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The Effectiveness of Various Bimetallic on Iron-Zeolite Catalyst by Carbon Dioxide Hydrogenation

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Abstract. Nowadays, the concentration of carbon dioxide (CO₂) getting worse and increasing year by year due to the open burning, transportation, deforestation, use of synthetic fertilizer and industrial process. The concentration of CO₂ has reached 406.99ppm since August 2018. This can cause global warming, rising sea level, climate change and etc. Therefore, an intensive research was done to control this issues on hydrogenation of CO₂ reaction by using composite catalyst. A series of X/Fe-Zeolite (X=Co, Cu, Pd and Ni) were synthesized by sol-gel method that using oxalic acid and precursors of nitrate. The Fe-Zeolite act as both a support and a co-catalyst while bi-metal served as promoter for CO₂ hydrogenation. Parameters that involved for synthesized the composite which are fixed weight ratio of X:Fe:Zeolite (0.1:1.25:2), the polyethylene glycol (PEG) of 2 mL and calcine temperature of 500°C. Then, the composite was evaluated on CO₂ hydrogenation at temperature reaction of 130°C, pressure CO₂:H₂ of 1:3.5 bar, weight catalyst of 0.2g and time reaction of 6 hours in liquid 1,4-dioxane solvent. Formic acid (FA) was the major product in this research. The effectiveness of composite was studied after addition of bi-metal onto the surface area Fe-Zeolite can boosted the production of FA or not. Transmission Electron Microscopy (TEM) determined the morphological and textural properties of the synthesized catalysts and X-Ray Diffractometer (XRD) while the formation of FA from CO₂ hydrogenation reaction was evaluated using High Performance Liquid Chromatography (HPLC). By this way it can reduced the concentration of CO₂ at atmosphere and getting value-added product from the reaction.

1. Introduction

Major anthropogenic source for global warming arise from an increasing level of concentration carbon dioxide (CO₂) at atmosphere that causes many problems such as hotter days, rising sea levels, droughts and climate change [1]. Nowadays, utilization on CO₂ has been an interesting issue to overcome global warming by the CO₂ hydrogenation reaction for the production of valuable chemicals [2]. An efficient catalyst is required for the CO₂ hydrogenation reaction because of CO₂ is a kinetically and thermodynamically stable molecule to broke up the double bond (C=O) and to increase the product yield [3,4]. The present study was designed to determine the effectiveness of the series of bi-metal on



Fe-zeo through sol-gel method in the presence of polyethylene glycol (PEG) and oxalic acid. α -Fe₂O₃ elected as catalyst due to its characteristic of non-toxic material, inexpensive and thermodynamically stable at ambient temperature among iron oxide [5,6]. Zeolites made of crystalline microporous aluminosilicates that forming a three-dimensional network between aluminum [AlO₄]⁵⁻ and silicon [SiO₄]⁴⁻ tetrahedral linked by oxygen [7,8]. α -Fe₂O₃ and zeolites have wide application and one of it is catalysis. In the previous study, both of them shows a higher activity in catalysis and because of that we modified and synthesize composite Fe-zeolite with various bi-metal through sol-gel method. Sol-gel method is a uncomplicated, quick and be able to synthesized on huge scale compared to other method [5,9]. Formic acid is considered product formed from the conversion of CO₂ hydrogenation. Formic acid is a main chemical and have diverse application in production of food, leather, agriculture, cleansing solution and act as starting material to produced other chemical [10,11]. The conversion reaction can reduce the concentration of CO₂ at atmosphere, thereafter can reduce pollution and increase the country's revenue. In the presents study, an investigation about the effect of crystal size on production of formic acid was done. The activity of catalyst depending on their crystallite size, the bigger crystallite size will decrease the surface area and catalytic activity will decreases [12].

2. Materials and Methods

2.1. Preparation of synthesize Fe-Zeolite and bi-metal Fe-Zeolite

Initial materials to synthesized Fe-zeolite through sol-gel method by using Zeolite X from Fluka BioChemika, Fe (III) nitrate nanohydrate from R&M Chemical, oxalic acid dehydrate from R&M Chemical, polyethylene glycol (PEG 2000) from Merck and absolute ethanol from HmbG Chemicals without any auxiliary purification. First of all, 2 g of zeolite was dissolved in 50 mL absolute ethanol with a continuing stirred at 60 °C for 10 min. After that, add 1.25 g of Fe (III) nitrate into a solution continue stir for 10 min. Then, slowly added 2 mL of PEG. Next, 0.75 g of oxalic acid was heated with 40 mL absolute ethanol in another beaker and poured into previous beaker until a gel formed. An oven with the temperature of 105 °C was set up to dry the produced gel. Finally, further calcination in furnace at 500 °C for 2 h.

The bimetal Fe-Zeolite were also prepared with sol-gel method by using the similar constituent as stated above by adding 0.1 g of Cobalt (II) nitrate hexahydrate from Merck, Palladium (II) nitrate dehydrate from Sigma Aldrich, Nickel (II) nitrate hexahydrate from R&M Chemicals and Copper (II) nitrate trihydrate from Bendosen without any further purification as second metal or promoter as indicated in Figure 1.

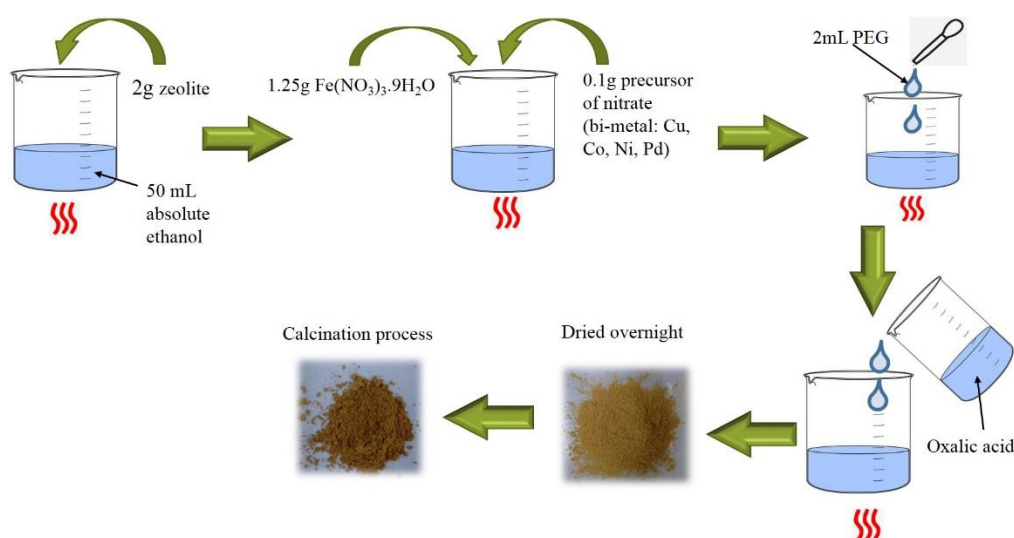


Figure 1. Experimental procedures of bi-metal of Fe-Zeolite

2.2. Hydrogenation of CO₂

After synthesized, the activity of each prepared catalyst was undergo CO₂ hydrogenation reaction. The reaction was running in an autoclave reactor by using 1,4-dioxane from Fisher Chemical as solvent without any purification. This reaction used 0.2 g catalyst and 35 mL of 1,4-dioxane, followed by flushing H₂ for 1 min to remove air. Then, the CO₂ and H₂ gases were occupied with the molar ratio of 1:3.5, heated to 130 °C and 6 h time framed was needed for the mixture to be stirred. High Performance Liquid Chromatography (HPLC) was used to analyzed the production of formic acid.

3. Results and Discussions

3.1. FTIR Analysis

The formation of oxalates by the reaction of bi-metal Fe-zeolite with oxalic acid as shown in Figure 2 (a). Before calcination, it shows a broad peak at ~3401-3430 cm⁻¹ was referred to O-H stretching due to the moisture of water as the temperature increases the peak gradually decreases. The strong stretching peak at ~1698-1704 cm⁻¹ was referred to C=O group and ~1416-1418 cm⁻¹ dint to the presence of C-O bonds. The vibration of C-H bonds of all oxalates occur at ~900-675 cm⁻¹. The final peaks of aluminosilicate from zeolites occur at ~987-1039 cm⁻¹. After calcination all organic compound were decomposed. This is proving that the transformation from oxalates to oxide as shown in Figure 2 (b). Finally, four set of two absorption peak at ~3384-3429 cm⁻¹ and ~973-977 cm⁻¹ due to stretching vibration of bi-metal Fe-O and aluminosilicate bond, respectively.

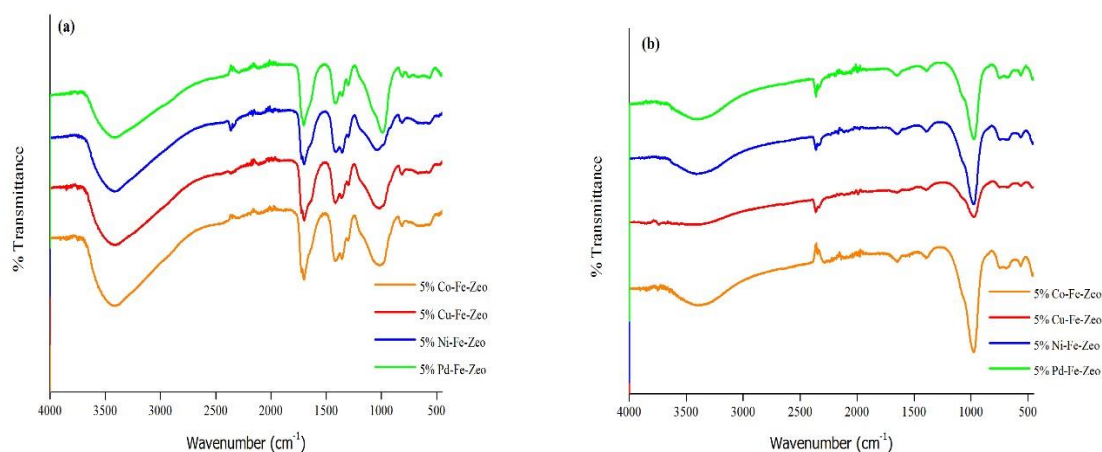


Figure 2. FTIR Spectra of (a) oxalates of 5% Co-Fe-Zeo, 5% Cu-Fe-Zeo, 5% Ni-Fe-Zeo and 5% Pd-Fe-Zeo at 105 °C, and (b) 5% Co-Fe-Zeo, 5% Cu-Fe-Zeo, 5% Ni-Fe-Zeo and 5% Pd-Fe-Zeo at 500 °C

3.2. XRD Analysis

The XRD pattern of Fe-zeolite and bi-metal X/Fe-Zeolite (X=Co, Cu, Pd and Ni) are shown in Figure 3 without any detectable impurities. The characteristic 2θ peaks at 6.1°, 15.4°, 23.2°, 26.6° and 30.9° corresponded to (111), (331), (533), (642) and (751) planes, respectively. Table 1 shows their intensity and crystallite size on each planes. Figure 3 shows the increasing intensity by adding bi-metal due to the oxidized zeolite supported catalyst that had various composition on iron phase [13]. The modification with bi-metal resulted in a huge increment in the substance Fe₂O₃ phase in zeolite supported iron catalyst and in a much lower concentration of iron aluminosilicate [13]. 5% Pd-Fe-

Zeolite indicates a significant increase compared to others bimetal. The modification Fe-zeolite with palladium significantly enhance intensity peaks compared to others bi-metal, thereby increase the catalytic activity and improve their performance in the conversion of CO₂ hydrogenation [14].

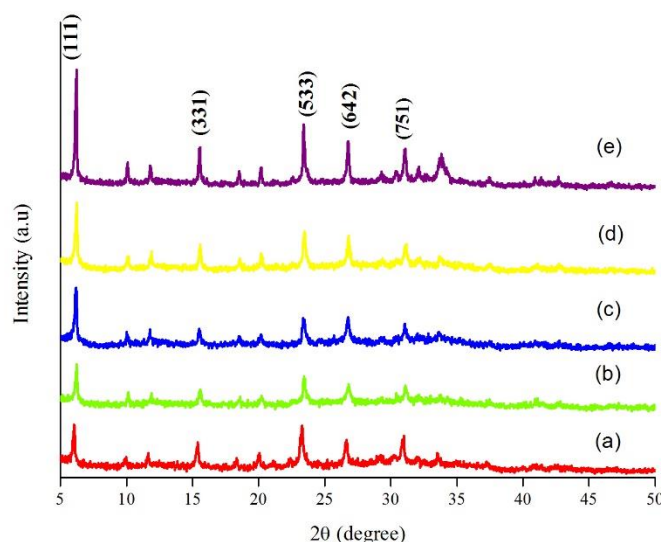


Figure 3. X-ray pattern (a) Fe-Zeo (b) 5% Ni-Fe-Zeo (c) 5% Cu-Fe-Zeo (d) 5% Co-Fe-Zeo (e) 5% Pd-Fe-Zeo

Table 1. Intensity and crystallite size of catalyst

h	k	l	2θ	Fe-Zeo		5% Ni-Fe-Zeo		5% Cu-Fe-Zeo		5% Co-Fe-Zeo		5% Pd-Fe-Zeo	
				Inten.	C. size (nm)	Inten.	C. size (nm)	Inten.	C. size (nm)	Inten.	C. size (nm)	Inten.	C. size (nm)
1	1	1	6.19	291.0	63.98	277.0	42.56	367.0	46.58	414.0	41.79	674	54.77
3	3	1	15.61	191.0	43.33	135.0	46.10	140.0	44.27	184.0	47.52	241	52.52
5	3	3	23.58	282.0	37.75	212.0	44.68	200.0	35.49	257.0	32.74	374	39.77
6	4	2	26.97	207.0	37.35	171.0	44.90	212.0	34.98	234.0	38.46	275	41.32
7	5	1	31.31	229.0	40.03	154.0	48.43	175.0	43.14	180.0	33.55	233	47.09

3.3. Surface Morphology

The particle size was evaluated using TEM under 28 000x magnification are shown in Figure 4 (a). Figure 4 (a) shows that Fe particles have covered the zeolite surface. Thus, the agglomeration was occurred due to the smaller particles that combine together. The range of particle size from ~22-48 nm. While Figure 4 (b1, c1) illustrate the FESEM images under 5 000x magnification for the zeolite and Fe-Zeolite, respectively. The zeolite showed octahedral structure and it nearly orbicular appearance as shown in Figure 4(b1) [14]. Figure 4(b2) illustrate the particles of iron and zeolite agglomerated within the particles. The final composition of zeolite and Fe-zeolite as shown in Figure 4 (c1, c2), respectively. The sample was analyzed using EDX. The results show that the composition of zeolite only has O, Si, Al and Na while for Fe-zeolite shows the addition element of iron it proves that they are no impurities in a sample.

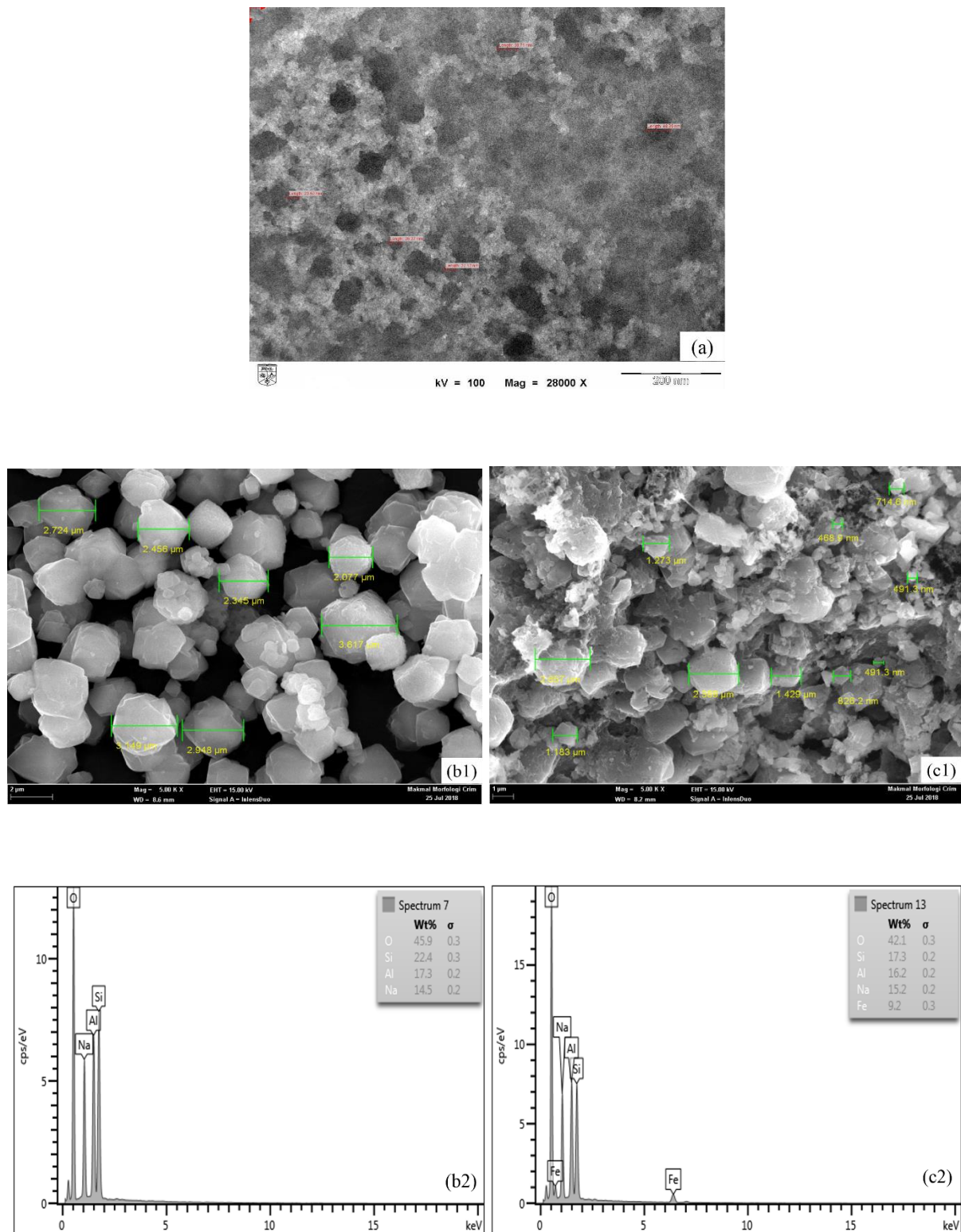


Figure 4. (a)TEM image of Fe-zeolite, FESEM images and EDX of (b1, b2) zeolite and (c1, c2) Fe-Zeolite

3.4. Effect of crystal size on Catalytic Activity

Figure 5 indicates the activity of the catalyst. It shows that the increment of production formic acid after adding bi-metal. The presence of bi-metal on the Fe-Zeo surfaces was successfully improved the CO₂ hydrogenation to produce formic acid may due to difference of band gap energy between bi-metal Fe-Zeo compared to Fe-Zeo [15]. According to Table 1, crystallite size on plane (111) of Fe-Zeolite decreased after modification with bi-metal. Therefore, the amount of metal loading of bi-metal decreases the crystallite size and increase the surface area that enhanced the catalytic activity [16]. 5% Pd-Fe-Zeolite produced the highest concentration of formic acid (ppm or mg/L) which is 275.91 ppm. The utmost concentration of formic acid produced in the crystal size of 54.77 nm [plane (111)], with the subsequent independent variable: weight ratio of Pd: Fe: zeolite (0.1:1.25:2), PEG volume of 2 mL and calcine temperature of 500 °C.

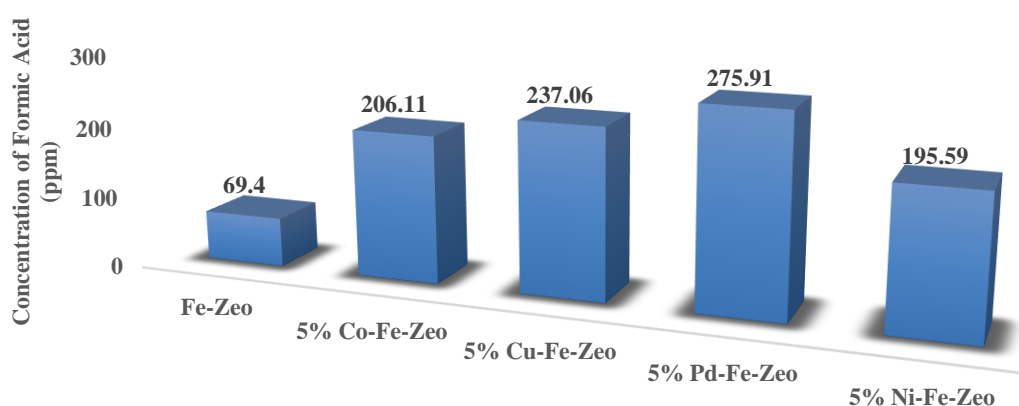


Figure 5. Activity of the catalyst on the production of formic acid

4. Conclusions

In summary, bi-metal on Fe-zeolite through sol-gel method was successfully synthesized. A series of bi-metal on Fe-zeolite was evaluated for CO₂ hydrogenation at 130 °C in 35 mL of 1,4-dioxane solvent with total pressure of 35 bar and reaction time of 6 h. The highest concentration of formic acid at 275.91 ppm under the subsequent condition: weight ratio of Pd: Fe: zeolite (0.1:1.25:2), PEG volume of 2 mL and calcine temperature of 500 °C.

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