Study of the acidic properties of ZrO$_2$-pillared bentonite

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Abstract. Research on pillared clays prepared from purified bentonite of Boyolali Central Java, Indonesia, and polycation Zr at various concentration and calcination temperature had been done. Effect of acidity characteristic and structure of resulting materials were studied. The nature of acidic site of the material was identified on the basis of FTIR spectra of pyridine adsorbed on ZrO$_2$-pillared bentonite catalysts. Analysis showed that increasing calcination temperature was followed by decreasing acidity and increasing ZrO$_2$ content in the pillared bentonite accompanied by the increase of its acidity. FTIR spectra showed there was an intensity increase of the characteristic band of 1635 cm$^{-1}$ that indicates a Brønsted acid.

1. Background

Zirconium pillared clay is a microporous solid with a large surface area. The nature of zirconium itself is good as acid sites or as co-catalysts. Zirconium chloride octahydrate solution (ZrOCl$_2$.8H$_2$O) has been used to form stable oxide pillars between layers in bentonite clays. Pillarization impact is able to increase the surface area, acidity, and high selectivity. A ZrOCl$_2$.8H$_2$O solution is normally used in ion exchange. However, the hydroxy zirconium structure on intercalation process and its transformation into ZrO$_2$ are not so easy to understand until at present [1-4]. In pillared clays, it was shown that the number of acid-Lewis centers that are present in the pillars predominates over that of Brønsted type, which mainly arises from the structural hydroxyl groups of the layers [5-7]. Acidity properties of catalyst surface play an important role in bringing various organic transformations. The nature of the acidic site in clays is different from that of metal oxides and zeolites. The study of acid centers on clays is still a subject of investigation primarily due to the presence of different kinds of water molecules and their indefinite contribution to a different type of acidities on the surface. Desorption analysis of pyridine can also be used for rapid evaluation of the amount and type of acid sites in clay minerals [8]. Brønsted and Lewis acid sites can be distinguished from FTIR spectrum of pyridine adsorbed on the clay surface. The spectrum shows well resolved and characteristic peak for pyridine adsorbed on both the types of acid sites [9].

The acidity characterization of pillared clays is frequently made by commonly used methods of acidic characterization of solids, namely, adsorption of basic molecules followed by FTIR spectroscopy analysis [10-11]. The present study focuses characterization of the surface acidity adsorbed pyridine, basal spacing ($d_{001}$) and morphology after pillarization process of ZrO$_2$/bentonite.
2. Experiment

2.1. Clay source and sampling
A sample of natural clay was collected from an open clay deposit in Boyolali, Central Java, Indonesia. The clay sample was dissolved using 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.

2.2. \( \text{ZrO}_2 \)-pillared bentonite synthesis
Transformation of natural bentonite into pillared clay required the use of pillaring solution prepared at a variation in concentrations of 0.05; 0.10; and 0.20 M \( \text{ZrOCl}_2\cdot8\text{H}_2\text{O} \) for 2 hours as well as refluxed it under constant stirring at 70 °C. Thereafter, the pillaring solution was added dropwise to ca. 4 g of clay in 200 mL suspensions with constant stirring and aged overnight at room temperature. Afterward, the pillared clay suspension was filtered and washed with distilled water and neutralized until Cl− free. The pillared clay was air-dried at ambient temperature and 80 °C for 8 hours, then calcinated at 400 °C for 4 hours. The resulting product were sequentially named as BZR05; BZR10; BZR20. Furthermore, calcination was performed at temperature variations of 400 °C, 500 °C, 600 °C. The product were sequentially named as BZR10-400; BZR10-500; BZR10-600.

2.3. Pyridine adsorption
Bentonite and \( \text{ZrO}_2 \)-pillared bentonite samples prepared by the above process were exposed to pyridine vapor. In vacuum desiccator, 25 mL of dry pyridine and 0.3 g of bentonite were kept under vacuum overnight. Subsequently, the samples were evacuated for 3 hours at room temperature to desorb physisorbed pyridine.

2.4. Characterization of \( \text{ZrO}_2 \)-pillared bentonite
The vibrational framework of the clay samples was studied using FTIR Spectroscopy (Shimadzu 8201 PC). Determination of basal spacing of the product were characterized by X-ray diffraction (XRD Shimadzu model X-RD 6000 using Cu Kα radiation). The Transmission Electron Microscopy (TEM) micrographs were obtained using JEOL Hitachi H-600 at 120 kV to observe the surface morphology of the pillared clays.

3. Results and discussion
Results of infrared spectra of bentonite are presented in figure 1 and 2. Considering the figures it can be seen that the peak of bentonite spectra which occur in the wave numbers of 3626.17 cm\(^{-1}\) and 3448.72 cm\(^{-1}\) that are identified as a \(^{\text{OH}}\) band stretching vibrations of octahedral and \(^{\text{OH}}\) band stretching vibration of water molecules, respectively. Pyridine vibration bands appear in the IR region of 1400–1700 cm\(^{-1}\). The IR bands at 1637 and 1545 cm\(^{-1}\) are assigned to \(^{\text{Brønsted}}\) acid. The IR bands at 1450–1455cm\(^{-1}\) are characteristic for Lewis acid sites and band at 1490 cm\(^{-1}\) indicates the combined presence of all acid sites. The absence of a band at 1450–1455 cm\(^{-1}\) which is characteristic for Lewis acid showing that at 1640 and1540 cm\(^{-1}\) correspond to \(^{\text{Brønsted}}\) acid sites. The band at 1540 cm\(^{-1}\) is attributed to \(^{\text{–NH\}}\) bending of pyridinium ions is characteristic of \(^{\text{Brønsted}}\) acid sites [12-13].

In this method, the number of \(^{\text{Brønsted}}\) or Lewis acid sites was determined and depended on pyridine bonded on the sites in mmol/g catalyst. Acid site or acidity of zirconium-pillared bentonite are related to three sources, namely cations \( M^{n+} \) that equilibrate the electrical charges of the material, specific sites at the edge of the crystal due to bond breaking or crystal defect, and pillaring metal oxide. Dehydration process may cause \(^{\text{Brønsted}}\) sites of Si-OH-Al change to Lewis acid. Besides, those processes remove water molecules from its coordination bond to metal \( M^{n+} \) leaving the ion as Lewis acid [14]. Therefore, the change in the acid properties is related to dehydration process of Si-OH-Al group. Considering gravimetric acid analysis as depicted in table 1 it comes to the conclusion that the more pillaring metal oxide, the more acidic the material is, the increase was from 1.1490 to 1.5488 mmol/g (BZR20).
Moreover, increasing in calcination temperature was followed by decreasing its acidity, from 1.2772 to 0.9072 mmol/g.

Figure 1. IR spectra of pyridine adsorbed on Bentonite and ZrO$_2$-Bentonite.

Figure 2. IR spectra of pyridine adsorbed on ZrO$_2$-Bentonite with different calcination temperature.

| Table 1. Determination of acidity with pyridine adsorption |
|---------------------------------------------|
|                                          | Acidity (mmol/gr) |
| Bentonite                                | 1.1490            |
| BZR05                                    | 1.5558            |
| BZR10                                    | 1.2771            |
| BZR29                                    | 1.5488            |
| BZR10-400                                | 1.2771            |
| BZR10-500                                | 0.9130            |
| BZR10-600                                | 0.9072            |

| Table 2. Basal Spacing $d_{001}$ of Bentonite and ZrO$_2$-pillared Bentonite |
|---------------------------------------------|
|                                          | 20  | $d_{001}$ (Å) |
| Bentonite                                | 7.74| 11.41         |
| BZR05                                    | 4.32| 20.41         |
| BZR10                                    | 4.01| 22.01         |
| BZR29                                    | 4.42| 19.96         |
| BZR10-400                                | 4.01| 22.01         |
| BZR10-500                                | 4.19| 21.03         |
| BZR10-600                                | 4.14| 21.29         |
The identification results of bentonite and ZrO$_2$–pillared bentonite with X-ray diffraction methods can be seen in figure 3 and 4. From the diffractogram can be seen abroad reflection on the regions of 2$\theta$ = 7.74° and 19.43° with a values of d= 11.41 Å and 4.56 Å which area typical reflection of montmorillonite sample. From these results can be concluded that the bentonite contains montmorillonite minerals. In addition, bentonite also composes of feldspar and quartz minerals as impurities. The X-ray diffraction analysis shows that there has been peak shifting of bentonite on angle 2$\theta$ of 7.74° to 2$\theta$ = 4.01° in pillarization of BZR10 stage which means the pillarization process has been done. Characterization of zirconium pillared product into silicate bentonite interlayer using X-ray diffraction are shown in figure 3 and 4. It is characterized by increasing in basal spacing of bentonite $d_{001} = 11.41$ Å to $d_{001} = 22.01$ Å for pillared bentonite. Pillarization result at different concentration of zirconium shows similar effects, an increase in basal spacing.

On the other hand, the changes in temperature of calcination at ZrO$_2$–pillared bentonite (BZR10-400; BZR-500; BZR10-600) does not change the structure and the basal spacing, it indicates that the product pillarization has a good thermal stability as shown in table 2. The basal spacing change is determined by calculating the difference between basal spacing $d_{001}$ of point of zirconia-bentonite intercalation product with the thickness of the silicate–bentonite interlayer hydrated or usually written as $\Delta d=(d_{001}–9.6)$ Å[15]. The results of the analysis for pillarization stage as shown in table 2 also showed that there has been shifting the peak of bentonite before pillarization at an angle of 20 = 7.74° shifted towards conditions ZrO$_2$ - bentonite of 20 = 4.01° (BZR10). The shifting peak was followed by a shifting in basal spacing bentonite $d_{001} = 11.41$ Å or $\Delta d_{001} = (11.41 – 9.6)$ Å = 1.81 Å basal spacing ZrO$_2$-bentonite into $d_{001}=22.01$Å or $\Delta d_{001} = (22.01 – 9.6)$ Å = 12.41 Å. The changes in basal spacing showed that pillarization zirconia oxide in silicate interlayer of bentonite had been successfully carried out with an increase in the silicate interlayer distance of (12.41–1.81) Å = 10.60 Å.

**Figure 3.** XRD pattern of Bentonite (a); BZR05 (b); BZR10 (c); BZR20 (d).

**Figure 4.** XRD pattern of ZrO$_2$- Pillared Bentonite (a); BZR10-400 (b); BZR10-500 (c); BZR10-600.
4. Conclusion
Zirconium pillared bentonite has been synthesized successfully as proved by characterization result performed using XRD and acidity of pyridine adsorption. The analysis showed that the presence of metal oxide ZrO$_2$ was able to increase the basal spacing of 11.41 Å to 22.01 Å and related to the raising damage of the bentonite structure. Moreover, increasing in calcination temperature is followed by decreasing in its acidity, from 1.2772 to 0.9072 mmol/g.

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