic Measurements.** The CO<sub>2</sub>/H<sub>2</sub> reaction was carried out in a vertical down flow U – tube natural quartz reactor (with inner diameter of 12 mm) at atmospheric pressure. In a typical experiment, ca. 50 mg of sieved catalyst was placed in U-tube between two quartz wools. The reactor was placed vertically inside a programmable cylindrical furnace, which was heated electrically. Before the reaction, the catalyst was pretreated under flowing reductive mixture (Ar/H<sub>2</sub>, 3 L h<sup>-1</sup>) at 600 °C for 60 minutes. The reaction went on under flowing gas mixture (CO<sub>2</sub>/H<sub>2</sub> ratio of <sup>1</sup>/<sub>4</sub>, 50 mL min<sup>-1</sup>). In reaction, the product stream coming from the reactor was passed through collector tube with water as a trapper which is immersed into ice cubes. Then, the products were analyzed by gas chromatography with thermal conductivity detector (TCD).

Acid sites analysis of catalyst. After heating on  $120^{\circ}$ C, sample is inserted in vaccum (ASTM, 2005). Then, liquid aniline is fluidized into crucible located inside of vaccumized dessicator. After contacting for 24 hours, catalyst's sample is taken out from dessicator and allowed on air for 2 hours. Finally, a small amount of sample is mixed to KBr powder (sample/KBr ratio = 1/9) and is ready to analyze by putting it on quartz cell of FTIR (Shimadzu).

**SEM Analysis.** 0.1 g of catalyst's sample is put on sample holder containing Cu sticking tape, Then sample is coated by thin layer of gold or other conducting materials (Drbohlavova *et al.*, 2009; and Hanke, 2001).

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### **Results and Discussions**

### Catalyst Characterizations.

**X-Ray Diffraction Analysis.** In Figure 1, it is shown that  $Ni_{0.2}Fe_{0.8-x}Co_xO_{3\pm\delta}$  (where x = 0.1 – 0.3) catalysts consist principally in NiFe<sub>2</sub>O<sub>4</sub> crystalline phase which has representative peaks corresponding to JCPD file no. 10-0325. However, other crystalline phases are also identified such as CoFe<sub>2</sub>O<sub>4</sub> (JCPDF 22-1086), Co<sub>3</sub>O<sub>4</sub> (JCPDF 42-1467 and JCPDF 09-0418), Fe<sub>3</sub>O<sub>4</sub> (JCPDF 19-0629),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDF 33-0664), and NiO (JCPDSF 44-1159 and PDF 47-1049) as a minor phases. Furthermore, It has to be noted that crystalline phases of NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> are superimposed and have a similar spinel crystal structure.



Figure 1. Fitting of  $Ni_yCo_xFe_{(1-x-y)}O_4$  diffractograms {(a)  $Ni_{0,2}Fe_{0,7}Co_{0,1}O_4$ , (b)  $Ni_{0,2}Fe_{0,6}Co_{0,2}O_4$  dan (c)  $Ni_{0,2}Fe_{0,5}Co_{0,3}O_4$ } with references of  $NiFe_2O_4$  and  $CoFe_2O_4$  data.

**FTIR Analysis of Bronsted-Lowry and Lewis acid sites.** Both BrØnsted – Lowry and Lewis acid sites of Ni<sub>0.2</sub>Fe<sub>0.8-x</sub> Co<sub>x</sub>O<sub>3± $\delta$ </sub> catalysts (where x = 0,1 – 0,3) was investigated by FTIR instrument. Infra red spectrum showed that Lewis acid sites' peak of Ni<sub>0.2</sub>Co<sub>0,1</sub>Fe<sub>1,7</sub>O<sub>4</sub>, Ni<sub>0.2</sub>Co<sub>0.2</sub>Fe<sub>1,6</sub>O<sub>4</sub>, and Ni<sub>0.2</sub>Co<sub>0.3</sub>Fe<sub>1,5</sub>O<sub>4</sub> catalyst appears at wavenumber of 1634,95 ; 1630,03 and 1633,90 cm<sup>-1</sup>, respectively. However, a peak of Bronsted-Lowry acid sites on Ni<sub>0.2</sub>Co<sub>0.1</sub>Fe<sub>1,7</sub>O<sub>4</sub>, Ni<sub>0.2</sub>Co<sub>0.2</sub>Fe<sub>1,6</sub>O<sub>4</sub>, Ni<sub>0.2</sub>Co<sub>0.2</sub>Fe<sub>1,6</sub>O<sub>4</sub>, and Ni<sub>0.2</sub>Co<sub>0.3</sub>Fe<sub>1,5</sub>O<sub>4</sub> catalyst appears at wavenumber of 1537,26 ; 1519,90 and 1510,25 cm<sup>-1</sup> respectively, as shown in Figure 2 below.

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Figure 2. IR spectra of several nano-catalysts : (a)  $Ni_{0,2}Co_{0,1}Fe_{1,7}O_4$ ,

(b)  $Ni_{0,2}Co_{0,2}Fe_{1,6}O_4$ , and (c)  $Ni_{0,2}Co_{0,3}Fe_{1,5}O_4$ .

Furthermore, as shown on Figure 2, increasing Co-content in  $Ni_{0.2}Co_xFe_{(1.8-x)}O_4$  structure decreasing its Lewis acid strength. The same pattern appeared on its BrØnsted – Lowrey acid strength.

**Micrograph analysis of SEM.** As shown in Figure 3, distribution of catalyst particles is relatively homogeneous as Co content is increased in  $Ni_{0.2}Fe_{1.8-x}Co_xO_4$  (where x = 0,1 - 0,3), especially in  $Ni_{0.2}Fe_{1.6}Co_{0.2}O_4$  catalyst. The particle size of this middle catalyst is around 85 nm.



Figure 3. Micrograph of various  $Ni_{0.2}Fe_{1-x}Co_xO_4$  catalysts (where x=0,1-0,3; from left to right).

However, the other catalysts have a particle size of 100 nm. In general, the shape of these particles is cubic eventhough there is impurities hiding those particles'shape.

**Catalyst activity.** Figure 4 shows that all catalysts such as  $Ni_{0.2}Fe_{1.7}Co_{0.1}O_4$ ,  $Ni_{0.2}Fe_{1.6}Co_{0.2}O_4$ , and  $Ni_{0.2}Fe_{1.5}Co_{0.3}O_4$  are active in  $CO_2/H_2$  reaction to produce alcohol compounds in the range of reaction temperature. The most selective catalyst is actually

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Ni<sub>0.2</sub>Fe<sub>1.6</sub>Co<sub>0.2</sub>O<sub>4</sub>, except at 200°C, since it produced both ethanol, C<sub>2</sub>H<sub>5</sub>OH and propanol,

C<sub>3</sub>H<sub>7</sub>OH. Other catalysts are also active to produce both ethanol and propanol.



Figure 4. ethanol formation (yields in ppm) by some catalysts in different reaction temperature.

Other catalysts are also active to produce both ethanol, C2H5OH and propanol,

In general, it can be said that the quantity of ethanol formed is affected by the reaction temperature. As temperature increased ethanol augmented. The clear tendency appeared on both  $Ni_{0.2}Fe_{1.6}Co_{0.2}O_4$  and  $Ni_{0.2}Fe_{1.5}Co_{0.3}O_4$  catalysts.

The formation propanol on  $Ni_{0.2}Fe_{1.6}Co_{0.2}O_4$  catalyst is only observed at 300°C (see Figure 5) compared to other catalysts. However, its amount is relatively higher (almost 14 ppm) than the others. Concerning the propanol formation, it can be said that cobalt content in  $Ni_{0.2}Fe_{1.8-x}Co_xO_4$  catalysts plays a role to form  $C_3^+$  species eventhough the propanol formation is still low. In other words, since increasing Co- content in the catalyst decreasing the acid strength, it can be implied that the acid sites of the catalyst is not strong enough to bind  $C_2^+$  in order to form  $C_3^+$  species furthermore.

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Figure 5. Propanol formation (yields in ppm) by some catalysts in different reaction

On the whole, it is observed that, among the various  $Ni_{0.2}Fe_{1-x}Ni_xO_4$  catalysts investigated in this study, in order to produce ethanol,  $Ni_{0.2}Fe_{1.7}Co_{0.1}O_4$  catalyst is a promising system for performing the  $CO_2/H_2$  reaction under mild conditions of temperature and pressure.

### Conclusion

Based on this worked, we can conclude that both the cobalt content in  $Ni_{0.2}Fe_{1-x}Ni_xO_4$  catalysts and the temperature reaction affect the formation of alcohol compound on  $CO_2/H_2$  reaction. In general, all catalysts such as  $Ni_{0.2}Fe_{1.7}Co_{0.1}O_4$ ,  $Ni_{0.2}Fe_{1.6}Co_{0.2}O_4$ , and  $Ni_{0.2}Fe_{1.5}Co_{0.3}O_4$  are active in this  $CO_2/H_2$  reaction. In fact,  $Ni_{0.2}Fe_{1.7}Co_{0.1}O_4$  catalyst is a promising system for performing the  $CO_2/H_2$  reaction under mild conditions of temperature and pressure.

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