

The effect of the process condition on synthesis amorphous silica alumina from metakaolin on pore structure and crystallinity of product

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Abstract. The objective of the research to study the effect of amorphous silica alumina (ASA) synthesis condition on pore structure and crystallinity. Synthesis of ASA was done by co-precipitation method, that preceded by neutralization to form a sol phase, followed by introducing a silica solution, and then aging to form an amorphous phase. Alumina solution is resulted by leaching of metakaolin from kaolin Belitung, Indonesia. The use of alumina source from this kaolin is a novelty method. Process conditions synthesis of ASA were varied on Si /Al ratio, time of neutralization and time of aging. While, a pH and temperature of neutralization are as independent process variable, of 7-8 and 50-55 °C, respectively. Characterization of ASA was performed using XRD, surface area and pore analyzer. The increasing of Si/Al ratio in starting material affects on the surface area of ASA, as well as with aging time. The best product of ASA with a specific surface area of 510 m²/g, average pore diameter of 85 Å, a total pore volume of 1.1 mL/g, and an amorphous phase of 53%-mass were observed.

1 Introduction

Amorphous Silica Alumina (ASA) is an inorganic polymer, composed of components identical to zeolites. The ASA structure is irregular, in its structure there are also tetrahedral units of SiO₄ and AlO₄ which build a three-dimensional framework. ASA has a mesopore-sized diameter, greater than the pore diameter of the zeolite Y of 7.4 Å [1-3]. The nature of ASA is strongly influenced by the methods and operating conditions of the manufacturing process [4].

Amorphous Silica Alumina (ASA) are built by atoms of Al, Si and O, accordingly it can be synthesized with raw materials such as kaolin. Kaolin is an inert and inactive material, so it requires activation to convert to metakaolin by calcination. The silica and alumina content in the metakaolin can be separated through leaching by acid, to obtain a rafinat namely Leached Metakaolin (LMK) and extract that contain a high of alumina. Both of the process conditions of calcinating kaolin and leaching metakaolin will affect the results of the separation of silica and alumina.

There are few papers reporting on leaching metakaolin. Ajayi [5], Mamani [6] and Adeoye [7] have successfully separated silica and alumina in metakaolin using acid and reported the result a silica-rich solid as source of SiO₂ for synthesis zeolite. However, they did not regard to the importance of alumina-rich solutions that can be used as a source of Al₂O₃ for ASA. Based on this description, researcher have used valuable opportunities to use kaolin in total, using extracts from

the metakaolin leaching process as an alumina source for ASA synthesis.

The main purpose of this paper is to present the results of synthesis ASA using extract leaching metakaolin, that focus on studying the effect of ASA synthesis condition on pore structure and crystallinity.

2 Materials and methods

2.1 Materials and reagents

The material and chemical used in ASA synthesis include: Indonesian Kaolin Belitung, a technical grade of chemicals HCl 10%, Ammonia solution 10 %, Sodium Silicate and aquademineral.

2.2 Experimental set-up

Synthesis ASA uses the extract of metakaolin leaching as alumina source, consisting of several working steps, namely:

2.2.1 Preparation of alumina solution from metakaolin

The process starts with activating kaolin through calcination process in the furnace at a temperature of 700°C for 2 hours, so that the amorphous phase of metakaolin is formed. The separation of alumina content was done from metakaolin through a leaching process. The suspension of metakaolin in HCl 2.5 M was determined with weight ratio of HCl 2.5M / metakaolin

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solids at 10 w/w [6], at a temperature of 100°C, for 2 hours, by stirring speed of 170 rpm. Furthermore, the leaching products are separated by filtration. Leaching extracts were characterized using the Atomic Absorption Spectrophotometer (AAS) to determine SiO₂ and Al₂O₃ content.

2.2.2 Synthesis of ASA

Synthesis of ASA was done by co-precipitation method, by adopting a *US Patent* 6399530 [4], that preceded by neutralization process to form a sol phase, stabilizing, followed by introducing a silica solution, and then aging to form an amorphous phase.

Synthesis with a co-precipitation method, using acid of alumina solution and base of Ammonia solution 10 %, for neutralizing step. Neutralizing time, ratio of Si/Al and aging time were used as variable process. While, a pH and temperature of neutralization are as independent process variable, of 7-8 and 50-55 °C, respectively.

The equipment for ASA synthesis shown in Figure 1 includes a laboratory glass reactor and support tool such as hot plate, magnetic stirrer, thermometer. The others else, such as universal pH paper, Buchner funnel, Whatman filter paper, vacuum pump, mortar, measuring cup, impermeable plastic, oven and furnace.

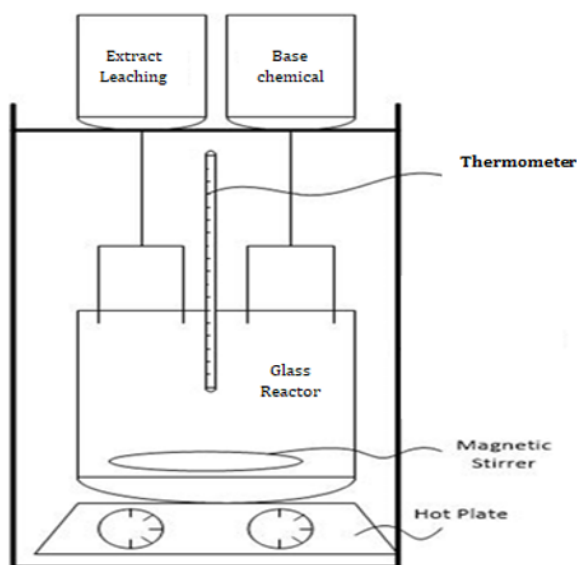


Figure 1. Typical reactor and support tools

2.2.3 Characterization of ASA

The product was filtered and rinsed to a neutral pH, dried in an oven with a temperature of 110°C for 8 hours, and analyzed by a NovaWin Quantachrome for pore structure, mineralogy analysis with instrument of XRD Brucker, and morphology analysis with instrument of SEM JEOL.

3 Results and discussion

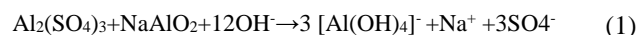
3.1 Dealumination metakaolin by leaching

The alumina concentration in the extracts of metakaolin leaching in between 20-24 g / L was obtained by using HCl 2.5 M at temperature of 100°C during 2 hours, which is used as an alumina source in ASA synthesis. Extracts of metakaolin leaching also contain SiO₂ about 0.09 g / L.

3.2 Synthesis of ASA from kaolin

The synthesis of ASA using alumina from extract of metakaolin leaching was carried out by co-precipitation method, at temperature of 50-55°C and pH in between 7-8 for neutralizing stage using 10% ammonia solution to form sol, and at temperature of 50-55°C and pH 8-9 for aging stage to form gel. The results of pore structure ASA shown in Table 1 and diffractogram of ASA in FIG.2.

In the reaction of ASA synthesis, formation of sol and gel is written in equations (1) and (2), respectively:



The effect of the Si / Al ratio in the starting material on the ASA pore structure is not significant, as well as the influence of aging time. The Si / Al ratio is predicted to be more likely to affect ASA acidity.

In general, the ASA products with base chemical of NH₄OH solution have good pore structure, by using alumina solution of 20 g/L. It have a high of specific surface area and average pore diameter, which suited as a hydrocracking catalyst support. The ASA results are almost the same as the results obtained by C. Song (2002) that using Al₂O₃ solution above 40 g/L. As a comparison, Rahayu [8] produces a pore structure of ASA with a lower surface area of 372 m²/g, when using a base chemical of NaOH, a higher neutralization temperature and an aging temperature of 65°C and 60°C, respectively. Therefore, in this study was used ammonia solution as a base chemical, which has proven its superiority to get a better pore structure, in addition to being supported by a lower process temperature.

Table 1. Pore structure ASA

Synthesis Process ASA			Pore Structure of ASA		
Neutralizer	Rasio Si/Al (g/g)	Aging Time (Hour)	Average Pore Diameter (Å)	Specific Surface Area (m ² /g)	Tot Pore Vol (mL/g)
Neutralizing, 60 meimutes					
NH ₄ OH	0.11	1	79	446	0.88
		3	80	462	0.95
		5	70	480	0.85
	0.22	1	85	510	1.10
		3	80	535	1.07
		5	82	535	1.10
	0.33	1	97	485	1.18
		3	90	544	1.22
		5	88	536	1.17
Neutralizing, 40 minutes					
NH ₄ OH	0.11	1	61	458	0.70
		3	59	463	0.93
		5	48	479	0.57

Even, Rahayu [9] has also done the synthesis of ASA by using chemicals synthetic of aluminum sulphate $[Al_2(SO_4)_3 \cdot xH_2O]$ and Sodium Aluminate ($NaAlO_2$), and the ASAs product with an average of specific surface area of $383.5 \text{ m}^2/\text{g}$, average pore diameter of 80.7 \AA , and total pore volume of 0.78 ml / g were obtained. This result is lower than the results of the study using extracts of metakaolin leaching. The possibility is the alumina in the extract of metakaolin leaching is more homogeneous than alum solution from synthetic chemicals, even this still has to be verified.

The diffractogram pattern of the synthesized ASAs are shown in Figure 2a, Figure 2b and Figure 2c, that similar to the commercial ASA. Silica is required to provide acidic properties of ASA, however, the addition of Si in the synthesis of ASA may destroy the pore structure and affects the pore structure. In addition, the replacement of the Al atomic site by the Si atom can excessively remove the Bronsted acid-forming group (Si-OH-Al), which will decrease the Bronsted acid concentration [10].

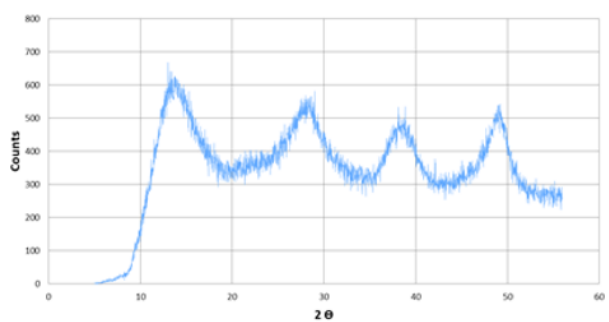


Figure 2a. The ASA with mass ratio Si/Al of 0.11/1 w/w

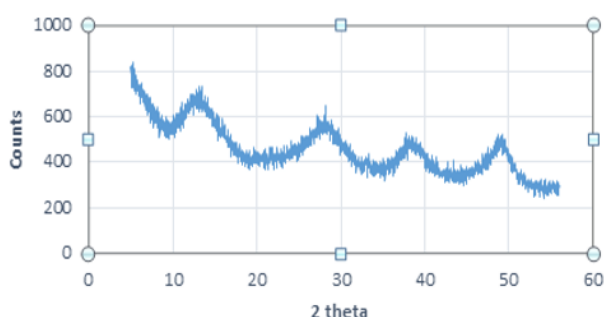


Figure 2b. The ASA with mass ratio Si/Al of 0.22/1 w/w

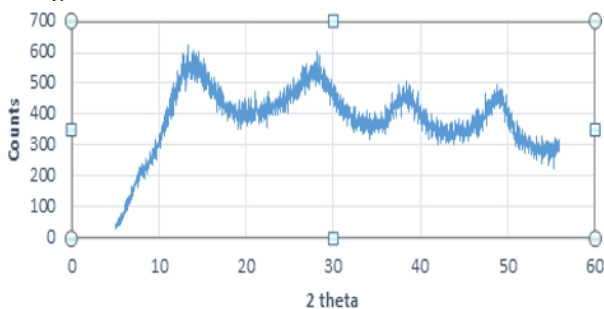


Figure 2c. The ASA with mass ratio Si/Al of 0.33/1 w/w

Figure 2a, Figure 2b and Figure 2c show that the greater Si content in starting material in ASA synthesis, Si will occupy the Al place in the ASA with the greater

amount too, so it adds an amorphous phase in ASA or less in crystallinity.

Conclusion

The results of ASA synthesis with a new method that is using extracts of metakaolin leaching from Indonesian origin Belitung kaolin was obtained, with a good pore structure and a low crystallinity. The increasing of Si/Al ratio in starting material affects on the specific surface area of ASA, as well as with aging time. The product of ASA with a specific surface area of $510 \text{ m}^2/\text{g}$, an average pore diameter of 85 \AA , a total pore volume of 1.1 mL/g , and an amorphous phase of 53%-mass were observed. The effect of Si / Al ratio and aging time in ASA synthesis is not significant to the pore structure, but apparently the time of neutralization can affect the pore structure significantly. The results of the ASA synthesis using this new method can match to the synthesis results of ASA using synthetic chemicals. It obtained a good pore structure, even alumina concentrations in the extract of metakaolin leaching lower than by using synthetic chemicals. It is predicted that the solubility of alumina in the metakaolin leaching extract is higher than when using synthetic chemicals.

Authors would like thanks to Directorate General of Research Reinforcement & Development for funding this research through the National Competition Grants Program, PSN, 2018.

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