

Effect of physical and chemical modification on surface area of low-grade bauxite

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Abstract. In this research, the effect of physical and chemical modifications of low-grade bauxite (LB) with particle size of 200 mesh were studied. Here, we demonstrate chemically technique to synthesize low-grade bauxite/CeO₂ composites using Ce(NO₃)₃.6H₂O with weight variations of 0.5, 1 and 2 g. The effect of Ce(NO₃)₃.6H₂O concentrations on BET surface area of prepared low-grade bauxite/CeO_{2(0.5)} (ALB0.5), low-grade bauxite/CeO₂₍₁₎ (ALB1), and low-grade bauxite/CeO₂₍₂₎ (ALB2) composites were observed. The results showed the BET surface area of LB is 59.85 m²/g. After acid activation with 1M HNO₃, activated low-grade bauxite (ALB) has BET surface area of 101.6 m²/g. By chemically modification with Ce(NO₃)₃.6H₂O in concentration ranging from 0.5; 1 and 2 g, the BET surface areas were reduced in the respectively order of 94.5, 87.9, and 85.5 m²/g for ALB0.5, ALB1, and ALB2. With the increase of the Ce(NO₃)₃.6H₂O concentration, the BET surface area reduced compare to those found in the ALB. The acid activation treatment has significant effect compare to the chemical modification using Ce(NO₃)₃.6H₂O.

1. Introduction

The bauxite exploitation increased significantly due to high demand of alumina and aluminum for various applications [1]. This exploitation process generated huge quantities of mining wastes such as low-grade bauxite. Therefore, there is an increasing interest in the utilization of low-grade bauxite waste. For this purpose, further application of low-grade bauxite is needed to be explored.

As our previous report [2], low-grade bauxite (LB) was collected from Bintan islands, Indonesia, consists essentially of SiO₂, Al₂O₃, and Fe₂O₃, which makes it possible to use it as source materials for some industrial applications such as synthetic zeolites, adsorbent and catalyst support. Low-grade bauxite with alumina content of ~44% was used for the present study. It contained a small amount of rare-earth elements including Y₂O₃ (0.0052%) and La₂O₃ (0.0041%). Mineral composition was determined using X-Ray Fluorescence with a proprietary software based on data reconciliation including multiple inputs such as chemical analysis, LOI and so on. Detail mineral composition of the low-grade bauxite used in this report is presented in table 1.



Table 1. Chemical composition of low-grade bauxite (mass fraction, %)

| Oxide | % Composition |
|--------------------------------|---------------|
| SiO ₂ | 24.09 |
| Al ₂ O ₃ | 44.11 |
| Fe ₂ O ₃ | 9.77 |
| LOI | 20.05 |
| TiO ₂ | 0.912 |

The mineral composition of low-grade bauxite was determined by XRD analysis. The mineral composition of LB is listed in table 2. It is found that kaolinite, and gibbsite are the major components. Other minerals such as cristobalite, hematite, anatase, muscovite and quartz are also present in low quantity. The combination of chemical and mineral composition of the LB make it as a suitable candidate for catalyst support.

Table 2. XRD analysis of low-grade bauxite [2]

| Sample | Clay Mineral (%) | | | | | Other Minerals (%) | | | | |
|--------------------------|------------------|--------|-----------|---------|--------|--------------------|----------|----------|-----------|---------|
| | Ectite | Illite | Kaolinite | Calcite | Quartz | Cristobalite | Gibbsite | Hematite | Muscovite | Anatase |
| Low-grade bauxite | * | * | 42 | * | 2 | 8 | 30 | 7 | 4 | 7 |

Cerium oxide has been reported as good catalyst for various application and/or catalyst supporter [3]. As we know that, CeO₂ can provide favorable catalytic activity and provide a large area of chemical surface absorption and improve reducibility [4]. The addition of CeO₂ will also increase the number of Ce³⁺ ions that provide redox-active sites and also provide a large surface area for physical and chemical adsorption [5-7]. Therefore, in this research, we used Ce(NO₃)₃·6H₂O for the modification of low-grade bauxite (LB) to increase the BET surface area.

In this study, we explored the effect of physical and chemical treatments on the surface area properties of low-grade bauxite (LB), activated low-grade bauxite (ALB). Also, we prepared composites of low-grade bauxite/CeO_{2(0.5)} (ALB0.5), low-grade bauxite/CeO₂₍₁₎ (ALB1), and low-grade bauxite/CeO₂₍₂₎ (ALB2).

2. Experimental

2.1. Materials

Low-grade bauxite was obtained from Madong located in Bintan island, Indonesia. Other chemicals and materials were used in this study without purification.

2.2. Characterization

Mechanical treatment of low-grade bauxite was done in a laboratory scale using *Planetary ball mill* (NOAH NQM-4). Two stainless steel balls of 30 mm diameter with weight of 111 g and six stainless steel balls of 20 mm with weight of 32.5 g were used in the milling experiment. The stirrer speed used was 660 rotations per min (11 Hz) during 120 min.

The surface area of each powder sample was determined using a BET analyzer (model: ASAP 2020 V4.02 (V4.02 E), Micromeritics, US) with analysis adsorptive N₂, equilibration interval of 5 second, no low-pressure dose and analysis bath temperatures at -195.858; -195.822; -195.791; -

195.794 and -195.814°C (77K). Prior to BET analysis, the sample was subjected to degassing under high vacuum at 350°C for 4 hours.

The characteristics of the LB has been evaluated using XRD, XRF and BET analysis. Whereas, the characteristics of ALB and the prepared composites have been analyzed only using BET analyzer.

2.3. Preparation of ALB

Low-grade bauxite (LB) was milled to obtain the fine powder and sieved to obtain a 200 mesh (75 μm) particles size. The sieved low-grade bauxite powder using *Humboldt Motorized Siever Shaker* and then was kept in sealed plastic container. Low-grade bauxites (200 mesh) were washed with distilled water several times to remove any other impurities and allowed to dry at 110°C for 6 hours. Then sample was activated with 1 M HNO_3 solution in ratio of acid: solid of 20 mL/g, followed was stirred continuously for 8 hours at 80°C, then the powders were filtrated and washed with distilled water several times until reached the pH at 7. The obtained solid was transferred to an oven at 110°C for 24 hours. Then sample was transferred to a furnace at 500°C for 3 hours to perform calcination process. For low-grade bauxite (LB), and activated low-grade bauxite (ALB) were stored in desiccator to further characterization.

2.4. Preparation of ALB/ CeO_2 composites

The ALB composites are prepared according to the method reported by Kusriani *et al.* [7,8]. The obtained activated low-grade bauxite (ALB) samples were chemically modified using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The weight of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was varied at 0.5, 1 and 2 g, and NH_3 solution (1M) were added drop-wisely into the sample solution for 30 min and stirred slowly with a magnetic stirrer, and the pH was adjusted to 9. After mixing for one hour, all samples were dried for 12 hours at 110°C, and then calcined in the furnace at 500°C for 5 hours. All samples of low-grade bauxite/ $\text{CeO}_{2(0.5)}$ (ALB0.5), low-grade bauxite/ $\text{CeO}_{2(1)}$ (ALB1), low-grade bauxite/ $\text{CeO}_{2(2)}$ (ALB2) were stored in a desiccator to further characterization.

3. Results and Discussion

This study presents the properties of Indonesian low-grade bauxite sample after physical treatment (ball mill) and chemical modifications using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. After the treatment, samples were subjected to a surface area and porosity characterization.

The N_2 adsorption isotherms at 77K of activated and treated sample are shown in figure 1, and the properties including BET surface area, nanoparticle size, surface from external and microporous calculated from t-plot are summarized in table.1. As seen from Figure 1, the adsorption isotherm of N_2 at 77K for all samples showed type II of sorption isotherms, typical pattern for nonporous material [8].

BET results show good correlation between the mill treatment and surface area of the samples, ; Also the material after chemical modifications have significant difference compare to the raw material. The various $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ weight ratio was ranging from 0.5 to 2 g resulted in different BET surface area, external surface and average particle size. Increasing of adsorbed N_2 to the samples indicates the increasing of surface area and diminished bauxite particle size. Activation process by milling and acid treatment using 1M HNO_3 increased surface area of low-grade bauxite (LB) significantly up to almost twice in activated low bauxite (ALB) (see table 3). BET surface area of LB has sharply increased after acid activation using 1M HNO_3 (101.60 m^2/g), but after chemical modifications using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was reduced eventually. Increasing concentration of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was ranging from 0.5 to 2 g, the BET specific surface area reduced, namely 94.523; 87.925 and 85.467 m^2/g , respectively. The increasing amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ used in chemical treatment causes a decrease in the number of adsorbed N_2 which indicates decreasing surface area and increasing particle size. A quite similar was observed for modification of graphite waste using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to produce graphite/ CeO_2 composites [7,8]. The largest surface area that is found in graphite/ CeO_2 composite with variation concentration of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ of 2 g is equal to 26.82 m^2/g [7].

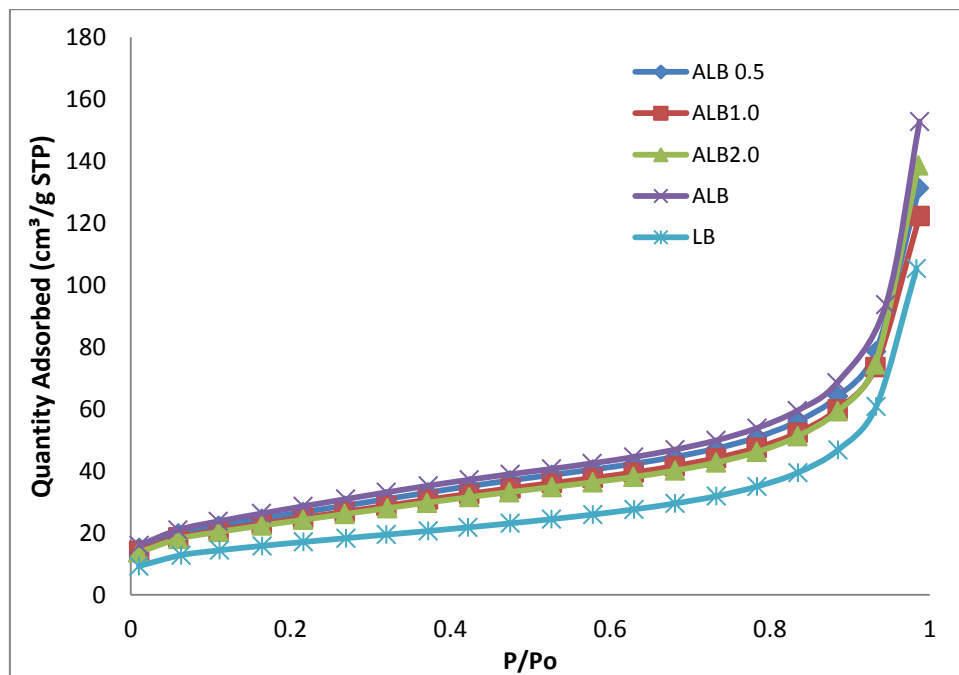


Figure 1. Isotherm adsorption using N_2 gas of quantity adsorbed vs relative pressure (P/P_o)

Tabel 3. BET surface area characterization for all samples

| | LB | ALB | ALB 0.5 | ALB 1.0 | ALB 2.0 |
|-------------------------|---------|---------|---------|---------|---------|
| S_{BET} | 59.849 | 101.602 | 94.524 | 87.925 | 85.467 |
| S_{ext} (m^2/g) | 57.625 | 104.852 | 95.583 | 87.914 | 85.016 |
| S_{micro} (m^2/g) | 2.225 | - | - | 0.0107 | 0.451 |
| Average Size (nm) | 100.251 | 59.054 | 63.476 | 68.240 | 70.203 |

In LB contained t-plot small micropore of $2.225 \text{ m}^2/\text{g}$, whereas for ALB1 and ALB2 are 0.0107 and $0.451 \text{ m}^2/\text{g}$, respectively. A t-plot micropore area for ALB and ALB0.5 are not present. It is confirmed that ALB and ALB0.5 are non-porous. The t-plot external surface area of ALB after milled process and acid activation is the highest ($104.852 \text{ m}^2/\text{g}$). If we compare both t-plot micropore area and t-plot external surface area for all samples, confirmed that all samples are non-porous. Because no micropore is present in all samples. t-plot external surface area is contributed from the average particle size of samples. The LB has average particle size of 100.25 nm . The acid activation using 1 M HNO_3 has significant effect on the BET surface area as well as t-plot external surface area. We observed all samples are non-porous because increasing surface area is contributed from decreasing average particles size. From the pattern of isotherm adsorbed N_2 and the calculated particle size after chemical treatment, it can be assumed that core shell of $\text{CeO}_2@$ bauxite was formed, where the core is bauxite and CeO_2 coated it. Increasing amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ increases the particle size of $\text{CeO}_2@$ bauxite formed, indicating CeO_2 growth on outer side of bauxite particles.

4. Conclusion

The physical and chemical treatments were used to modify the surface properties of low-grade bauxite. With increasing $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ concentration, the BET surface area reduced compare to those found in the activated low-grade bauxite (ALB).

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