



Synthesis of γ - Al_2O_3 Catalyst Support from Kaolin of Indonesian Origin

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Abstract. Kaolin has been identified as a potential raw material for the production of γ - Al_2O_3 for hydrotreating catalyst support. This work explores the technical feasibility of applying the potassium hydroxide (KOH) extraction synthesis route on kaolin from the Belitung Island in Indonesia. The application of a published synthesis method to Belitung kaolin requires an approximately twofold increase in kaolin calcination time, an increase in kaolin calcination temperature from 950 to 1000°C, and a tenfold increase in metakaolin extraction time, to obtain a specific surface area higher than 200 m²/g. The highest specific surface area of 233 m²/g was obtained when the kaolin was calcined at 1000°C for 24 hours, and the metakaolin was extracted by concentrated KOH solution for 12 hours. Phase characterization of the final product confirmed the formation of γ - Al_2O_3 , but with the inclusion of low-surface area α - Al_2O_3 phase.

Keywords: acid leaching; γ -alumina; catalyst support; hydrotreating; kaolin.

1 Introduction

The global petroleum-based energy market has recently been marked by several opposing trends. Market demand has been characterized with a generally increasing demand volume for various petroleum fuels, and regulatory shift towards cleaner-burning fuels with lower sulfur and heavy metals content. The latter trend is primarily due to the need to reduce emission levels generated by combustion engines and to increase the thermal efficiency of the engines. On the other hand, fuel production has been characterized by a shift in the global crude oil supply towards heavier, more difficult-to-refine crudes with increasing concentrations of impurities such as sulfur, metals, oxygen, and nitrogen compounds.

These opposing trends have increased the prominence of refinery process technologies that rely on hydrogen to convert crude oil fractions into valuable fuels and other derivative products. To date, the so-called hydroprocessing is still regarded as the most effective process technology when dealing with high impurity, heavy to extremely heavy crude oils. Hydroprocessing encompasses a

wide range of process objectives, including cracking (hydrocracking), removal of impurities (for example the hydrodesulfurization, hydrodemetallization, hydrodeoxygenation processes), and improvement of fuel physical properties (generally known as hydrotreating process).

Among the wide range of hydroprocessing technologies, hydrotreating ranks as among the most widely employed. Global capacity data of catalytic processing units in petroleum refineries collected by Silvy [1] indicate that hydrotreating boasts the highest global capacity and fastest growth compared to other major catalytic processes such as fluid catalytic cracking, hydrocracking, reforming, and isomerization (see Figure 1).

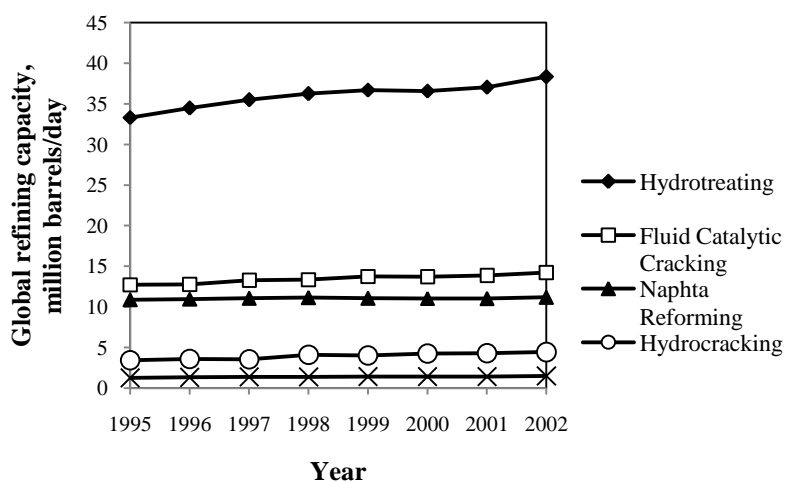


Figure 1 Global capacity trend of major catalytic units in petroleum refineries in 1995-2002 [1].

This global increase in hydroprocessing capacity is naturally accompanied by an increase in the demand of solid catalysts required by these processes. As an indicative trend, the Shell multinational oil company has forecasted that the global demand for hydrotreating catalysts is likely to increase at an annual growth rate of 3-5% in the foreseeable future [2].

The objective of this experimental research is to evaluate the technical feasibility of the utilization of Indonesian kaolin as a raw material for the manufacture of hydrotreating catalyst support. This process is regarded as having a strategic importance in the national fuel supply security, since it is responsible for the improvement of physical properties of petroleum fuels

through the reduction of sulfur and metals, and through the reduction of polymerization susceptibility of the fuels.

This research shall involve the utilization of kaolin as a precursor for the synthesis of γ -Al₂O₃, one of the most widely used catalyst support material for hydrotreating. While the selected synthesis route is not a novel technology, properties of naturally-occurring minerals are highly dependent on their origin and mineralogy. This implies that even a highly detailed synthesis method that has been established for a specific mineral has to be verified (and often needs to be adjusted) when the source of mineral is altered. Therefore, proving that available synthesis methods are applicable to Indonesian minerals is of utmost practical significance.

As a preliminary developmental study, the technical feasibility of γ -Al₂O₃ is synthesized from Indonesian kaolin in this work is judged by the key physical properties that characterize its role as a catalyst support, namely its specific surface area, pore volume, and crystalline phase distribution. If the physical properties of the Indonesian kaolin-derived γ -Al₂O₃ are deemed competitive, then this study may form a basis for the development of a high added-value alternative processing route for the Indonesian mineral industry.

The low cost of kaolin and the existence of large, good quality kaolin reserves in the Bangka Belitung, South Kalimantan, and West Kalimantan provinces as listed in Table 1, suggest the prospect for long-term production of γ -Al₂O₃ to bolster the domestic fuel refining industry.

Table 1 Major kaolin reserves in Indonesia [3-5].

| Province | Estimated reserve, tons |
|------------------|-------------------------|
| Bangka Belitung | 224,300,000 |
| South Kalimantan | 194,187,800 |
| West Kalimantan | 317,000,000 |

2 Literature Review

Commercial hydroprocessing catalysts are typically Ni/Co-promoted Ni/W sulfide supported by γ -Al₂O₃ or silica-alumina (SiO₂-Al₂O₃). The main purpose of catalyst support is to disperse the active catalytic metal particles and to absorb heat during operation. The nanometer-sized active metal particles are susceptible to sintering (agglomeration of particles due to partial fusion at high temperatures). Thus, the presence of the catalyst support with its large specific surface area serves to protect the active metal particles from sintering which reduces the activity of the catalyst [6].

As a catalyst support, γ - Al_2O_3 offers several advantages. This material provides a large specific surface area of 50-300 m^2/g , mesopore size in the 5-15 nm range, a pore volume of approximately 0.6 cm^3/g , a high thermal stability, and the ability to be formed into various geometries for fixed bed reactors by extrusion or pelletizing. As catalyst support for fixed bed reactors, γ - Al_2O_3 provides good mechanical integrity [6].

Large-scale production of γ - Al_2O_3 generally utilizes boehmite (AlOOH) or gibbsite ($\text{Al}(\text{OH})_3$) as precursors. Under heating, these hydrated aluminas undergo removal of crystalline water, followed by a series of polymorphic transitions as described in Figure 2. Boehmite and gibbsite are themselves intermediate materials in the production of metallic aluminum from raw minerals such as bauxite.

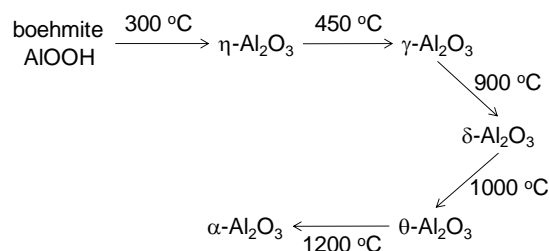
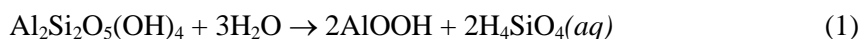


Figure 2 Boehmite dehydration and polymorphic phase transition route in the Al_2O_3 system [7].

In his study on soil chemistry, Huang [8] described the formation of boehmite from kaolinite and water under hydrothermal conditions through the following reaction:



The reaction was undertaken in dilute KCl solution at temperatures between 200-275 $^\circ\text{C}$ and a pressure of 500 bar. The X-ray diffraction pattern of the solid reaction product resembled that of commercial boehmite.

As outlined below, several authors have described the direct conversion of kaolin into γ - Al_2O_3 without the formation of boehmite. This is achieved by reacting kaolin with concentrated base solution.

Okada, et al. [9] described the synthesis of γ - Al_2O_3 from calcined kaolin via the selective extraction of the amorphous SiO_2 phase by concentrated KOH solution. The solid residue remaining after the extraction was identified as having a spinel structure, containing γ - Al_2O_3 and a minor content of crystalline

SiO₂. Saito, et al. [10] studied the effect of kaolin calcination temperature on the pore structure of γ -Al₂O₃ produced via extraction by KOH solution. At calcination temperatures in the 950-1050°C range, these authors obtained a specific surface area of 250 m²/g.

Extraction by acidic solution represents another route for the synthesis of γ -Al₂O₃ from kaolin. Contrary to the basic solution extraction route, the acidic solution extracts the alumina phase from the kaolin crystal structure. This implies that the acid extraction route necessarily involves additional steps to recover the alumina from the extract, and to convert the recovered solid material to γ -Al₂O₃ by calcination.

Belver, et al. [11] described the reaction between a Spanish kaolin calcined between 600-900°C and concentrated HCl solution. This reaction removes most of the octahedral Al³⁺ from the kaolin crystal structure, leaving behind a network structure consisting of amorphous silica phase.

Yang, et al. [12] also described a synthesis route of γ -Al₂O₃ from kaolin by acid extraction. The suspension extract produced by contacting kaolin and concentrated HCl solution was filtered and precipitated by adding ammonia. The obtained precipitate contained boehmite and aluminum hydroxide, which started to form γ -Al₂O₃ at 537°C during calcination.

3 Methodology

3.1 Materials and Equipment

The kaolin utilized in this study was obtained from the Belitung island via the Center for Ceramic Research (*Balai Besar Keramik*) of the Ministry of Industry of the Republic of Indonesia in the city of Bandung. Oxide composition of this material was characterized by the wet chemical method at the Mining Engineering Program laboratory facility in Bandung Institute of Technology, and the results are presented in Table 2. As a comparison, typical composition of Georgia (USA) fiberglass-grade kaolin [13] is included in the table. The oxide compositions of the two minerals are generally similar, except for the higher CaO and Na₂O contents of the Belitung kaolin.

Concentrated aqueous solution of KOH was selected as the solvent to extract the silica phase, in accordance to Okada's method [9] which served as the baseline synthesis method. Selection of KOH was also based on unpublished preliminary trials by one of the co-authors, which in general produced less than

satisfactory specific surface areas. An analytical grade KOH (Merck Emsure[®]) was used to prepare the KOH solution.

Table 2 Oxide composition of the Belitung kaolin sample.

| Component | Belitung | Georgia, USA |
|--------------------------------|----------|--------------|
| SiO ₂ | 46.77 | <45.0±0.6 |
| Al ₂ O ₃ | 38.17 | >38.5±0.5 |
| Fe ₂ O ₃ | 0.37 | <0.50±0.05 |
| TiO ₂ | 0.22 | <1.4±0.03 |
| CaO | 0.64 | <0.2±0.05 |
| MgO | 0.14 | <0.3±0.1 |
| Na ₂ O | 0.12 | <0.03±0.01 |
| K ₂ O | 0.10 | <0.20±0.1 |
| Loss on ignition | 13.47 | >14.0±0.5 |

3.2 Synthesis Method

The base extraction method described by Okada, et al. [9] was selected as the basis of the processing route of the Belitung kaolin. This synthesis route was selected due to its simplicity and lower consumption of reagents compared to the acid extraction route. The base extraction method based on the work of Okada, et al. [9] is outlined in Table 3.

Table 3 Base extraction route used as the baseline synthesis procedure.

| Step no. | Description |
|----------|---|
| 1 | Raw kaolin is comminuted in a ball mill for 15 minutes to remove agglomerates |
| 2 | Kaolin is calcined in an electric furnace at 950°C for 24 hours in ambient air atmosphere |
| 3 | One gram of calcined kaolin is extracted by 250 mL 4.0 M KOH solution at 90°C for 1 hour in a beaker glass on an electric plate heater equipped with a magnetic stirrer |
| 4 | The remaining solid residue is separated by centrifuging and decantation, followed by washing by 0.5 M KOH solution, and double-washing with demineralized water |
| 5 | The washed residue is then dried in an electric oven at 110°C overnight and stored for characterization |

Since the objective of this preliminary research stage is to demonstrate the technical feasibility of Belitung kaolin utilization as a γ -Al₂O₃ precursor, modifications to the baseline method outlined in Table 3 were undertaken to obtain a specific surface area of at least 200 m²/g, which refers to the intermediate value of that of hydrodesulfurization and hydrodenitrogenation catalysts for distillates [14]. These modifications were explored by the one-factor-at-a-time method as described by Montgomery in his classic text on statistical experimental design [15], in which the calcination temperature and time were varied alternately. While not as efficient as a statistically designed experiment, the one-factor-at-a-time was selected due to the lack of published

data on the range of values within which calcination temperature and time should be varied for Belitung kaolin.

3.3 Sample Characterization

Solid-phase physical properties characterization included morphological evaluation by scanning electron microscopy (SEM), phase identification by X-ray diffraction (XRD) and specific surface area and pore volume measurement by inert gas adsorption. These characterizations were aimed at evaluating the changes occurring during processing and to measure the key engineering properties of the product.

The XRD characterization was undertaken for the kaolin raw material, metakaolin intermediate, and γ -Al₂O₃ product. The XRD instrument unit was a Phillips PW1710 operated by the Mining Engineering Program in Bandung Institute of Technology. The 2θ angle range was set between 5 to 75°, with a step size of 0.02° and dwell time of 0.50 second. The SEM analysis was undertaken at the Environmental Geology Research Center facility of the Ministry of Energy and Mineral Resources in Bandung.

The inert gas adsorption measurement was undertaken on a Quantachrome Nova 1000 high-speed gas sorption analyzer at the Chemical Engineering Program in Bandung Institute of Technology. High-purity nitrogen (BOC Gases/PT. Aneka Gas, Bandung) was used as the sorbent inert gas. Treatment of the nitrogen adsorption-desorption data resulted in specific surface area determination by the BET (Brunauer-Emmett-Teller) method, mesopore size distribution by the BJH (Barnett-Joyner-Halenda) method, and pore volume.

4 Results and Discussion

4.1 Product Properties from the Exploratory Experiment

To evaluate the applicability of the base extraction route for Belitung kaolin as measured against the targeted specific surface area, modifications on the synthesis variables in the original procedure by Okada, et al. [9] were undertaken. The calcination temperature was varied at 950 and 1000°C, the calcination time was varied at 1, 12, and 24 hours, and the extraction time was varied at 1 and 12 hours. These relatively large ranges of variation were selected to create a substantial change in the specific surface area of the final product.

Table 4 presents the combinations of calcination temperature, calcination time, and extraction time selected in this exploratory study. Three sets of experiments were undertaken. Characteristics of the synthesized products are also listed in

the table, which include specific surface area, median size of the mesopores, and pore volume.

Table 4 Summary of the exploratory experiment results.

| Experi-ment no. | Batch no. | Calcination T, °C | Calcination time, hrs | Extraction time, hrs | Specific surface area, m ² /g | Median mesopore size, Å | Pore volume, cm ³ /g |
|-----------------|-----------|-------------------|-----------------------|----------------------|--|-------------------------|---------------------------------|
| I | 1 | 950 | 22 | 1 | 21.2 | 14.4 | 0.012 |
| | 2 | 950 | 24 | 1 | 50.0 | 14.6 | 0.030 |
| | 3 | 950 | 25 | 1 | 54.8 | 14.5 | 0.033 |
| II | 4 | 950 | 6 | 12 | 160.0 | 14.6 | 0.10 |
| | 5 | 950 | 24 | 12 | 182.9 | 14.4 | 0.12 |
| | 6 | 950 | 42 | 12 | 220.0 | 14.4 | 0.14 |
| III | 7 | 750 | 24 | 12 | 91.6 | 14.0 | 0.055 |
| | 8 | 850 | 24 | 12 | 112.3 | 14.0 | 0.068 |
| | 9 | 1000 | 24 | 12 | 233.5 | 14.1 | 0.14 |

The first experiment listed in Table 4 was a first attempt at proving the direct applicability of the method described by Okada, et al. [9] to the Belitung kaolin sample. Thus, the calcination time was varied in a relatively narrow range, *i.e.* between 22-25 hours. Calcination temperature was kept at 950°C due to risk of mullite (3Al₂O₃.2SiO₂) formation in the vicinity of 980-1000°C as described by several authors (see, for example, classical papers by Brindley and Nakahira [16], Chakraborty and Ghosh [17], and MacKenzie, et al. [18]). Mullite is a well-crystallized refractory aluminosilicate phase, considered to have a low reactivity towards chemical attack. The specific surface area data obtained from the first experiment clearly indicate that the base extraction method described by Okada, et al. [9] cannot be applied to Belitung kaolin without any modification, since it only produced a specific surface area of 22-52 m²/g.

In the second experiment, the effect of calcination time was evaluated by varying this variable between 6 to 42 hours while keeping the temperature constant at 950°C and extraction time of 12 hours. Longer calcination time increased the specific surface area and pore volume, while the pore size did not appear to be substantially impacted. With a calcination time of 42 hours, a specific surface area of approximately 220 m²/g was obtained, thus exceeding the minimum target of 200 m²/g. Compare with the first experiment suggests that increasing the calcination time from 1 to 12 hours resulted in a substantial increase of surface area. However, the same comparison also suggests that an increase of calcination time alone is not likely to be sufficient to produce the desired minimum specific surface area (compare Batch no. 2 and 5 in Table 4).

The third experiment included in Table 4 was undertaken to measure the effect of calcination temperature, which was varied at 750, 850, and 1000°C. As the numbers in Table 4 clearly suggest, an increase in calcination temperature improves the specific surface area and pore volume. Similar to the first and second experiments, the median pore size did not appear to be substantially impacted by any changes in calcination process parameters. Calcination temperatures of 750 and 850°C were apparently not high enough to produce the desired surface area. When the kaolin calcination was undertaken at 1000 °C, the specific surface area of the final product was approximately 233 m²/g. This value is substantially higher than the targeted 200 m²/g, and was the highest surface area obtained in this preliminary study.

4.2 Phase and Morphological Development during Conversion of Kaolin to γ - Al_2O_3

Figure 3 presents the X-Ray diffractograms of the three materials representing the phase development occurring during the conversion of kaolin into γ - Al_2O_3 . These are the raw Belitung kaolin, the metakaolin or calcined kaolin, and the γ - Al_2O_3 product. Phase designations of the diffraction peaks are included in Figure 3. These diffractograms were measured using the same instrument, at the identical operating parameters setting.

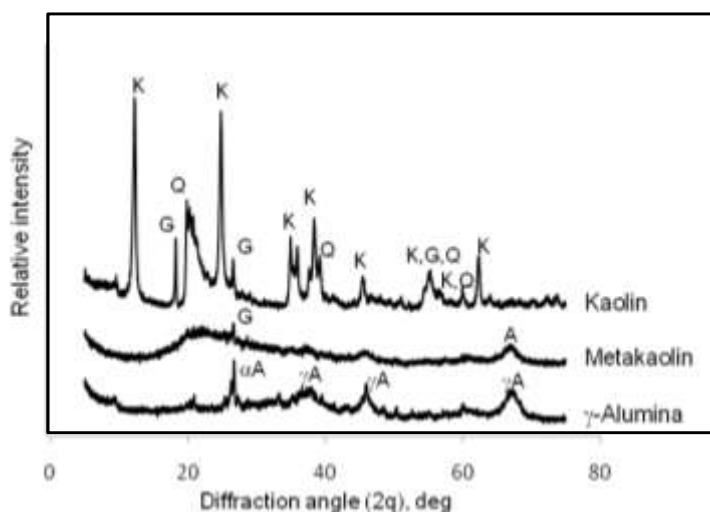


Figure 3 X-ray diffractograms of Belitung kaolin, metakaolin (calcined at 950°C for 24 hours), and the final γ - Al_2O_3 product (Note: A = alumina, α A = α - Al_2O_3 , γ A = γ - Al_2O_3 , G = gibbsite, K = kaolinite, Q = quartz).

The particular metakaolin in Figure 3 was produced by calcining the raw kaolin at 950°C for 24 hours as described by Okada, et al. [9]. The near-amorphous nature of this intermediate material is implied by the disappearance of kaolinite peaks. The sharp quartz peak near $2\theta = 20^\circ$ in kaolin was broadened, suggesting a substantial shift in the long-range order of the crystalline silica phase towards a predominantly short-range order, albeit with the preservation of the SiO_4^- tetrahedra as the smallest repeating unit containing Si atoms. As described by Lee [19], the dehydroxylation of kaolin during calcination destroys the hexagonal $\text{Al}(\text{O},\text{OH})_6$ octahedral sheet, but does not have much effect on the SiO_4 tetrahedral sheet. A new phase also appeared in the metakaolin, indicated by the rather faint Al_2O_3 peak at $2\theta = 66^\circ$.

The phase identity of the synthesized product is presented as the bottom graph in Figure 3. The list of diffraction peaks of the product in Figure 3 is presented in Table 5. With the exception of the peak at 26.7° , the peaks observed for the final product are quite consistent with those of the pure $\gamma\text{-Al}_2\text{O}_3$ phase described by Meephoka, et al. [20], which exhibits diffraction peaks at 2θ angles of 32, 37, 39, 45, 61, and 66° . Yang, et al. [12] also observed a rather weak peak in the vicinity of $2\theta = 27^\circ$ in their boehmite phase. These authors observed that this peak intensifies after calcination at 1000°C, and assigned this peak to the $\alpha\text{-Al}_2\text{O}_3$ phase.

Table 5 X-ray diffraction peak angles and relative intensities of $\gamma\text{-Al}_2\text{O}_3$ product obtained by calcination at 950°C for 24 hours.

| Diffraction angle (2θ) ($^\circ$) | Relative intensity (%) |
|---|---------------------------|
| 26.72 | 100.0 |
| 33.2 | 55.4 |
| 36.6 | 65.1 |
| 37.8 | 64.5 |
| 45.9 | 65.6 |
| 60.0 | 42.6 |
| 66.6 | 60.8 |

The morphological changes occurring during the conversion of kaolin to metakaolin, and after the subsequent leaching by KOH solution are described by scanning electron micrographs in Figure 4(a) through 4(c). Comparison of the morphology of the Belitung kaolin and metakaolin obtained after calcination at 1000°C for 24 hours indicates the breakdown of the layered kaolinite structure.

Qualitatively, the microstructure of the metakaolin was dominated by acicular particles with relatively rounded edges. Figure 4(c) is the electron micrograph of the product obtained by leaching the metakaolin in Figure 4(b) for 12 hours. The morphology of the solid phase remaining after leaching by KOH solution exhibited a cubic crystal habit, consistent with the crystal structure of the γ -Al₂O₃ [21].

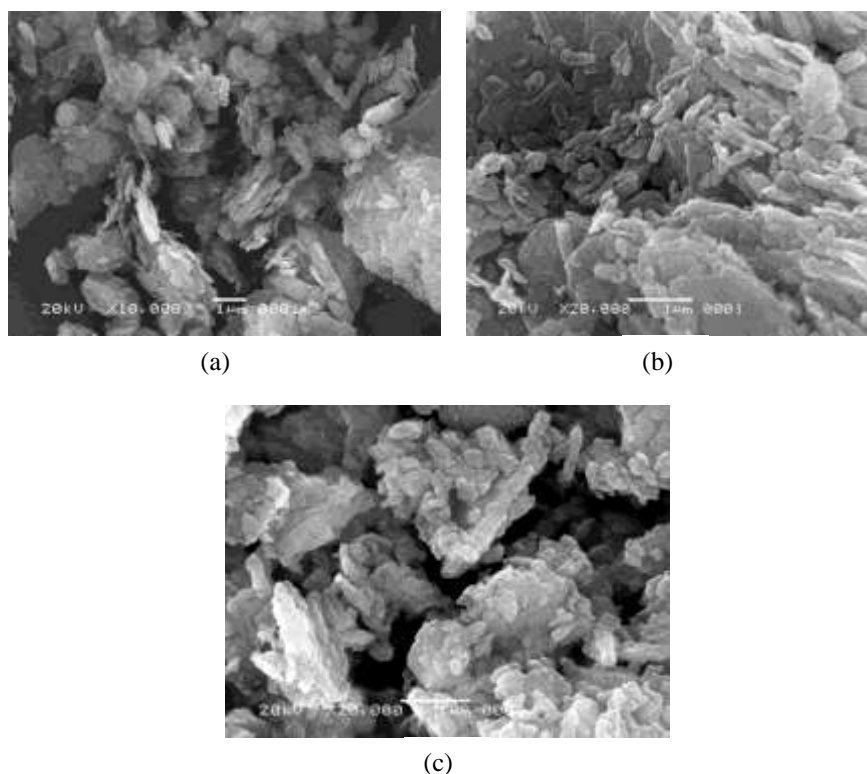


Figure 4 Scanning electron micrographs of: (a) raw Belitung kaolin (b) metakaolin obtained after calcination of kaolin at 1000°C and 24 hours (c) γ -Al₂O₃ obtained after leaching with 4.0 M KOH for 12 hours.

5 Conclusions and Recommendations

The technical feasibility of applying the base extraction process to produce γ -Al₂O₃ suitable for hydrotreating catalyst support material from Belitung kaolin has been verified. Three key synthesis variables (kaolin extraction time, and metakaolin calcination time and temperature) have been identified in this work. Compared to the published synthesis method, this study suggests that a very large increase (approximately tenfold) in kaolin extraction time and a moderate

increase (approximately twofold) in metakaolin calcination time are necessary to obtain the desired minimum specific surface area of 200 m²/g. Substantial increase in the specific surface area may be obtained by a relatively small increase in metakaolin calcination temperature from 950 to 1000°C.

Recommended items for future work include performing a statistically designed experiment to quantify the effects of the above variables, validating the improved base-extraction synthesis route, and evaluating the extrusion / shaping behavior of the bulk γ -Al₂O₃. Finally, the need for a study on the formulation and performance evaluation of the hydrotreating catalyst using the obtained γ -Al₂O₃ as the support material is imminent.

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