

Effect of Hydrothermal Time on The Character of High Silica Sodalite

Sriatun¹ and Ranu Luthfi Ananto²

¹Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Indonesia

sriatun71@gmail.com

²P.T. Pan Brothers Tbk, Indonesia, Ranulutfi96@gmail.com

Abstract: Zeolites are aluminosilicate microporous crystals with intrinsic properties of acidity, high surface area, high thermal stability, and shape selectivity. Synthetic zeolite is engineered to obtain a better character than natural zeolite. High Silica synthetic zeolite is hydrophobic. It can interact with non-polar molecules. This study aims to determine the effect of hydrothermal time on the character of high silica Sodalite. The synthesis is preceded by a sodium aluminate solution reacted with sodium silicate at a Si/Al 20 mole ratio. The gel was heated using the hydrothermal method in an autoclave at 200 °C for 12, 18, 24, and 48 hours. Furthermore, the hydrothermal product was neutralized, dried, and analyzed using X-ray Diffraction (XRD) and Fourier Transform InfraRed (FTIR). The FTIR analysis shows that all products of hydrothermal time variations have O-T-O bending vibration absorption at wavenumber 500-420 cm⁻¹ and Single four-ring (S4R) at 650-500 cm⁻¹. Internal asymmetric stretching vibrations of O-Si-O or O-Al-O at wavenumbers 1250-950 cm⁻¹. Based on FTIR deconvolution, the increase in hydrothermal time causes the Si-OH/Si-O-Si ratio to decrease, which indicates an increase in hydrophobicity. The XRD analysis showed that the hydrothermal time products of 12 and 18 hours were still amorphous, while the hydrothermal times of 24 and 48 produced crystalline products, but the intensity was still low.

Keywords—high silica sodalite; hydrothermal time; crystallinity; hydrophobicity; deconvolution

1. INTRODUCTION

Zeolite Sodalite (SOD) is a zeolite material obtained as a single crystal. Sodalite is an important host molecule for creating a simple periodic arrangement of various types of synthetic zeolites. Sodalite is not only a framework for zeolite A (LTA), but zeolite is a skeleton building unit for other types of zeolites. Sodalite is one of the ten types of framework CRCs (compound-related cancrinite and sodalite). The difference is the aluminosilicate framework, composition and distribution of components in the extra-framework [1].

In general, zeolites are divided into two, namely natural zeolites and synthetic zeolites. Natural zeolites usually contain K⁺, Na⁺, Ca²⁺, or Mg²⁺ cations, while synthetic zeolites usually only contain K⁺ or Na⁺ cations. In natural zeolites, the presence of water molecules in the pores and free oxides on the surface such as Al₂O₃, SiO₂, CaO, MgO, Na₂O, and K₂O, can cover the pores or active sites of the zeolite to reduce adsorption. capacity and properties of zeolite catalysts. One type of synthetic zeolite is a zeolite with a high silica content, this type of zeolite absorbs non-polar molecules so it is very well used as an acid catalyst for hydrocarbons. The type of zeolite is Sodalite zeolite with high silica [2].

Luo et al. [3] have researched the synthesis of Sodalite without a template, the method used is the hydrothermal method. The hydrothermal process was carried out at 100 °C for 18 hours. In this study, coal fly ash was used as a source of silica and alumina, while the FTIR, XRD and SEM characterizations were used. The results showed that Sodalite with high crystallinity at the crystallization time of 12 hours, SEM showed a change in morphology from fly ash to Sodalite which was initially in the form of fine and round particles and

amorphous morphology to petals and the particle size was around 1 μ.

Mohiuddin et al. [4] synthesized zeolite by hydrothermal method using kaolin from Grahams City, South Africa, at hydrothermal time variations of 120, 150 and 190 °C with time variations of 24, 48 and 96 hours. The results obtained indicate that temperature and time are very important for the formation of crystallinity, zeolite purity and optimal conditions are at 150 °C and 48 hours. At 120 °C the gel mixture remains largely amorphous and at 190 °C the zeolite changes to a more stable phase such as quartz. Crystallization time was also shown to influence the physical properties of the zeolite, where the optimal temperature at 150 °C and 48 hours showed a hexagonal-shaped lump morphology with crystal sizes ranging between 1 and 5 μ.

The synthesis of sodalite from kaolinite using hydrothermal temperatures at 200 -800 °C for 5 minutes to 60 minutes has been carried out by Song et al. [5]. The results show that at high temperatures 700 °C – 800 °C the sodalite contain are higher. Hartanto et al. [6] used kaolin from Bangka, Indonesia, as a source of aluminium and silica in the synthesis of high-silica zeolite, without an organic template but using a seeding technique with variations in the H₂O/SiO₂ molar ratio 15, 25, 30, and 35. The hydrothermal process was carried out at 175 °C for 72 hours. In this study, it has been proven that kaolin from Bangka, Indonesia can be used as a source of aluminum and silica in zeolite synthesis without using an organic template, indicating that zeolite synthesis takes place optimally with a molar ratio of H₂O/SiO₂ 30, has the largest crystallinity 59.44% and crystal size 3.795 μm.

Sriatun et al. [7] have investigated the manufacture of zeolite from bagasse ash using the hydrothermal method at a temperature of 100 °C for 3 days. In this study, a high Si/Al

ratio (15 and 25) resulted in NaP1 type zeolite. In another study, sodalite with a high Si/Al 30 ratio also has been synthesized hydrothermally at a temperature of 200 °C for 24 hours [8].

Wei et al. [9] have researched the effect of Si/Al ratio on acid site accessibility and catalytic performance in 2D and 3D MFI Zeolite. the method used is the hydrothermal method, at a temperature of 180 °C for 48 hours. Meanwhile, the ratio of Si/Al was varied with ratios of 15, 30, 50 and 87. The results showed that when the Si/Al ratio increased, the ratio of the number of strong acid sites decreased, while the average strength and accessibility of acid sites increased.

Jiang et al. [10] conducted a study in which high silica zeolite synthesized from palygorskite (PAL), previously used PAL was prepared with acid as the source of silica and aluminium. The method used in this research is hydrothermal and using a template tetrapropylammonium bromide (TPABr), the hydrothermal process is carried out at 180 °C for 48 hours. The results showed that the high temperature and length of hydrothermal time were beneficial for the transformation of PAL into zeolite as well as increasing the crystallinity of the zeolite. High silica sodalites have also been successfully prepared using TPABr and CTABr templates by the hydrothermal method at 200 °C for 24 hours [8]. Meanwhile, mesoporous sodalite has been prepared using inorganic salts by hydrothermal method at 90 °C for 36 hours [11]. Even hydroxy sodalite has been developed through the pore-plugging hydrothermal (PPH) method [12].

Based on this background, this report examines the effect of hydrothermal time on the character of high silica Sodalite.

2 METHODOLOGY

Tool: Analytical balance Ohaus, Autoclave, Whatman 42 filter paper, Teflon container, pH meter, hot plate JLabTech, magnetic stirrer, oven Shimadzu. X-Ray Diffraction (XRD) (Philip Analytical JOEL JDX-3530), Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu).

Material: Aquadest, sodium silicate (Merck), Sodium hydroxide (Merck), Aluminum hydroxide (Merck, powder).

Synthesis of high silica sodalite: Sodalite was synthesized by hydrothermal method with the Si/Al 20. First, NaOH was dissolved with aquabidest. After the NaOH dissolves, Al(OH)₃ is added by heating until dissolved. Then sodium silicate solution was added. The mixing was carried out with a magnetic stirrer at room temperature. The result is an aluminosilicate gel which is then stirred to form a thick solution. The mixture was transferred to an autoclave and heated at a temperature of 200 °C for 12 hours, 18 hours, 24 hours, and 48 hours. The product from the autoclave was filtered and washed with distilled water until neutral. The product as a white solid was dried at 90 °C for 2 hours. Product characterization using X-ray Diffraction (XRD), and Fourier Transform Infra-Red (FTIR).

3 RESULTS AND DISCUSSION

3.1 Product Crystallinity

Characterization using XRD instruments aims to identify the crystalline phase of the product and determine the type of mineral constituent. After the synthesis process, XRD identification results were obtained from samples of high silica Sodalite zeolite with a ratio of 20:1 at 200°C with time variations of 12 hours, 18 hours, 24 hours, and 48 hours. The results of the XRD diffractogram are shown in Figure 1.

The diffractogram of the XRD test results in Figures 1 shows that at the hydrothermal time variation of 12 hours and 18 hours, no crystal peaks were formed, even though at 12 hours 1 very low peak appeared sample was still amorphous. From the graph of the diffractogram, it can be seen that the crystallinity peak began to be seen at the 24-hour hydrothermal time variation and showed the most optimal crystal peak at the 48-hour hydrothermal time variation. This is in accordance with the research conducted by Mohiuddin, et al. [4], the results of the study show that hydrothermal time greatly affects the crystallinity and the resulting zeolite product. Hydrothermal time affects the occurrence of nucleation and crystallization of zeolite synthesis results.

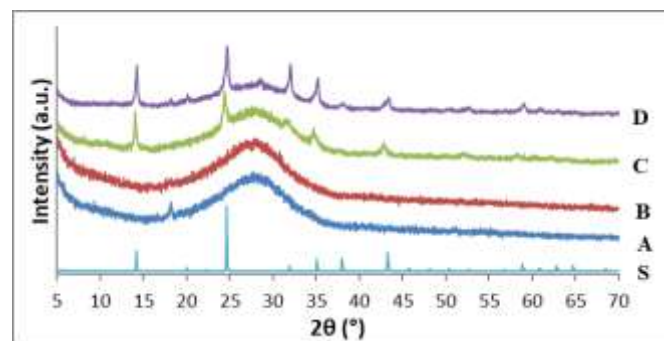


Fig. 1. Synthesized high silica sodalite XRD diffractogram at time variation S: Standard, A: 12 h, B: 18 h, C: 24 h, D: 48 h

Based on Figure 1, the overall crystallinity of the synthesized High Silica Sodalite is still quite low. Therefore, to find out more about the types of zeolites, a manual qualitative analysis is needed. XRD of synthesized zeolite Sodalite was compared with XRD of standard zeolite Sodalite obtained from RRUFF ID R060436 at a diffraction angle of $2\theta = 14.1^\circ; 24.5^\circ; 31.9^\circ; 35.1^\circ$ and 43.2° which are typical peaks of Sodalite zeolite. The diffraction angle data of synthesized high silicate Sodalite and sodalite RRUFF ID R060436 are presented in Table 1.

Table 1. The diffraction angle data of synthesized high silicate Sodalite

	High silica sodalite				Sodalite RRUFF
	12	18	24	48	
	-	-	14.05	14.28	14.1
Diffraction	-	-	24.37	24.70	24.5

angle (2θ)	-	-	31.57	32.0	31.9
(°)	-	-	34.69	35.22	35.1
	-	-	43.59	43.43	43.2

The crystallinity of the synthesis product increased with increasing hydrothermal time. The hydrothermal process for 48 hours produces high silica Sodalite synthesized with the best crystallinity. These data indicate that the longer the hydrothermal time is carried out, the better the energy and rate of formation of zeolite crystals.

3.2. FTIR characterization results

Qualitatively, Infrared (IR) spectrophotometer characterization aims to identify the functional groups present in the synthesized high silica Sodalite zeolite and to determine the formation of the alumina silicate zeolite framework structure. In general, zeolites have a typical absorption region around the wave number 400-1400 cm-1 which refers to the fundamental vibration of the tetrahedral framework (Si and Al). Where these units are zeolite framework development units. The vibration of 400-1400 cm-1 also provides information about the composition and condition of the SiO44- or AlO45- tetrahedral in the synthetic zeolite [13]. The results of the IR spectra are shown in Figure 2.

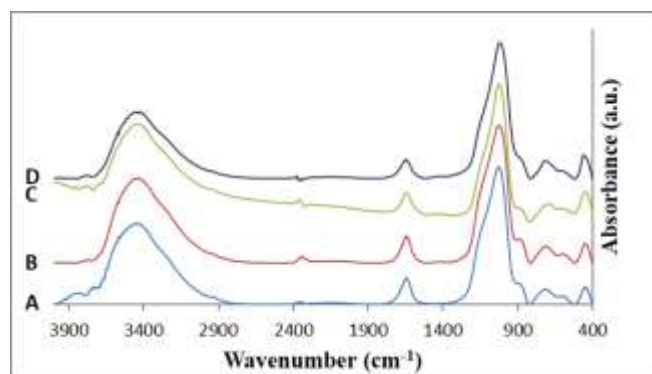


Fig. 2. FTIR spectra of synthesized high silica sodalite A: 12 h, B: 18 h, C: 24 h, D: 48 h

Figure 2 shows strong absorption at wavenumbers 1027, 1023, 1025, and 1019 cm⁻¹, for 12 h, 18 h, 24 h, and 48 h respectively. Strong absorption in this range is a characteristic of internal asymmetric stretching vibrations, namely the O-Si-O or O-Al-O asymmetric strain of the zeolite framework [14].

The absorption band at wavenumbers 720, 715, 690 and 720 cm⁻¹ indicate the external symmetrical stretching of O-Si-O or O-Al-O. The peak spectra in this region are typical peaks of zeolite which are sensitive to changes in structure and composition. zeolite framework [13]. The absorption at wavenumbers 454, 450, 450 and 459 cm⁻¹ indicate a tetrahedral internal bond, namely bending vibrations of O-Si-

O or O-Al-O. Meanwhile, the peak at wavenumbers 597, 595, 583 and 599 cm⁻¹ indicate the external vibration of Single 4 ring (S4R) in the zeolite framework structure.

The absorption formed in the 3600-3100 cm⁻¹ region is identical to the O-H bending vibration. The O-H group is owned by zeolite in the form of Si-OH as well as other groups that may still be left from the synthesis process. This can be strengthened by the absorption of 1670-1600 cm⁻¹ which is the peak absorption of H₂O.

Meanwhile, quantitative analysis of FTIR is used to determine the magnitude of the change in intensity and to determine the effect of functional groups. For this reason, the FTIR spectra were deconvoluted using the Fityk application program by comparing the area of a particular cluster. The area is calculated using the Gaussian method with the same HWHM value for each peak component. The graph of the processing results with the Fityk application can be seen in Figure 3.

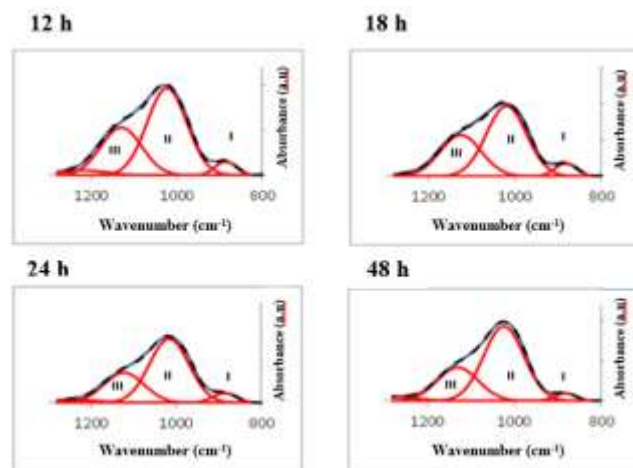


Fig.3. FTIR deconvolution of synthesized high silica sodalite I: Si-OH area, II: Si-O-T area, III: Si-O or Al-O area

The ratio of Si-OH/Si-O-Si is equal to the area of Si-OH (deconvolution peak I) divided by the area of Si-O-T (peak deconvolution II). While for the deconvolution peak III is the peak of the bending vibration of the T-O group where Si-O or Al-O. The results of the calculation of the area are presented in Table 2.

Table 2. The Si-OH and Si-O-Si deconvolution and Si-OH/Si-O-Si ratio of high silica sodalite

Hydrothermal Time (hours)	Area		Si-OH/Si-O-Si Ratio
	Si-OH	Si-O-Si	
12	953.436	11267.7	0.084617
18	878.454	11242.3	0.078138
24	590.752	10955.8	0.053921
48	542.109	11496.6	0.047154

Table 2 shows the extension of the hydrothermal time, the ratio of Si-OH/Si-O-Si decreased. This means that the number of Si-OH groups is much less than the Si-O-Si groups in that time variation. The Si-OH group is easy to interact with water due to the presence of the -OH group. The more Si-OH groups formed, the more amorphous the phase is because it is more soluble in water. Meanwhile, the more Si-O-Si groups formed, the more the framework structure of the zeolite and it can be ascertained that the crystalline phase also increased. The results of the lowest Si-OH/Si-O-Si ratio are at 48 hours variation, this is directly proportional to the data obtained by XRD where 48 hours variation has the best crystallinity.

4 CONCLUSIONS

Based on the description of the results and discussion, it can be concluded that the hydrothermal time greatly affects the crystallinity and structural properties of high silica sodalite. At a Si/Al ratio of 20 and a hydrothermal time range of 12 h, 18 h, 24 h, and 48 h and a temperature of 200 °C, a hydrothermal time of 48 hours produced high silica Sodalite with the best crystallinity and hydrophobic properties, where this obtained the smallest of Si-OH/ Si-O-Si ratio is 0.047.

References

- [1] N. V. Chukanov, S. M. Aksenov, and R. K. Rastsvetaeva, "Structural chemistry, IR spectroscopy, properties, and genesis of natural and synthetic microporous cancrinite- and sodalite-related materials: A review," *Microporous Mesoporous Mater.*, vol. 323, p. 111098, 2021, doi: <https://doi.org/10.1016/j.micromeso.2021.111098>.
- [2] Y. Li, H. Sun, R. Feng, Y. Wang, F. Subhan, Z. Yan, Z. Zhang, Z. Liu, "Synthesis of ZSM-5 zeolite from diatomite for fluid catalytic cracking (FCC) application," *Appl. Petrochemical Res.*, vol. 5, no. 4, pp. 347–353, 2015, doi: [10.1007/s13203-015-0113-2](https://doi.org/10.1007/s13203-015-0113-2).
- [3] J. Luo, H. Zhang, and J. Yang, "Hydrothermal Synthesis of Sodalite on Alkali-Activated Coal Fly Ash for Removal of Lead Ions," *Procedia Environ. Sci.*, vol. 31, pp. 605–614, 2016, doi: <https://doi.org/10.1016/j.proenv.2016.02.105>.
- [4] E. Mohiuddin, Y. M. Isa, M. M. Mdleleni, N. Sincadu, D. Key, and T. Tshabalala, "Synthesis of ZSM-5 from impure and beneficiated Grahamstown kaolin: Effect of kaolin content, crystallisation temperatures and time," *Appl. Clay Sci.*, vol. 119, pp. 213–221, 2016, doi: <https://doi.org/10.1016/j.clay.2015.10.008>.
- [5] Q. Song, J. Shen, Y. Yang, J. Wang, Y. Yang, J. Sun, B. Jiang, Z. Liao, "Effect of temperature on the synthesis of sodalite by crystal transition process," *Microporous Mesoporous Mater.*, vol. 292, p. 109755, 2020, doi: <https://doi.org/10.1016/j.micromeso.2019.109755>.
- [6] D. Hartanto, O. Saputro, W.P. Utomo, A. Rosyidah, D. Sugiarto, T. Ersam, H. Nur, D. Prasetyoko, "Synthesis of ZSM-5 Directly from Kaolin without Organic Template: Part-1: Effect of Crystallization Time," *Asian J. Chem.*, vol. 28, no. 1, pp. 211–215, 2016, doi: [10.14233/ajchem.2016.19348](https://doi.org/10.14233/ajchem.2016.19348).
- [7] Sriatun, Taslimah, and L. Suyati, "Pemanfaatan Katalis Silika Alumina Dari Bagasse Pada Pembuatan Biodiesel Dari Minyak Goreng Sisa Pakai," *J. Teknol. Ind. Pertan.*, vol. 25, no. 1, pp. 35–42, 2015.
- [8] S. Sriatun, H. Susanto, W. Widayat, A. Darmawan, S. Sriyanti, R. Kurniasari, R. Kurniawati, "Synthesis of silica-rich zeolite using quaternary ammonium-based templates," *J. Phys. Conf. Ser.*, vol. 1524, no. 1, pp. 0–11, 2020, doi: [10.1088/1742-6596/1524/1/012087](https://doi.org/10.1088/1742-6596/1524/1/012087).
- [9] R. Wei, H. Yang, J. A. Scott, K.-F. Aguey-Zinsou, and D. Zhang, "2D versus 3D MFI zeolite: The effect of Si/Al ratio on the accessibility of acid sites and catalytic performance," *Mater. today Chem.*, vol. 8, pp. 1–12, 2018.
- [10] J. Jiang, C. Duanmu, Y. Yang, X. Gu, and J. Chen, "Synthesis and characterization of high siliceous ZSM-5 zeolite from acid-treated palygorskite," *Powder Technol.*, vol. 251, pp. 9–14, Jan. 2014, doi: [10.1016/j.powtec.2013.10.020](https://doi.org/10.1016/j.powtec.2013.10.020).
- [11] L. Cui, R. Han, L. Yang, Y. Wu, R. Pei, and F. Li, "Synthesis and characterization of mesoporous sodalite and investigation of the effects of inorganic salts on its structure and properties," *Microporous Mesoporous Mater.*, vol. 306, p. 110385, 2020, doi: <https://doi.org/10.1016/j.micromeso.2020.110385>.
- [12] O. Eterigho-Ikelegbe, S. Bada, M. O. Daramola, and R. Falcon, "Synthesis of high purity hydroxy sodalite nanoparticles via pore-plugging hydrothermal method for inorganic membrane development: Effect of synthesis variables on crystallinity, crystal size and morphology," *Mater. Today Proc.*, vol. 38, pp. 675–681, 2021, doi: <https://doi.org/10.1016/j.matpr.2020.03.693>.
- [13] S. Sriatun, "Sintesis Zeolit A dan Kemungkinan Penggunaannya Sebagai Penukar Kation," *J. Kim. Sains dan Apl.* vol. 7, no. 3, pp. 61–67, Dec. 2004, <https://ejournal.undip.ac.id/index.php/ksa/article/view/3324>.
- [14] C. Wang, J. Zhou, Y. Wang, M. Yang, Y. Li, and C. Meng, "Synthesis of zeolite X from low-grade bauxite," *J. Chem. Technol. Biotechnol.*, vol. 88, no. 7, pp. 1350–1357, Jul. 2013, doi: <https://doi.org/10.1002/jctb.3983>.