



Synthesis and Characterization of Ni-Cu doped Zirconia-pillared Bentonite

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ABSTRACT

Copper doped Ni/zirconia-pillared bentonite prepared using pillarization-impregnation method and its application as heterogeneous catalyst for hydrocracking of cooking oil to biogasoline has been investigated. Several zirconia-pillared bentonite supported Ni-Cu catalyst (Ni-Cu [x:y])/zirconia-pillared bentonites; where x and y represent the mass ratio of Ni and Cu, respectively) were prepared by the impregnation method and used for hydrocracking of cooking oil to biogasoline. The Ni-Cu/zirconia-pillared bentonite samples were characterized by TEM, SEM, TGA, while the surface area by N₂ adsorption, GC-MS was used to evaluate the product. The catalytic activity was assessed in view of the effects of different mass ratios of Ni and Cu, temperature. Among all the samples, the Ni-Cu(3:1)/zirconia-pillared bentonite catalyst showed the highest catalytic ability.

Keywords: Zirconia-pillared bentonite, Ni-Cu catalysts, Mass ratios, Biogasoline.

INTRODUCTION

The supports are used for deposition of the nickel phase range from conventional carriers, i.e., TiO₂, SiO₂, Al₂O₃ and ZrO₂, to become mixed oxide systems and molecular sieves^{1,2}. We have shown³ that nickel can also be deposited within the highly porous structures of pillared interlayered clays (PILCs). PILCs are synthesized from natural layered minerals, such as bentonite, by replacement of the interlayer cations with positively charged oxohydroxy

oligomeric species of the desired pillar-forming cation⁴. After calcination, the cationic oligomers turn into oxidic pillars firmly bound to the silicate sheets leading to rigid porous structures opened to gases and vapours. Alumina, Titania and Zirconia pillared clays are among the most widely studied⁴. In this study, we report the use of bimetallic Ni-Cu catalysts for the catalytic hydrocracking of cooking oil of palm. Nickel is a cheap metal compared to noble metals and is known for its high hydrogenation activity for a broad range of organic groups. Copper is applied



as a promoter, primarily to improve the distribution of Ni on the support, and to prevent excessive carbon deposition on Ni⁵. Nickel and copper can be incorporated into the PILC structure during the pillaring procedure. This work aimed to design and synthesized supported Nickel and Copper catalysts using zirconia-pillared bentonite as a carrier. The obtained materials were tested hydrocracking of palm cooking oil. The catalytic results were are discussed regarding to the physicochemical properties of the samples.

EXPERIMENTAL

A sample of natural clay was collected from an open clay deposit in Boyolali, Central Java, Indonesia. The commercial zirconia chloride $ZrOCl_2 \cdot 8H_2O$ of industrial grade was supplied by Jiaozou Huasu Chemical Co. Ltd (purity 99%). The analytical grade of $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were obtained from Merck & Co. All chemicals were used without further treatment. Starting from ZrO_2 -pillared bentonite was prepared by following the procedure described^{4,6}. The transformation of natural bentonite into pillared clay required the use of pillaring solution prepared by 0.10M $ZrOCl_2 \cdot 8H_2O$. The pillared clay was air-dried at ambient temperature and 80 °C for 8 h, then calcinated at 400°C for 4 hours. The product is referred to as BZR. Ni-Cu samples were prepared by the wet impregnation method, where $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were mixed to obtain the following Ni:Cu molar ratios: 1:0, 3:1, 1:1, and 1:3. Every solution should contain as much as metal nitrate to get 2 wt% metal in the final catalyst powder. The synthesis catalyst had the same composition as sample of NiCu11/ ZrO_2 -pillared bentonite and was designated as Ni-Cu11/BZR in

the following discussion. Finally, the pellet catalyst was obtained by a pellet printing device. Catalytic activity tests were performed in a continuous tubular fixed-bed micro-reactor with a catalyst weight, temperature, and H_2 gas rate of 0.1 g, 350 °C, and 20 cc/s, respectively. The characterization of the specific surface area and porosity of the bentonite used N_2 adsorpsi-desorpsi method (Bet Nova 1994-2010 Instrument version 11:0). The morphology and elemental analysis of the test samples were estimated by SEM-EDX (JEOL JED-2300 Analysis Station, 20 kV) and TEM (JEOL JSM -6510 at 100 kV). The product was analysed by GC-MS (GCMS-QP2010 plus) to confirm the biogasoline formation in this reaction. The thermal analysis method (DTA) was used to distinguish the type of coke deposit formed on the surface of the used spent catalyst.

RESULTS AND DISCUSSION

Texture Properties

The adsorption isotherms give a good fit on the BET equations for the Zr-pillared bentonite materials. Furthermore, Table 1 shows an increase in surface area along with an increase in the ratio of Cu content obtained from a plot of BET equation with different pore size distribution. The increasing ratio of Cu content (NiCu13) has led to different interactions so that the pore size distribution and the surface area become larger. In contrast, the increased Ni content ratio (NiCu31/BZR) results in a lower surface area than before the addition of Cu (Ni/BZR)^{7,8,9}. This situation was due to pore blocking by metal species dispersed in the interlayer of supports material^{10,11}. The composition of Ni-Cu ratio becomes strategic because it affects the catalyst activity as shown in the Fig. 4, Table 1.

Table 1: Textural properties of ZrO_2 -pillared Bentonite and Ni-Cu/BZR

Sample	Zr (M)	Ni%	Ni-Cu%	SBET(m ² /g)	Vp(cc/g)	V _{μp} (cc/g)	Pore Radius
(Å)							
BZR	1.0	-	-	194.800	0.151	0.045	17.280
Ni/BZR	1.0	2.0	-	111.567	0.340	0.027	16.889
NiCu31/BZR	1.0	-	2.0(3:1)	107.488	0.317	0.056	18.978
NiCu11/BZR	1.0	-	2.0(1:1)	132.970	0.122	0.082	15.306
NiCu13/BZR	1.0	-	2.0(1:3)	322.754	0.930	0.085	19.089

Microscopic Analysis

The results of the analysis using TEM show apparently that there is no damage to the pillared bentonite structure of ZrO_{26} . The texture conditions between the layers of the bentonite still look right that the impregnation process of Ni and Cu metal does not cause bentonite destruction as support. Also, the used catalyst texture used has shows black blocking which is indicated as carbon compounds as in Figure 1.

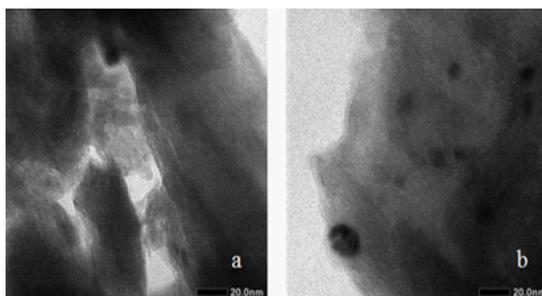


Fig. 1. TEM image of (a) fresh and (b) used catalyst NiCu31/ BZR

Strong indications of carbon deposits on used catalysts are strengthened in thermal analysis. DTA analysis suggests the energy release process ($\Delta H = \text{negative}$) as well as weight reduction at temperatures around 400-600 °C. The morphological analysis of the NiCu/ZrO₂-Bentonite catalyst use SEM method as shown in Fig. 2. The Figure shows the presence of layers on the surface of the used catalyst which reinforces the prediction that the carbon deposit is indeed present. The SEM image very clearly indicates a parallel correlation TEM and DTA analysis which states that carbon deposits occur during the catalyst test process.

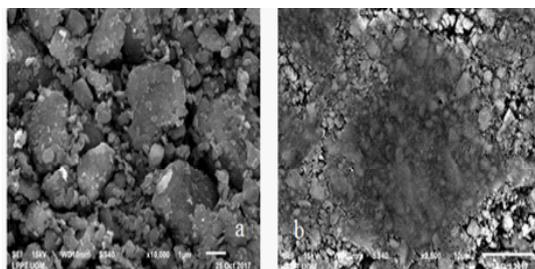


Fig.2. SEM image of (a) fresh and (b) used catalyst NiCu31/ BZR

Analysis of precursor of coke

The result of elemental analysis using EDX shows the previous assumption that there is an increase of carbon content (5.93% to 32.25%) in the catalyst after being used for hydrocracking reaction

of palm cooking oil into biogasoline as shown in Table 2. A more in-depth analysis of carbon deposits has been analyzed using DTA data showing in Fig. 3 that coke releases from the catalysts that occur at different temperatures for each sample.

Table 2: Elemental analysis of Catalyst of NiCu31/ BZR

Elements	NiCu31/BZR (fresh)% massa	NiCu31X/BZR (used)% massa
C	5.93	32.25
Mg	1.41	0.99
Al	6.79	4.83
Si	18.2	12.92
K	0.39	0.38
Fe	1.95	1.45
Ni	2.86	2.03
Cu	1.49	0.74
Zr	16.67	11.14

The heat of coke combustion illustrates how high the interaction occurs on the cauldron surface with coke. The massive release of combustion energy symbolized by the combustion enthalpy is ΔH with joules/g^{12,13}. Based on Fig. 3 the temperature of the combustion process is divided into two parts. The first part occurs at a temperature interval of 350-400 °C where ΔH for NiCu31/BZR and NiCu13 /BZR catalysts are -215.3553 and -76.2515 J/g, the coke at that temperature often referred to as softcoke. While the second part of the combustion process occurs at a temperature interval of 550-600 °C, where ΔH for Ni/BZR and NiCu13/BZR catalysts are -1261.2932 J/g for the former and -1457.7797 J/g and the coke that burns at that temperature referred to as hardcoke.

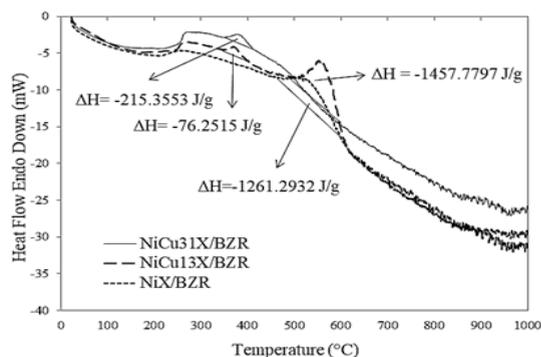


Fig. 3. DTA Analysis of used catalysts of NiCu31/BZR; NiCu13/BZR and Ni/BZR

The phenomenon of the coke combustion process on the catalyst surface may provide information on the catalytically activated model which for the NiCu31/BZR catalyst undergoes a slower deactivation process compared to NiCu13/BZR and Ni/BZR catalysts¹⁴. Thus the mass ratio of Ni:Cu metal catalyst of 3:1 are more resistant to deactivation caused by hydrocracking of palm cooking oil conversion reactions.

Catalytic cracking of palm cooking oil

The hydrocracking process using a catalyst aims to cut long, cyclic and branched saturated carbon chains to form carbon chains with a lighter molecular weight. Fig. 4 shows the conversion of hydrocracking of cooking oil product at 350 °C that includes gases, liquid hydrocarbon fuel and coke.

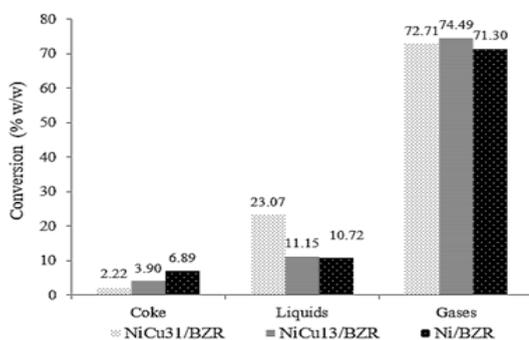


Fig. 4. The conversion of hydrocracking of palm cooking oil at 350 °C using different catalysts

The liquid hydrocarbon fuel yield increases with increased mass ratio of nickel. The increase mass ratio of Ni to the NiCu/BZR catalyst could enhance the yield of hydrocarbon biofuel due to the increase of acid site, which will do transformation of fatty acid to hydrocarbon-based biofuels. The product of liquid hydrocarbons on NiCu/BZR catalysts has increased along with higher mass ratio Ni:Cu. However, Ni catalysts without the addition of Cu result in lower yields of the hydrocarbon product. These facts show that the synergic interactions between Ni and Cu to produce acid sites on the catalysts that promote cracking reactions of palm cooking oil during the conversion of triglyceride molecules into hydrocarbon-based biofuels¹⁵. The bimetallic catalysts are more active than the monometallic ones, an indication for a synergic effect between nickel and Copper. The coke increase that produced

by the catalyst with a higher Cu content compared to a catalyst with a higher Ni content. This phenomenon may be due to the high Cu mass ratio of catalyst that causes high activity of producing aromatics.

Table 3: The product yield of biogasoline fraction

Catalyst	Product Yield biogasoline % (w/w)
BZR	8.64
NiCu31/ BZR	25.07
NiCu13/BZR	11.05
Ni/ BZR	8.72

The amount of the gasoline fraction yield of each liquid hydrocarbon fuel product is shown in Table 3. The amount of total biogasoline fraction is calculated based on the ratio of % (w/w) of the resulting liquid fraction, then done by fractionation distillation process at 130 °C. Based on the GC-MS analysis, the distillation product is biogasoline fraction (C₅-C₁₂). Table 3 shows the catalyst selectivity to the highest gasoline fraction is indicated by the NiCu31/BZR catalyst. The metal ratio of 3:1 for Ni and Cu shows that the primary metal of the catalyst is Ni, where as Cu metal with a smaller amount of percentage is a promoter which can improve the catalytic function of Nickel metal. As a comparison for catalyst activity in producing biogasoline fraction on Ni/BZR catalyst produced only 1.69% which is of course much smaller than on NiCu31/BZR catalyst that of 3.08%.

CONCLUSION

The catalytic effect of Ni/BZR and Ni-Cu/BZR catalysts on textural properties and catalyst activity has shown an increase in surface area along with an increase in the Cu content ratio, however the ratio with high Ni content can increase the liquid hydrocarbon fuel product. Through TEM and SEM on the analysis on used catalysts indicates the presence of coke deposits that cover a portion of the zirconia pillared bentonite surface that causes deactivation process. The best outcome confirmed the conversion of hydrocracking palm cooking oil and selectivity for biogasoline could be simultaneously more than 20% by employing the NiCu31/BZR catalyst at 350°C. Besides having excellent activity, the NiCu31/BZR catalyst also has a higher deactivation capability than other catalyst types.

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