

Characterization Of Silica-Alumina Synthesized From Glass Waste By Double Templates *Cetyltrimethylammonium Bromide* (Ctab) And *Trimethylammonium Chloride* (Tmacl)

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Abstract: Synthesis of silica-alumina was done to overcome the limitations of pore diameter of natural zeolite as a catalyst. Due to the effectiveness of catalysis was constrained by the pore size, therefore, some efforts are needed to increase the pore size by using a double template, namely cetyltrimethylammonium bromide (CTAB), which was as a templating agent and trimethylammonium chloride (TMACl) as co-surfactant. Silica was extracted from the glass by Na_2CO_3 to form sodium silicate. Sodium aluminate was obtained from the reaction of $\text{Al}(\text{OH})_3$ with NaOH . The synthesis of silica-alumina $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 7:1, 7:2, and 7:3 with surfactant concentration of 0.6 M CTAB and 0.3 M TMACl. The hydrothermal processes at 100 °C for 72 hours. The mixture was filtered and washed until neutral pH, then they calcined at 550 °C for 5,5 hours. The results of all samples had a functional group (1080.14 cm^{-1}). The nature of crystallinity by XRD showed that the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ 7:1 with 0.6 M CTAB had a good crystallinity with the types of nepheline, syn minerals. Characterization of surface properties with a BET surface area analyzer showed that the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ 7:1 with 0.6 M CTAB had the largest pore size of 14.487 Å.

Keywords—silica-alumina, glass waste, double templates, CTAB, TMACl

1. INTRODUCTION

Natural zeolites used as catalysts generally have a pore diameter of less than 8 Å (micropores) so that the catalysis process is constrained by pore size and effectiveness [1]. The larger pore sizes can be formed with pore template, generally in the form of quaternary surfactant such as cetyltrimethylammonium bromide (CTAB) [2][3] and trimethylammonium chloride (TMACl) [4]. Both of the surfactants could produce material with a pore diameter of > 20 Å (mesoporous).

On the other hand, glass material is widely used in everyday life and waste of broken glass from household is not used and can even be harmful to the environment. The silica content in glass is between 65-80%, so that glass waste can be used as an alternative source of silica.

Alumina silica material has the advantage of a combination of large surface area, high porosity and high thermal stability [5]. Silica alumina has been synthesized using many variables, especially the type of crystal structure-forming materials, surfactants as pore molds (templates), solvents and base conditioners used so that it is expected that the pore size and reactivity of new materials are as needed. In addition, to obtain silica alumina material with good crystallinity and large pore diameter, the synthesis factors were examined, namely the use of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, pH, temperature, and surfactant concentration [6].

According to Sarti et al. [7] studied the effect of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and thermal treatment of zeolite on the adsorption of toluene. The amount of silica and alumina in the silica alumina material which can affect the nature of hydrophobicity. Furthermore, they affected the pore size, crystallinity and has a role in determining the structure and composition of the alumina silica material product. The characteristics of silica alumina material with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio have hydrophobic characters and organophilic surface properties and low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio have hydrophilic characters and polar surface properties and usually a low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can be used as a cation exchanger with the tetrahedral silica alumina molecular framework.

According to Tengker and Falah [8] the concentration of surfactants in the synthesis of silica alumina material also affects the resulting synthesis product, namely the greater the concentration of surfactants used, the better the resulting product includes pore size and crystallinity. Previous research conducted by Dipowardani et al. [4] examined the effect of double template concentrations of CTAB and TMACl on the synthesized of crystalline silica. CTAB concentrations of 0.6 M and TMACl 0.3 M produced a product with the largest surface area and pore volume compared to others.

Critical Micellization Concentration (CMC) is the minimum concentration of surfactant molecules required for the formation of micelles from monomer aggregates [9]. The CMC 1 CTAB and CMC 1 TMACl values (from pre-micelle to spherical micelle) were 8×10^{-4} M and 2×10^{-4} M, respectively, while the CMC 2 CTAB and TMACl (spherical

micelle to rodlike micelle) are 2.0×10^{-2} M and 1.2×10^{-1} M [10][11]. As the temperature increases, the concentration required for the transformation from CMC 1 to CMC 2 will increase. If the concentration and amount of surfactant needed is increasing, it is expected that the micelles formed to interact with the silica alumina framework will also be larger so that the pore mold is expected to be larger [12].

The use of cetyltrimethylammonium bromide (CTAB) and trimethylammonium chloride (TMACl) surfactants as pore-forming agents, which are cationic surfactants with positive characteristics, are expected to interact electrostatically with the silica alumina framework which is more negative in character. Based on this background, the research was carried out in the preparation of silica-alumina from household glass waste with a double template of CTAB and TMACl. It is expected to produce a pore size of $> 20 \text{ \AA}$ (mesoporous). This research also examines the effect of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on the crystallinity and pore size of the silica-alumina material.

2 METHODOLOGY

Tool: hot plate, Ariston oven, Vulcan furnace, Whatman 42 filter paper, nickel crucible, Teflon container, analytical balance, spectrophotometer FTIR (Fourier Transform Infrared) Thermo Nicolet Avatar 360, XRD (X-Ray Diffraction) Shimadzu 6000, GSA (Gas Surface Analyzer) NOVA 1000, and AAS (Atomic Adsorption Spectroscopy) Perkin-Elmer 26

Material: Used household glass waste, H_2O , Na_2CO_3 (Merck), Tetraethylortosilicate (TEOS) (Merck), NaOH (Merck), Trimethylammonium-Chloride (TMACl) (Merck, 99%), Cetyltrimethylammonium-Bromide (CTAB) (Merck, 99%), $\text{Al}(\text{OH})_3$, CH_3COOH , and NH_3

Preparation of Sodium silicate: The glass waste is cleaned from impurities and then dried. Clean and dry glass is digested until it forms a fine glass powder. Then sieved using a 100-mesh sieve. Ten grams of glass powder were added 17.6 g Na_2CO_3 and heated in a furnace at a temperature of $900 \text{ }^\circ\text{C}$ for 5.5 hours. The solid product was dissolved in distilled water, and filtered until a sodium silicate filtrate was obtained. The dissolution was repeated until 200 ml. Determination the dissolved silica content by AAS spectrophotometer.

Preparation of Sodium aluminate: Thirty grams of NaOH were dissolved into 100 mL of distilled water then stirred and heated until boiling. Twenty grams of $\text{Al}(\text{OH})_3$ added to the solution, stirring gradually until dissolved. Then it was diluted to 250 mL.

Synthesis of silica alumina: In this study we used double templates, namely cetyltrimethylammonium bromide (CTAB) and trimethylammonium chloride (TMACl) surfactants with a concentration ratio of 2:1. The first step was dissolving the surfactants cetyltrimethylammonium bromide (CTAB) and trimethylammonium chloride (TMACl)

with the addition of each of 20 mL of distilled water. Furthermore, for $\text{SiO}_2/\text{Al}_2\text{O}_3=7:1$ was synthesized by 17.18 mL of sodium silicate and 15.514 mL of TEOS were mixed into a mixed surfactant solution of CTAB and TMACl Then 9.77 mL of sodium aluminate was added into the mixtures. The addition of 15% CH_3COOH was carried out to reached the $\text{pH}=10$. The mixture was put into a Teflon container and heated at $100 \text{ }^\circ\text{C}$ for 72 hours. The solid product was washed and dried until constant weight. The final product was noted as SA-7163

In the same way, silica alumina the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3=7:2$ (SA-7263) and $\text{SiO}_2/\text{Al}_2\text{O}_3=7:3$ (SA-7363) was synthesized. The synthesized products were characterized by FTIR, X-ray diffraction, and GSA.

3 RESULTS AND DISCUSSION

3.1 Characters of functional groups

Characterization using a FTIR (Fourier Transform Infra Red) spectrophotometer to predict the functional groups present in the synthesized product. The wave number used to measure the absorption bands that occur between $300\text{-}4000 \text{ cm}^{-1}$. The vibration frequency of the middle or medium infrared region is in the wave number $300\text{-}1300 \text{ cm}^{-1}$. This region provides information about the tetrahedral state of aluminate and silicates $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$, while the vibrational region $1300\text{-}4000 \text{ cm}^{-1}$ provides information on other functional groups [13].

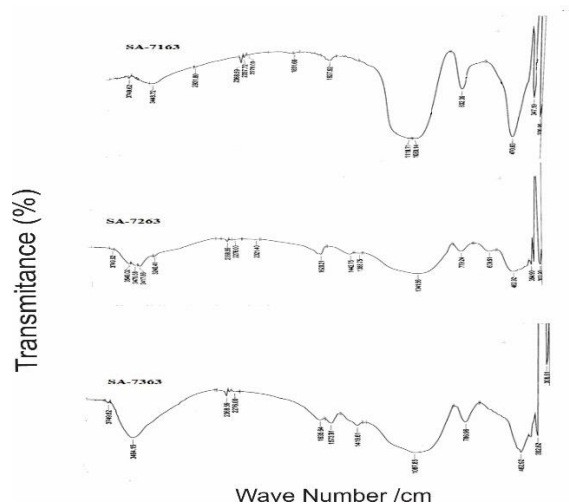


Fig. 1. FTIR spectra of silica alumina with $\text{SiO}_2/\text{Al}_2\text{O}_3=7:1$ (SA-7163), $7:2$ (SA-7263) and $7:3$ (SA-7363) with surfactant concentrations of 0.6 M CTAB and 0.3 M TMACl.

Figure 1 shows all the silica alumina produced by the synthesis show the presence of silanol groups, it proven by the appearance of the absorption band at the wave number $3700\text{-}3200 \text{ cm}^{-1}$ which is the $-\text{OH}$ symmetry stretch vibration of Si

– OH and in the 1700-1600 cm^{-1} region which is the bending vibration of –OH from Si – OH. The presence of siloxane groups can be seen by the appearance of the absorption band at wave number 1110 - 1000 cm^{-1} which is the asymmetric stretching vibration of Si – O from Si – O – Si, the wave number 900-800 cm^{-1} which is the stretching vibration of Si – O symmetry from Si – O – Si and at the wave number 500-400 cm^{-1} which is the bending vibration of Si – O – Si. The double ring is a specific character indicated by the appearance of absorption at the wave numbers 700–500 cm^{-1} . This double ring is an external braid between one layer and another. The absorption at this wave number is shown by the SA-7263 although the absorption peak is very low. The wave number 800 -700 cm^{-1} is the stretching vibration of Si-O from Si-O-Si shown by all the products which show that a stable silica alumina framework has been formed. The wave number 1110 - 1000 cm^{-1} is the strongest intensity of the internal and external Si-O tetrahedral stretching vibrations of Si-O-Si and is a characteristic of alumina silica products. In Figure 1 also observed the presence of absorption bands in the frequency area around 400 - 300 cm^{-1} which indicates an external vibration of the 12-ring, which indicates that the products formed pores.

The wave number 2450-2200 cm^{-1} , which is the vibration of atmospheric CO_2 molecules, it is still appears in product SA-7163, SA-7263, and SA-7363. This vibration strengthens the remaining decomposition of CTAB and TMACl surfactant molecules in the form of CO_2 which is still trapped in all products even though the calcination has been carried out at temperatures up to 550 °C. The absorption at 1475-1300 cm^{-1} indicated that there was a C-H bending vibration which further strengthened that in the SA-7263 and SA-7363, there were C-H groups from the surfactant molecules CTAB and TMACl which had not been evaporated completely during the calcination process. The incomplete removal of surfactant molecules is possible because of the damage to the silica structure of alumina when calcination reaches a temperature of 550 °C which is indicated by the lower absorbance in the area of asymmetric stretching vibration of TOT at the wave number 1250-800 cm^{-1} and the bending vibration absorption of TOT at 470-400 cm^{-1} . The breakdown and irregularity of the silica alumina framework is strengthened by the appearance of absorption at 3749.62 cm^{-1} which indicates the presence of free Si-OH on the surface of the synthesized products. The free Si-OH will block the surfactant molecules from being liberated in the calcination process.

3.2 Characters of the crystal of products

The result of characterization of X-ray diffractogram shows the relationship between the intensity of the reflected light and the angle of diffraction. The diffraction angle (2-theta value) indicates the dimension of the unit cell of the crystal, while the intensity of the reflected light represents the distribution of electrons in the unit cell crystal so that the characteristic characteristics of a particular crystal can be known [14]. The highest peaks at an angle of 2 θ are compared with the data

from the Joint Committee on Powder Diffraction Standards (JCPDS).

The diffractogram peaks of the silica alumina products are not too sharp, indicating that the crystallinity tendency is still low. In Figure 2 (a), the trend in the SA-7263 is amorphous. This is partly due to the imperfect hydrothermal process. The empirical data on the relationship between composition, temperature, reactant type and other factors are very influential in the synthesis of silica alumina types. Generally, the synthesis conditions depend on the starting material, pH system, hydrothermal temperature with a pressure corresponding to saturated water vapor pressure, high levels of saturation of the gel component which can lead to large amounts of crystal nucleation [15]. These complex synthesis conditions greatly affect the process of crystal formation and the product of synthesis. The product of the synthesis can be different if one of the factors at the time of synthesis is different.

Another factor that makes the less crystallinity is the condition at the calcination. According to Deng et al. [16], the presence of water vapor at calcination temperature besides hydrolyzing Al which has a Bronsted acid site in the framework also results in the lability of the oxygen skeleton. As a result, the silica alumina framework is easily shaken and damaged. Calcination also causes shrinkage of the walls of the framework for each unit cell and if the silica alumina framework is formed is unstable, the framework can be damaged.

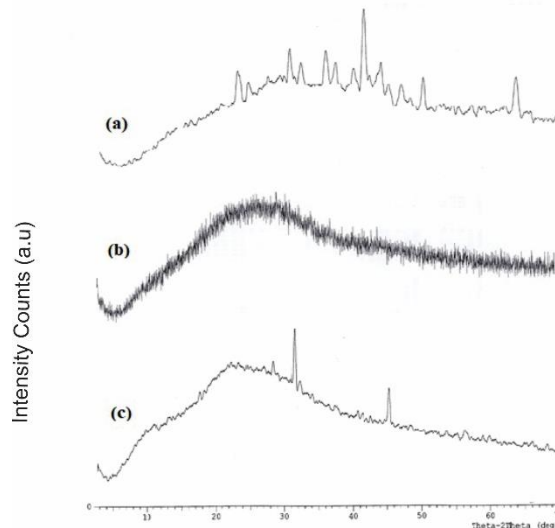


Fig. 2. The Diffractogram XRD of silica alumina $\text{SiO}_2/\text{Al}_2\text{O}_3$ (a) 7:1 (SA-7163), (b) 7:2 (SA-7263) and (c) 7:3 (SA-7363) with surfactant concentrations of 0.6 M CTAB and 0.3 M TMACl

Figure 2 shows that the diffractogram pattern of each alumina silica product has a different crystallinity which is indicated by the appearance of special peaks at a certain angle of 2 θ and the intensity of the diffractogram. The 2 θ data and the intensity obtained were then compared with the standard

data of the Joint Committee on Powder Diffraction Standards (JCPDS). The mineral type identified on SA-7163 and SA-7363.

The greater the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio, the better the crystallinity properties. This shows that the hydrothermal and calcination processes have been completed so that the silica alumina framework is stable. In addition, a few crystals are formed because there is still a lot of unreacted silica. According to Sriatun et al. [2] at least crystals are formed because they are still in a metastable phase, which is the phase where the embryo nucleus is formed. The metastable phase that appears can be formed at a low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [17] [18]. The formation of the crystal nucleus embryo in the synthesis of silica alumina is a metastable phase, where if the synthesis time is extended, the metastable phase will change to the silica alumina phase with the formation of crystal growth [13].

In product SA-7163, SA-7263, and SA-7363 used 0.6 M of CTAB. According to Sriatun et al.[3] the higher surfactant concentration would proceed the higher the relative intensity of the product. The increase of peaks was due to the structuring of the silica alumina framework by the CTAB and TMACl pore casters. The higher the crystallinity tendency, the clearer the peak separation in the silica alumina products. Increasing the concentration of CTAB and TMACl can increase the crystallinity of alumina silica. The number of silicate ions and aluminate ions surrounding the CTAB and TMACl template micelles will form silica alumina with almost the same size so that it will increase the crystallinity of the alumina silica material.

The identification of modified compounds aims to determine the specific types of product. Based on the data, it can be concluded that SA-7163 is similar to Nepheline, syn (ID 19-1176), SA-7363 is similar to Tetranatrolite (ID 33-1205),

3.3 Pore characters of the products

Gas surface analyzer is used to determine the pore size, total pore volume and pore surface area of the silica alumina product. The pore size classification according to IUPAC (Do, 1998) is: micropores ($d < 20 \text{ \AA}$), silica alumina (mesoporous) ($20 < d < 500 \text{ \AA}$) and macropores ($d > 500 \text{ \AA}$).

Table 1: Average pore radius, total pore volume and specific surface area of product

Code product	Average pore radius (\AA)	Total pore volume (cc/g)	Specific surface area (m^2/g)
SA-7163	14,487	21,8678	46,5234
SA-7263	13,552	6,5575	14,9487
SA-7363	14,219	9,8225	21,4590

Table 1 shows that the silica alumina products have micropore pore sizes because the average pore radius is less than 20 \AA [12]. This is not in line with expectations, namely with the

presence of CTAB and TMACl surfactants as pore-forming agents, it is expected that the resulting pore size will be more than 20 \AA (mesoporous), because CTAB and TMACl have micelle diameters of 23.36844 \AA and 4.19924 \AA which are capable of forming sizes. mesoporous pores.

The formation of micropore material occurs due to the uneven opening of the pore cavities. This is due to the factors that influence it. This factor is the inadequate calcination process, which causes the pores of the material to be completely unopened. Not decomposing the CTAB and TMACl surfactants will cause a decrease in the surface area of the resulting material because the pores that are formed will be filled with compounds from the surfactant residue. The large surface area can provide an advantage when applied as a supporting catalyst because it allows better interface contact of the substances to be reacted so that it is expected to increase the reaction [19].

In this study, the change of TEOS to silica SiO_2 oxidation occurred at a temperature of around $550 \text{ }^\circ\text{C}$, which is when the calcination process took place. The temperature at the time of calcination is also a factor that affects the results of the surface area of the formed sample material. A perfect calcination will leave open pores so that the surface area of the material increases. Characterization obtained in SA-7163, SA-7263, and SA-7363 shows that the greater the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the greater the resulting surface area. In addition, it also affects the total pore volume, which is also getting bigger and the average pore radius is also getting bigger even though there is no significant increase.

The factors that affect the surface area of the synthesized material apart from the above are the hydrothermal time which causes the crystallinity of the resulting material to increase so that more pores are formed which results in an increase in pore volume and an increase in surface area. Calcination temperature, that is, perfect calcination will leave open pores so that the surface area of the material increases. The use of the same guide molecule does not necessarily result in the same pore size and number because the pore formation of the material does not only depend on one factor.

The addition of different silica sources also causes the pore size of the yield material to be different due to the difficulty in the formation of the framework. The most influential factor here is the Si / surfactant ratio, because an excessive amount of Si and not balanced with the amount of pore forming (surfactant) will reduce the pore radius. Si that is free (Si that is not bound to the surfactant) will form amorphous silica.

4 CONCLUSIONS

Silica alumina has been successfully synthesized from household glass waste using a double template in the form of a mixture of surfactants cetyltrimethylammonium bromide (CTAB) and trimethylammonium chloride (TMACl). The product has the best crystallinity in the SA-7163 and the mineral is Nepheline, syn. With average pore radius of 14.487

Å, a specific surface area of 46.5234 m²/g and a total pore volume of 21.8678 cc/g.

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