Synthesis and characterization of Ni-promoted zirconia pillared bentonite

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Abstract. The aim of this study was to synthesize a catalyst applied to the cracking reaction and to characterize its physical-chemical properties. The catalyst is a zirconia-pillared bentonite with Nickel as a support metal (promoter). The catalyst is synthesized by pillaring bentonite with ZrOCl2·8H2O as a pillaring agent and then a calcination process for obtaining a zirconia pillared bentonite (ZrO2-bentonite). To obtain a catalyst with good cracking and hydrogenation activity, nickel metal (2% w/w) impregnation was performed using Ni(NO3)2·6H2O precursors. The next step is calcination and reduction to obtain a zirconia-pillared bentonite catalyst with Ni as a support metal (Ni/ZrO2-bentonite). To know the physical-chemical properties was characterized by XRF, XRD, acid properties test using ammonia absorption technique, FTIR and BET. The characterization results with XRF showed an increase of nickel metal content after impregnation process of 6.45%. The acidity assay with ammonia absorption technique showed an increase in the acid properties of the catalyst sample after pillaring and impregnation of 7.580 mmol/g. Analysis of sample diffraction patterns with XRD shows typical montmorillonite peaks still visible but shifts toward an angle of 2θ < 5°. Analysis of functional groups of catalyst with FTIR showed characteristic for Brønsted acid at wave number 1635.64 cm−1 after impregnation with nickel metal. Surface area analysis results show an increase in specific surface area after pillaring and impregnation of 96.307 m²/g.

1. Introduction

The production of pillared bentonite is based on an expanding phenomenon which is a special characteristic of smectite. Development occurs because parallel layers of this structure are bound to each other by electrostatic forces, so that they can be magnified by the inclusion of polar species between layers. Development is a process similar to what happens to the hydration of interlamellar cations. The hydrated cation becomes larger in volume. When dehydration at a temperature of 300-400 °C the lattice contracts to its original shape and the surface between layers cannot be used for chemical processes. To prevent this, found a way to still support the clay layer by placing a stable pillar in the area between layers and with this also obtained a high pore volume [1]. Pillar clay synthesis procedure consists of three stages, namely multivalent cation polymerization (Al3+, Zr4+, Ti4+, Fe3+) forming polycation; intercalation of polycation into clay interlayer space that is substitution with interchangeable cations; and calcination at certain temperatures [2]. The calcination process is carried
out because the intercalated clay is metastable as the cation itself, with calcination the polycation will turn into a stable oxy-hydroxide phase and is called a pillar [3].

ZrO$_2$ is chosen as a pillar agent because it is a pillar species that has good thermal stability (700-800 °C), besides the pillarization using ZrO$_2$ can increase basal spacing up to 19-20 Å and a large surface area (200 - 300 m$^2$/g) depends of some preparation variables [4]. Cracking reactions require bifunctional catalysts for cracking and high hydrogen activation, so to obtain such bifunctional properties, the catalyst used is a catalyst in the form of a metal-bearers [5]. Ni transition metal impregnation into the pillared bentonite is intended to increase the adsorption power and activation of the catalyst hydrogenation. Its strong adsorption capability is due to d orbitals with unfilled electrons. As a condition for the reaction, the reactants must be adsorbed on the catalyst. The role of the Ni metal active component on the surface of the catalyst is to adsorb the diffused reactants on the catalyst surface so as to speed up the reaction.

2. Experimental

2.1 Materials and Instrumentation
Bentonite Ni(NO$_3$)$_2$•6H$_2$O (Merck), ZrOCl$_2$•8H$_2$O (Merck), ammonia [25% (v/v)], AgNO$_3$, and distilled water. glassware, 200 mesh sieve, magnetic stirrer/hot plate, oven, desiccator, porcelain crucible, calcination furnace, centrifuge, XRF, XRD-Shimadzu X6000 X-ray Diffractometer, FT-IR Shimadzu 8201 PC, and BET NOVA package version 2.00.

2.2 Preparation of bentonite and ZrO$_2$-bentonite
Preparation of bentonite and zirconia pillared bentonite samples follow the stages of the procedure as in previous studies that have been done [6].

2.3 Synthesis of Ni/ZrO$_2$-bentonite catalyst
The metal impregnation of Ni [Ni 2% (w/w)] in the ZrO$_2$-bentonite was carried out by dissolving 2.9734 g Ni(NO$_3$)$_2$•6H$_2$O in 100 mL of distilled water on a round bottom flask. ZrO$_2$-bentonite was added, refluxed while stirring with a magnetic stirrer for 4 hours at a temperature of 80 °C. The impregnation result is then dried by oven for 3 hours at 110 °C. After that the sample was calcined at a temperature of 500 °C and flowed N$_2$ gas with a flow rate of 20 mL/min for 5 hours. After calcination, the sample was reduced by passing H$_2$ gas at 400 °C at a flow rate of 20 mL/minute for 4 hours. After that the sample is stored in desiccator. The obtained catalyst is called a zirconia pillared bentonite catalyst with nickel as a support metal (Ni/ZrO$_2$-bentonite).

3. Results and Discussion

3.1 Determination of Zr and Ni Metals with X-Ray Fluorescence
Table 1 shows the Zr and Ni metal content of the Ni/ZrO$_2$-bentonite sample. As in previous studies, the bentonite sample used in this study was detected to contain Ni metals of 0.20% and did not contain Zr metal. After pillarization with ZrOCl$_2$•8H$_2$O precursor obtained Zr metal concentration of 52.9% and Ni metal decreased to 0.04% in ZrO$_2$-bentonite sample [6]. In the Ni/ZrO$_2$-bentonite sample (2% Ni) there was an increase of Ni metal concentration after impregnation with Ni(NO$_3$)$_2$•6H$_2$O to 6.45% and Zr metal concentration to 54.5%.

| Sample                  | Zr (%) | Ni (%) |
|-------------------------|--------|--------|
| Ni/ZrO$_2$-bentonite (2% Ni)  | 54.5   | 6.45   |
Reduced concentrations of Ni metals in ZrO$_2$-bentonite samples may be caused by washing and heating processes at high temperatures (calcination) at the pillarization stage and impregnation of the catalyst [6].

3.2 Determination of Diffraction Patterns with XRD.

Figure 1 shows specific peaks for montmorillonite minerals that still appear after pillarization and impregnation at $2\theta = 5.32^\circ$ ($d = 16.58$ Å); $2\theta = 19.64^\circ$ ($d = 4.52$ Å); and $2\theta = 34.93^\circ$ ($d = 2.522$ Å) [7-9].

![Figure 1. Ni/ZrO$_2$-bentonite (2% Ni) Diffractogram](image)

Referring to previous studies, clay samples used in the study were clays of montmorillonite minerals. After the intercalation and pillarization process, the typical peak montmorillonite ZrO$_2$-bentonite sample ($d_{001}$) is still visible but shifts to the left ($\angle 2\theta < 5^\circ$) [6]. Theoretically, if the pillarization is able to increase the spacing between the silica montmorillonite layers, there will be a typical peak shift showing basal spacing $d_{001}$ ($2\theta = 5.29^\circ$) to the left [9].

3.3 Determination of Functional Groups with Fourier Transform Infrared.

The infrared spectra of Ni/ZrO$_2$-bentonite minerals are observed at 500-4000 cm$^{-1}$ wavelengths. Figure 2 shows the bentonite mineral absorption bands as in the 3425.58 cm$^{-1}$ wave number, which is the characteristic of OH from Si-OH stretching vibration and 3626.17 cm$^{-1}$ characteristic of OH from Al-OH stretching vibration. The absorption band at wave number 1635.64 cm$^{-1}$ is an OH bending vibration of water molecule, wave number 1442.75 cm$^{-1}$ which is a Si-O-Al stretching vibration is not visible on infrared spectra of Ni/ZrO$_2$-bentonite sample. The wave number 1041.56 cm$^{-1}$ is the stretching vibration of the Si-O-Si. The wave number 918.12 cm$^{-1}$ is characteristic for O-Al-O bending vibrations. and 794.67 cm$^{-1}$ characteristics for O-Si-O bending vibrations. The wave number 524.64 cm$^{-1}$ is characteristic for the bending vibration of Si-O-Al and 470.63 cm$^{-1}$ is the bending vibration of Si-O-Si [1, 10-13].

In a previous study conducted on bentonite samples showed that the characteristic wave number for stretching vibration OH of Si-OH were 3448.72 cm$^{-1}$ and 3695.61 cm$^{-1}$ characteristics for stretching vibration OH of Al-OH [6]. After bentonite has been modified by pillarization and impregnation, the characteristic absorption bands for bentonite undergo a shift. The characteristic absorption bands for stretching vibrations OH of Al-OH have shifted from wave numbers 3695.51 cm$^{-1}$ to 3749.62 cm$^{-1}$ on ZrO$_2$-bentonite and 3626.17 cm$^{-1}$ on Ni/ZrO$_2$-bentonite, whereas the characteristic band for stretching vibration OH of Si-OH has shifted from wave number 3448.72 cm$^{-1}$ to 3425.58 cm$^{-1}$ on ZrO$_2$-bentonite and Ni/ZrO$_2$-bentonite. This is probably due to the environmental change of the bond due to the formation of a bond between the ZrO$_2$ pillars and the silica tetrahedral layer.
Figure 2. FTIR spectra Ni/ZrO$_2$-bentonite (2% Ni)

Figure 2 also shows absorption bands at 1635.64 cm$^{-1}$ wave numbers indicating Lewis acid sites whereas Brønsted acid sites are not visible in the infrared spectra of Ni/ZrO$_2$-bentonite samples. This is caused by warming at high temperatures at the pillarization and impregnation stage resulting in dehydration process. Dehydration also causes the transformation of Brønsted acid sites to Lewis acid. The apparent Lewis acid site is also caused because ZrO$_2$ as a pillar agent is a transition metal oxide in which Lewis acid properties are derived from zirconium atoms [8]. The characterization results show that the IR spectra can hardly give a clear indication of the presence of zirconium oxide as a pillar within the interlayer of bentonite [9].

3.4 Determination of Catalyst acidity with ammonia absorption method.

Quantitatively the determination of the acidity of Ni/ZrO$_2$-bentonite sample was done by ammonia absorption method.

| Sample                  | Acidity (mmol/g) |
|-------------------------|------------------|
| Ni/ZrO$_2$-bentonite (2% Ni) | 7.580            |

The acidity value of Ni/ZrO$_2$-bentonite is: 7.580 mmol/g as shown in table 2. Previous research that has been done shows the value of acidity of bentonite and ZrO$_2$-bentonite respectively are 2.883 and 4.340 mmol/g [6]. Based on the result of determination of amount of acidity mentioned above, it appears that the process of pillarization and impregnation will increase the number of acid sites.

Qualitatively, IR spectra can be used to find out the distribution of Lewis and Brønsted acid sites on the surface of the catalyst. Figure 3 shows the changes occurring in the absorption bands with characteristic wave numbers for the slightly expanded Lewis acid (1635.64 cm$^{-1}$) site and the Brønsted acid site (1404.18 cm$^{-1}$) that reappears after ammonia absorption. The presence of a silanol (Si-OH) group resulting from the breakdown of Si-O-Si bonds in the tetrahedral layer through acid treatment or
contact with water contributes to Brønsted acidity in clay [14]. In the hydroxyl group will undergo proton transfer with a strong base such as ammonia. Pillarization significantly increases the acidity of the solids. Lewis's acidity ratio against Brønsted (L/B) is increased by the pillarization which means that Lewis's acidity distribution is greater than Brønsted acidity [15].

Figure 3. FTIR spectra Ni/ZrO$_2$-bentonite (2% Ni) after ammonia absorption.

Figure 3 also shows an absorption band showing the Brønsted acid site reappearing on a Ni/ZrO$_2$-bentonite sample (1404.18 cm$^{-1}$) after absorption of ammonia. This indicates the presence of H$^+$ in bentonite as a negative charge-balancing cation in the bentonite alumina silicate layer. The NH$_3$ gas (base) adsorbed on the bentonite surface will react with H$^+$ to form NH$_4^+$ (ammonium ion) [6].

3.5 Determination of Surface Area and Porosity Area with Surface Area Analyzer.

Table 3 shows the specific surface area of Ni/ZrO$_2$-bentonite of 96.307 m$^2$/g. Previous research on bentonite and ZrO$_2$-bentonite samples showed the specific surface area were 27.385 m$^2$/g and 89.115 m$^2$/g, respectively [6]. This shows that there is an increase in the specific surface area of the catalyst sample after the pillarization stage and the impregnation of Ni metal. This increase in surface area signifies the success of the ZrO$_2$ pillaring between the layers of bentonite, this is due to the increased spacing between silica layers due to the intercalation of polarity agents into interlayer silica in bentonite and the formation of delamination structures. Pillarization also leads to the formation of card house structures, through the formation of new pores into micropores, while the card structure causes pore size to be mesoporous [11].

Table 3. Surface surface results, pore diameter and pore volume average

| Sample                  | Surface Area (m$^2$/g) | Pore Diameter (Å) | Pore Volume (cc/g) |
|-------------------------|------------------------|-------------------|--------------------|
| Ni/ZrO$_2$-bentonite (2% Ni) | 96.307                 | 31.32             | 0.151              |

The isotherm adsorption-desorption pattern of the N$_2$ gas in the Ni/ZrO$_2$-bentonite sample is shown in figure 4. Based on the adsorption isotherm according to the BDDT classification, the isotherm pattern of the sample follows type IV indicating the adsorption of solids in the material with a pore
diameter greater than the micropore mesopores) and characterized by the presence of hysteresis loop [5]. The IV type isotherm pattern has four types of loop hysteresis according to IUPAC, the hysteresis loop type in Ni/ZrO$_2$-bentonite is a hysteresis type of H3 loop which indicates pore with slit size [15].

![Figure 4. Isotherm adsorption-desorption of Ni/ZrO$_2$-bentonite (2% Ni).](image)

4. Conclusion
From the results of this study can be taken several conclusions as follows:. The infrared spectra of the catalyst sample show a shift of some characteristic bentonite wave numbers after the impregnation step with the Ni metal. The catalyst synthesis produces a catalyst with increasing acid properties through acidity assay with ammonia absorption. There is an increase in specific surface area, pore diameter average, and pore volume after bentonite pillarization and after Ni metal impregnation step.

References
[1] Madejova J 2003 Vib. Spectro. 31, 1-10
[2] Figueras F 1988 Catal. Rev. Sci. Eng. 30 (3), 457-499
[3] Gil A, Korili S A, Trujillano R and Vicente M A 2011 Appl. Clay Sci 53 97-105
[4] Kloprogge J T 1998 J. Porous Mater 5 5-41
[5] Bartholomew C H, dan Farrayto R J 2006 John Wiley and Sons Inc; New Jersey
[6] Ruslan, Hardi J, and Mirzan M 2017 Proceedings of the National Seminar on Chemistry, State University of Yogyakarta, 325-334
[7] Tomlinson A G 1998 J.Por.Mat. 5 259-274
[8] Ward D A and Ko E I 1994 J. Catal. 150 18-33
[9] Wijaya K, Sugiharto E, Mudatsir, Tahir I and Liawati I 2004 Indonesian J. Chem 4 33-42
[10] Carrado K A, Xu L, Csencsit R, dan Muntean J V 2001 Chem. Mater. 13, 3733-3766
[11] Suseno A, Wijaya K, Trisunaryanti W, and Shidiq M 2015 Asian J. Chem, 27(7) 2619-2623
[12] Wijaya K, Pratiwi A S, Sudiono S, and Nurahmi E 2002 Indonesian J. Chem, 2(1) 20-25
[13] Xue W, He H, Zhu J, dan Yuan P 2006 Spectrochim. Acta Part A. 67 1030-1036
[14] Kou S M R, Mendioroz S, and Munoz V 2000 Clays Clay Miner, 48(5), 528-536
[15] Fatimah I 2010 Dissertation Chemistry Department of FMIPA UGM Yogyakarta.