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Hydrocracking of palm oil to gasoline on bimetallic Ni-Cu/zirconia pillared bentonite

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Abstract. Preparation and characterization of a catalyst based on bimetallic Ni-Cu over a zirconia pillared bentonite support were studied. Its catalytic activity had been tested for hydrocracking of palm oil as a model reaction. The cracking process of palm oil was carried out in the continuous micro reactor system with catalyst feed ratio 1:100 (w/w) for the reaction at 350°C for 30 min. The product of catalytic hydrocracking was evaluated by GC-MS. We found that a small loading addition of Cu to Ni catalyst increased the catalytic activity compared to the monometallic one. The characterization results using EDX map revealed that addition of copper metal with Ni:Cu mole ratio of 3:1, causes the amount of nickel metal seen is increasingly more evenly dispersed.

1. Introduction

Bentonite is a class of mineral aluminosilicates which contain montmorillonite and has the ability to expand. Related to its application the use of bentonite has limitations due to its low surface area and thermal stability. In general, bentonite will experience dehydration and structural damage at high-temperature reactions. Therefore, it is necessary to modify the clay structure to improve thermal stability and acidity by the pillarization method. Based on the ability to expand the structure between layers of silica, pillarization techniques can be modified according to the expected material character [1, 2].The main interest of the bentonite pillarization is to produce thermally stable structures by controlling the size and distribution of the pillars in the layers. Clay pillarization has become a new class in selective heterogeneous catalysts [3, 4] for cracking reactions [5], acid catalysts and hydro isomerization reactions.

The intercalation of the pillarization of clay using Al [6], Zr, Ga, Si, Fe, and Cr oxides has been widely published . Zirconia, a micropore solid with large surface area, is preferred to be a catalyst in various reactions [7, 8]. The characteristic property of ZrO_2-bentonite makes it possible as metal and metal oxide support materials [9]. Based on the structure of ZrO_2-bentonite, the metal dispersion in ZrO_2-bentonite becomes similar to the metal dispersion in the zeolite matrix. Metal distribution is carried out by utilizing solid pores on ZrO_2-bentonite. Several types of metals such as Co, Cu, Ni, Mo or Mn dispersed in the ZrO_2-Montmorillonite matrix have been reported by several researchers [10-13]. Nonetheless, nickel-based catalysts have been proven to be sensitive to doping, so structure modification is needed by adding other metals, such as Cu which affect the structure and morphology of the carbon produced [14]. Increased stability of deactivation can be achieved by adding a second metal component or known as a promoter [15-18]. This research will test the performance the activity of ZrO_2 pillared Ni-Cu/pillared bentonite on palm oil's hydrocracking reaction to the gasoline fraction and the catalyst's ability to deactivate coke formation.

2. Experiment

Natural bentonite was collected from an open clay deposit in Boyolali, Central Java, Indonesia. The clay sample was dissolved in deionized water for 24 hours. Furthermore, colloidal solution filtrate was centrifuged to obtain its precipitate that was separated from its filtrate by evaporation to get the bentonite. The solid bentonite was dried at 110°C and sieved to 150 mesh size, the resulting product was named as the resulting product was named as the activated natural bentonite. The activated natural bentonite was added $ZrOCl_2{\cdot}8H_2O$ with concentration of 0.1 M were refluxed at 70°C for 2 hours to convert $ZrOCl_2{\cdot}8H_2O$ · to poly-oxidation zirconia ($[Zr_4(OH)_8(H_2O)_{16}]^{8+}$). The mixture was stirred again for 24 hours at room temperature. Then washed repeatedly until the washing solution was no longer contained chloride ions [19]. The solid obtained was dried at 70°C for 12 hours and sieved with a 200 mesh sieve. Furthermore, the solid was calcined at a temperature variation of 400°C for 4 hours with a heating rate of 2°C/minute. The resulting product was then called ZrO_2-bentonite (BZR). A solid of of ZrO_2-bentonite was mixed with Ni $(NO_3)_2{\cdot}6H_2O$ and Cu $(NO_3)_2{\cdot}6H_2O$ containing nickel and copper metals with a total weight of 2% (b/b). The amount of nickel and copper metals used in the impregnation process was made with Ni:Cu mole ratio of (3:1); (1:1); (1:3) [14, 20]. The mixture was stirred for 24 hours at room temperature. Then the mixture was heated at 70°C for 12 hours. The solids obtained were calcined at 400°C for 4 hours with a nitrogen gas flow of 20 cc/min. Then the solids were reduced at 350°C for 3 hours with a hydrogen gas flow of 20 cc/min. The resulting product was called NiCu/ZrO_2-bentonite (NiCu/BZR) catalyst. The synthesized catalyst of 0.1 g was put into the catalyst reactor and the activity was tested using a feed of 10 g palm oil in a separate reactor. The reactor which has contained the catalyst was first heated at temperature of 350°C. Another reactor containing palm oil was heated at temperature of 300°C. The distribution of each type of atom on the surface of the catalysts was determined using EDX map analysis and the hydrocracking products of liquid fractions were analysed using GC-MS.

3. Results and Discussion

The catalyst activity test was carried out to determine the ability of the catalyst to convert palm oil to gasoline fraction in the hydrocracking reaction. Hydrocracking of palm oil thermally generated more gas fractions than the amount of gas fraction produced in hydrocracking using NiCu31/BZR, NiCu11/BZR, and NiCu13/BZR catalysts. Hydrocracking palm oil uses Ni/BZR catalyst, NiCu31/BZR and NiCu11/ BZR produced more liquid fractions (18.43; 20.18 and 14.99%) than the amount of liquid fraction produced in the palm oil hydrocracking process using bentonite and zirconia pillared bentonite (BZR) were 4.77 and 12.92%, respectively. The use of NiCu31/BZR and Ni/BZR catalysts was shown to produce the most liquid fractions in the palm oil hydrocracking process. This result is in accordance with the prediction explained based on the results of the EDX map catalyst where nickel metal is dispersed more evenly on the surface of the NiCu31/BZR catalyst compared to the surface of the Ni/BZR catalyst.

The liquid fraction obtained from the palm oil hydrocracking process both thermally and using a catalyst was distilled at 120°C to separate the gasoline fraction component (C5-C12) from the liquid product. The product selectivity of hydrocracking of palm oil at 350°C using different catalysts is shown in Fig. 1. The percentage fraction of the gasoline fraction obtained from the palm oil hydrocracking process using a catalyst synthesized in this study was only about 0.49 to 3.33%. However, this low percentage is still proportional considering the ratio of feed/catalyst used is still very large at 100/1 (b/b) with a reaction temperature of 350°C in 30 min. The results of other studies by Kadarwati *et al.* [21] using Ni/Zeolite catalyst produced gasoline fraction of 6.83% from palm oil with 10/1 (b/ b) feed/catalyst ratio and 60 min reaction time at 450°C. Meanwhile, although the hydrocracking process of palm oil thermally produces liquid fraction but it was no gasoline fractions. The percentage of gasoline fraction also increased when there was nickel metal in the catalyst used in the palm oil hydrocracking process (1.90%). The percentage of gasoline fraction increased, even more, when the hydrocracking of palm oil was carried out using NiCu31/BZR catalyst which was 3.33%. However, an increase in copper metal content in the catalyst causes a decrease in the percentage of gasoline fraction produced in the palm oil hydrocracking process. The composition of the gasoline fraction with the number of C5-C7 hydrocarbons was seen to increase when the bentonite used as catalyst pillared with zirconia (BZR). This phenomenon is caused by the acidity value of BZR which is higher (1.28 mmol/g) than the acidity value of bentonite (1.15 mmol/g). High acidity value indicates the possibility of BZR to break C8-C12 hydrocarbon molecules into C5-C7 hydrocarbon molecules compared to bentonite [22].

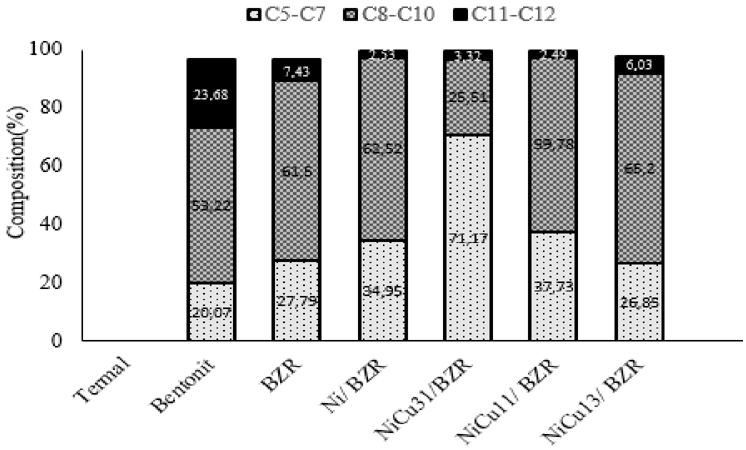

Figure 1. The product selectivity of hydrocracking of palm oil at 350°C using different catalysts.

Chew and Bhatia [23] also revealed that acidity affects the distribution of products and their selectivity. The selectivity of the fraction of gasoline fraction using NiCu31/BZR is greater than that of NiCu13/BZR catalyst. The number of C5-C7 hydrocarbon molecules has doubled amount when using NiCu31/BZR in the palm oil hydrocracking process. This result was obtained because the distribution of nickel metal which became more evenly distributed in the NiCu31/BZR catalyst according to the EDX map results. In contrast, the amount of C5-C7 hydrocarbons in the gasoline fraction decreased as the amount of copper metal in the catalyst was increased. However with no copper cokes formation occurs [24].

The EDX map results show the distribution of each type of atom on the surface of the fourth catalysts. Ni/BZR catalyst in Fig. 2a shows the distribution of dispersed zirconium and nickel atoms. Addition of copper metal with Ni:Cu mole ratio of 3:1 (Fig. 2b), the amount of nickel metal seen is increasingly more evenly dispersed and there is no agglomeration of nickel and copper metals on its surface. However, the addition of the Ni:Cu mole ratio to 1:1, metal agglomerations occur on the surface of the NiCu11/BZR catalyst (Fig. 2c). It clearly refers to the metal catalyst of copper. Furthermore, the mole ratio of Ni:Cu becomes 1:3, the green colour appears larger as shown in Fig. 2d.

The increase of copper metal on the surface of pillared bentonite causes the agglomerations of copper metals. This copper metal agglomeration is very unexpected because it reduces the surface area of the expected catalyst metal to interact with the feed in the activity test [24]. The addition of Cu metal on Ni catalyst is one of the factors that causes the deactivation process the catalyst by inhibition of coke formation, that makes the catalyst age becomes longer [14, 24].

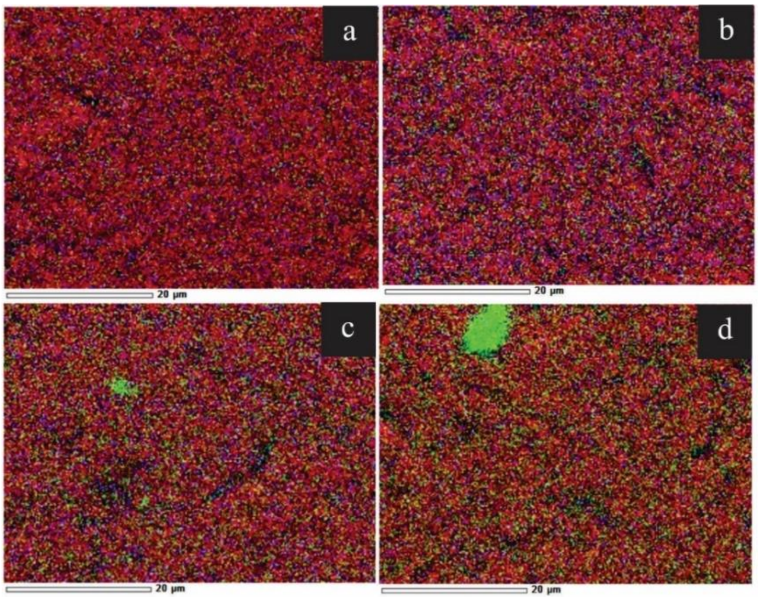

Figure 2. EDX map of (a) Ni /BZR, (b) NiCu31/BZR, (c) NiCu11/BZR and (d) NiCu13/BZR (Note: red = Zr, blue = Ni, Green = Cu).

4. Conclusion

The catalyst performance shows that the selectivity of the gasoline fraction for C5-C7 hydrocarbon molecules increases in the amount of palm oil hydrocracking process by decreasing the amount of Cu metal on the catalyst. The increase of copper metal on the surface of pillared bentonite causes the agglomerations occur on the surface of the catalyst.

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