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The Effect of Chemical Activation Using Base Solution With Various Concentrations Towards Sarulla Natural Zeolite

THE EFFECT OF CHEMICAL ACTIVATION USING BASE SOLUTION WITH VARIOUS CONCENTRATIONS TOWARDS SARULLA NATURAL ZEOLITE

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Abstract : Material characteristics analysis of Sarulla natural zeolite (SNZ) with base activation has been carried out. The base used was NaOH at various concentrations; 0.2 M, 0.5 M, and 2 M. Base activated catalysts were characterized by X-ray Fluorescence (XRF), X-ray diffractometer (XRD), Fourier-transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM) and gas adsorption analysis using BET method. The procedures applied have caused differences in adsorption and desorption rates as well as the crystallinity values of the catalytic materials. Moreover, the ratio of Si/Al contents has also changed at the lowest concentration. On the other hand, the crystallinity of catalysts has decreased at the highest concentration of base applied. The results are reinforced in FTIR characterization which shows the changes of silanol bonds to become silicate and aluminate. Furthermore, morphological analysis of the catalysts shows that homogenous surface was obtained at low concentration, while rough/lumpy surfaces was obtained at higher concentration.

Keywords : Sarulla natural zeolite, Base activation, Crystallinity

Abstrak : Analisis terhadap karakteristik material dari zeolit alam Sarulla (SNZ) dengan metode aktivasi basa telah dilakukan. Basa yang digunakan ialah NaOH dengan berbagai konsentrasi; 0,2 M; 0,5 M, dan 2 M. Katalis yang telah diaktivasi dengan basa kemudian dikarakterisasi dengan Analisis *X-ray Fluorescence* (XRF), *X-ray diffractometer* (XRD), *Fourier-transform Infrared* (FTIR) *Spectroscopy*, *Scanning Electron Microscopy* (SEM) dan *Gas Adsorption* menggunakan metode BET. Dari

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hasil penelitian, ditemukan perbedaan pada tingkat adsorpsi dan desorpsi, begitu juga dengan kristalinitas pada material katalis. Lebih jauh, rasio konten Si/Al juga berubah pada basa dengan konsentrasi terendah. Di sisi lain, tingkat kristalinitas dari katalis mengalami penurunan pada basa dengan konsentrasi tertinggi. Hasil ini diperkuat dengan data FTIR yang menunjukkan perubahan ikatan silanol menjadi silikat dan aluminat. Lebih jauh, analisis morfologi pada katalis menunjukkan bahwa permukaan yang homogen didapatkan dari penggunaan basa dengan konsentrasi rendah. Sebaliknya, basa dengan konsentrasi tinggi memberikan bentuk permukaan katalis yang tidak homogen serta kasar.

Kata kunci : Zeolit alam Sarulla, Aktivasi dengan basa, Kristalinitas

Introduction

Natural Zeolite (NZ) is usually formed as a secondary mineral in several geological activities in the Earth's crust. Indonesia has got many sources of natural zeolite which are widely spread across various regions such as Lampung (Elysabeth *et al.*, 2019), Bayah (Hartono *et al.*, 2019), Tasikmalaya (Dewi *et al.*, 2016), Ende-Flores (Noelaka *et al.*, 2018), Malang (Erlynata *et al.*, 2014), Gunung Kidul (Hernawan *et al.*, 2015) as well as in Sarulla – North Tapanuli (Sihombing *et al.*, 2020). NZ is available in large quantities at low-cost exploitation and until today, it has not been fully utilized.

NZ shows interesting structural properties like a large specific surface, good flexibility, well-defined micropores in molecular dimensions as well as high chemical and physical stability (Zhong *et al.*, 2019). Besides that, its cation exchange capacity selectivity and catalytic activity, especially of Bronsted Acid sites have allowed NZ to be widely used in various applications such as catalysts in oil industries, adsorbents in water treatment, production of cement, separation of gas and applications in biomedical (Gatta and Lee, 2014).

The utilization of NZ as catalysts is inseparable from activation processes, either physically or chemically. Zeolite chemical activation can be done by treatment with acid or base. In this study, SNZ was activated by using base. Lari *et al.* (2016) reported metal hydroxide of Group 1 in catalyst production by using a base, in which sodium hydroxide was identified to be the most suitable because it produces a stronger catalyst character, forms higher acid sites and minimizes damages in pores. This has led to superior catalytic performance. Rahmayani *et al.* (2020) has activated zeolite by using NaOH at concentration of 2 N, 4 N and 6 N to bind dissolved iron. The study reported that NaOH-activated zeolite can increase the amount of Fe attached to zeolite. This is shown by the changes of colors and morphology of the catalyst material analyzed by SEM. Sadowska *et al.* (2013) have done desilicalization of ZSM-5 zeolite by using NaOH and reported that all Al in the activated zeolite was able to form proton sites while some parts of them had gone through dihydroxylation during the thermal process to produce Lewis acid sites.

Therefore, in this research, material characteristics of SNZ activated by NaOH at various concentrations of 0.2 M, 0.5 M and 2 M will be examined. The produced material is expected to have better catalytic properties which are going to be observed by using SEM, XRD, BET, FTIR and XRF.

Materials and Methods

Materials

The materials used in this study were natural zeolites from Sarulla village, Pahae Jae sub-district, North Sumatra, NaOH (p.a), aquadest and aquabidest purchased from CV Bratachem Indonesia, also nitrogen gas from PT Aneka Gas.

Methods

First NZ is crushed and sieved to obtain 100 mesh size. Then it is soaked in aquadest for 24 hours at room temperature. Next zeolite is filtered and the precipitate is dried at 110 °C then calcined until active natural zeolite (ANZ) is obtained. Desilicalization is done next by using 100 ml NaOH 0.2 M, 0.5 M and 2 M is done subsequently with the same working procedure. ANZ is refluxed at 90 °C for 2 hours, and then it is filtered and washed by aquadest until neutral pH is reached. Next, the sample was dried and calcined for 2 hours at 500 °C along with nitrogen flow until the zeolites was activated by base (ZB). ZB 0.2 M, ZB 0.5 M and ZB 2 M were obtained. The catalyst is characterized by X-ray Fluorescence (XRF) to determine the chemical composition and X-ray diffractometer (XRD Shimadzu 6100) to determine the type and crystallinity by using Cu K α radiation at 40 kV and 30 mA. Functional group analysis was done by using FTIR (FT-IR Shimadzu type 8201-FC), while morphological analysis was done by using SEM type Zeiss EPOMH 10Zss. The surface areas, pore volumes and diameters are analyzed by gas sorption analyzer (NOVA 1200 e) with BET method.

Results and Discussion

XRD Analysis

NZ obtained from Sarulla village is a mordenite-type zeolite reported by Sihombing *et al.*, (2018). The changes of 2θ degree intensity are able to provide observations on the influence of base (NaOH) activation and calcination towards crystallinity, as shown in Figure 1. The level of NZ crystallinity is known from the high and low changes in peak intensity, by using crystallinity degree calculation based on Kaelble (1967). The result of the calculation is shown in Table 1.

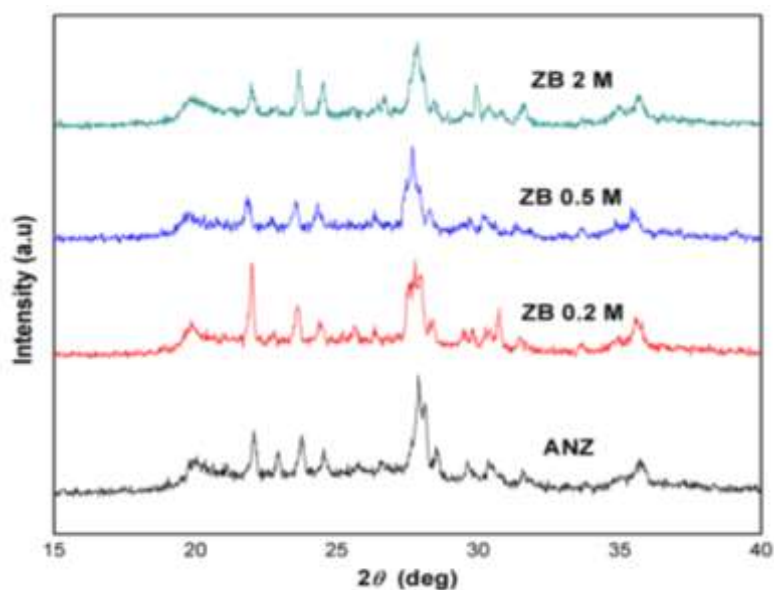


Figure 1. XRD diffractogram comparisons of ANZ ZB 0.2 M, ZB 0.5 M and ZB 2 M

From Table 1, catalyst ZB 0.2 M shows higher crystallinity than ANZ, ZB 0.5 M and ZB 2 M. The higher the intensity, the higher the crystallinity is possessed by zeolite. However, the use of NaOH with greater concentrations (0.5 M and 2 M) shows a decrease in the intensity of the main peak of zeolite compared to the use of 0.1 M NaOH and ANZ. The decrease in peak intensity can be seen at 2θ of 21.06° and 23.65° . The decrease in peak intensity and the shift of the 2θ angle indicate the changes in catalyst structure. This shows that the higher the use of NaOH base, the more Si can dissolve, causing changes in the zeolite structure. Desilicalization process at light (0.1 M and 0.2 M) conditions do not change the crystallinity and are able to maintain zeolite structures. Meanwhile, a higher concentration than 0.4 M will cause a reduction in crystallinity by 65% (Sadowska *et al.*, 2013).

Desilicalization process causes Al to be extracted in a relatively small amount (4 – 5%) with NaOH 0.1 and 0.2 M treatment. When zeolite is treated with 0.5 M concentration, Al loss can be up to 73% (Sadowska *et al.*, 2013). This is consistent with XRD data that shows a decrease in crystallinity of the structure treated with a 0.5 M base.

Table 1. 2θ (degree) peak intensity comparisons of ANZ ZB 0.2 M, ZB 0.5 M and ZB 2 M

ANZ		ZB 0.2 M		ZB 0.5 M		ZB 2 M	
2θ	Intensity	2θ	Intensity	2θ	Intensity	2θ	Intensity
21.06	22	21.97	203	21.81	54	21.99	48
23.65	74	23.58	87	23.50	46	23.63	67
24.47	33	24.41	42	24.31	39	24.47	49
27.93	196	27.94	175	27.64	146	27.80	150
Crystallinity	45.91%		49.50%		32.94%		49.11%

XRF Analysis

Both chemical and physical activations change the ratio of Si/Al of zeolites as shown in Table 2.

Table 2. Si/Al ratio comparisons of ANZ ZB 0.2 M, ZB 0.5 M and ZB 2 M

Composition	%Wt			
	ANZ	ZB 0.2 M	ZB 0.5 M	ZB 2 M
Al ₂ O ₃	38.28	24.06	24.44	26.48
SiO ₂	41.12	44.20	45.72	45.02
Ratio Si/Al	1	1.8	1.8	1.7

From Table 2, desilicalization process is known to increase the Si/Al ratio to be 1.8%. However, at a high concentration, there is a decrease in ratio to be 1.7%. Zeolites which were treated with NaOH contain more aluminium compared to other elements. These results are in accordance with previous studies (Wei *et al.*, 2011; Rownaghi *et al.*, 2011). The desiliconization leads predominantly to the removal of silicon from the zeolite body.

FT-IR Analysis

Figure 2 shows the asymmetric stretch of TO₄ functional group that appears at 900-1250 cm⁻¹ wavenumber (Rahmayani *et al.*, 2020). Asymmetric stretch in ANZ appears at 1042.35 cm⁻¹ wavenumber. While there are shifts to shorter wavenumber in ZB 0.2 M, ZB 0.5 M and ZB 2 M to 1041.22 cm⁻¹, 1038.76 cm⁻¹ and 1039.01 cm⁻¹ respectively with decreases in intensity. These results align with (Park and Kang., 2008 and Panagiotopoulou *et al.*, 2007) that stated shifts occur due to activation treatment with the base which has reorganized Si-O-Si and Al-O-Si bonds to form silicate and aluminate (Palomo *et al.*, 1999). As a result, zeolite structures become more negative. Base activation is not only caused by silanol structures presented in zeolites, but also by the changes in quartz structures such as silica mineral. This is shown by the appearance of 720-650 cm⁻¹ wavenumber in the catalysts.

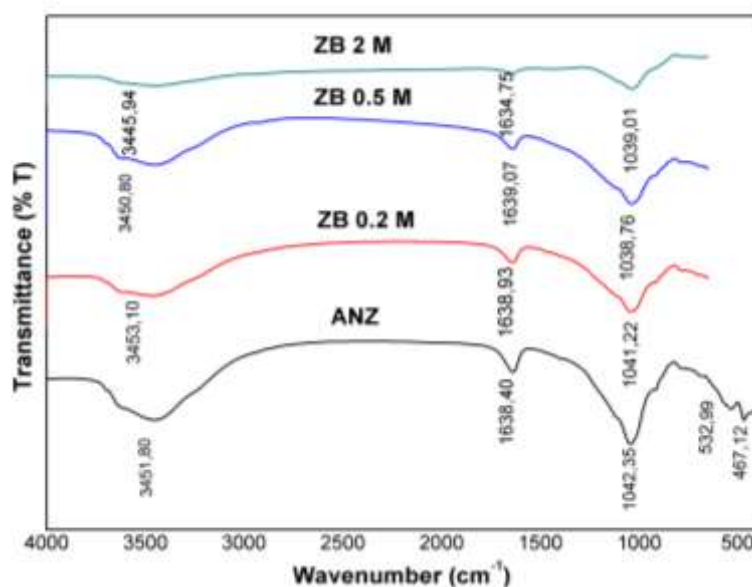


Figure 2. FTIR spectra comparisons of ANZ ZB 0.2 M, ZB 0.5 M and ZB 2 M

Brunauer-Emmett-Teller (BET) Analysis

Table 3 shows that ZB 0.2 M, ZB 0.5 M and ZB 2 M have got smaller surface areas than ANZ. Catalysts ANZ, ZB 0.2 M, ZB 0.5 M and ZB 2 M give the average pore radii of 1.7221 nm, 1.5989 nm, 1.5997 nm and 1.6038 nm respectively. The data illustrates that at the initial state, ANZ had a bigger pore diameter, but after the activation and calcination processes, changes took place and caused the pores of ZB 0.2 M, ZB 0.5 M and ZB 2 M to be tighter. From the results, the pore sizes of the catalysts are micropores and based on the classification from IUPAC (International Union of Pure and Applied Chemistry) they are categorized into Type 1. The size of micropore materials is less than 2 nm (Kanellopoulos, 2011). Adsorption-desorption isotherm graph of ANZ, ZB 0.2 M, ZB 0.5 M and ZB 2 M can be seen in Figure 3. Based on adsorption-desorption isotherm in Figure 3, the pattern in the diagram is categorized into Type IV with the presence of hysteresis loop and high rises in the graph at P/Po (Sihombing *et al.*, 2020; Sihombing *et al.*, 2018; Hasanuddin and Rahmat 2015; Fathi *et al.*, 2014). Moreover, the graph shows that the rate of adsorption is not the same as the desorption rate.

Table 3. Specific surface areas, pore volumes and average pore radii of ANZ ZB 0.2 M, ZB 0.5 M and ZB 2 M

Samples	Surface area (m ² /g)	Total pore volumes (cc/g)	Average pore radii (nm)
ANZ	59.602	0.152	1.7221
ZB 0.2 M	26.936	0.099	1.5989
ZB 0.5 M	22.723	0.090	1.5997
ZB 2 M	25.388	0.094	1.6038

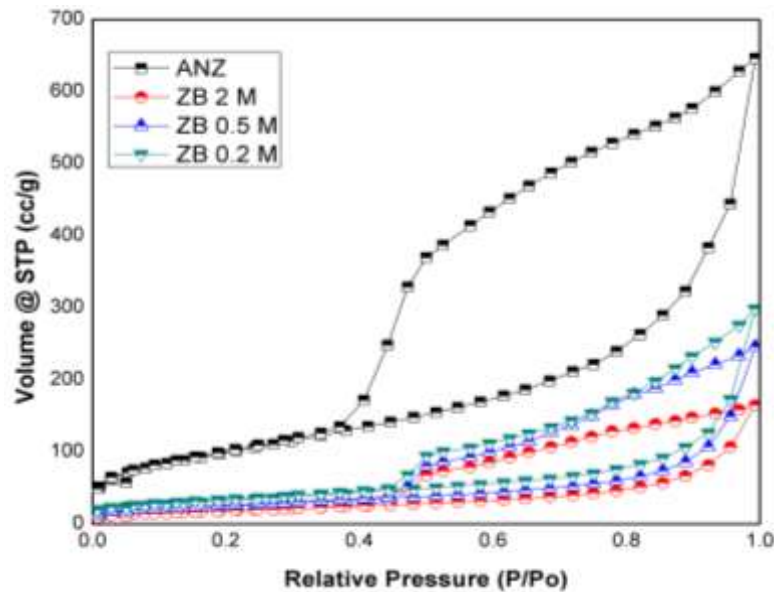


Figure 3. N₂ adsorption-desorption isotherm comparisons of ANZ ZB 0.2M, ZB 0.5M and ZB 2M

In figure 3, the adsorption volume of ANZ is greater than ZB 0.2 M, ZB 0.5 M and ZB 2 M. This data correlates to the previous data, that ANZ has a greater surface area and pore diameter than others.

Surface Morphology

SEM micrograph photos of ANZ, ZB 0.2 M, ZB 0.5 M and ZB 2 M are shown in Figure 4. Figure 4(a) shows that the surface morphology of ANZ is heterogeneous with impurities covering the pores. Figure 4(b) presents a more homogenous and equal morphology. While 4(c) and (d) show heterogeneous surfaces with a tendency to clot and form lumps. Pa and Chik (2018) reported that SEM micrograph of zeolites with 2 M NaOH was observed to have the tendency to be lumpy and rough and it follows the SEM photo of mordenite (Yuan *et al.*, 2007). The same thing has been reported by Fathi *et al.*, (2014), stating that the desilicization process shows a slightly coarser surface morphology, and is in accordance with the adsorption-desorption graph. This has also been reported by Schmidt *et al.* (2013).

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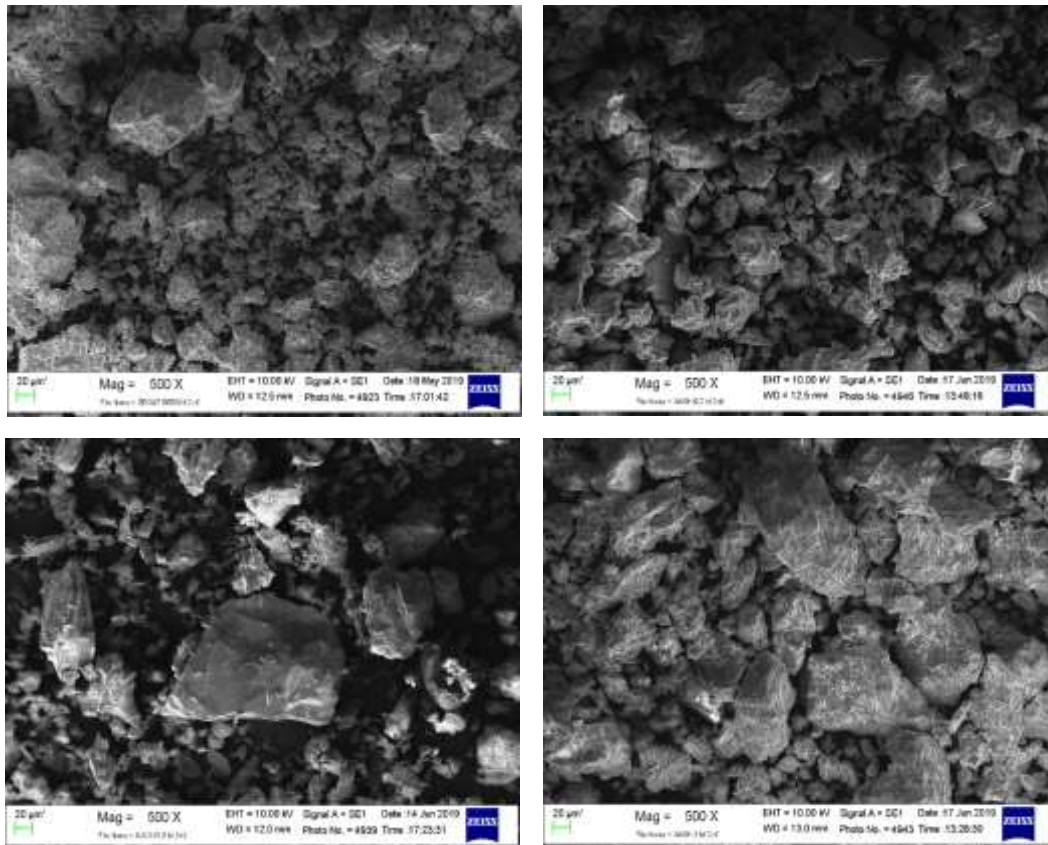


Figure 4. SEM micrograph images result with 500X magnification of (a) ANZ (b) ZB 0.2 M (c) ZB 0.5 M and (d) ZB 2 M

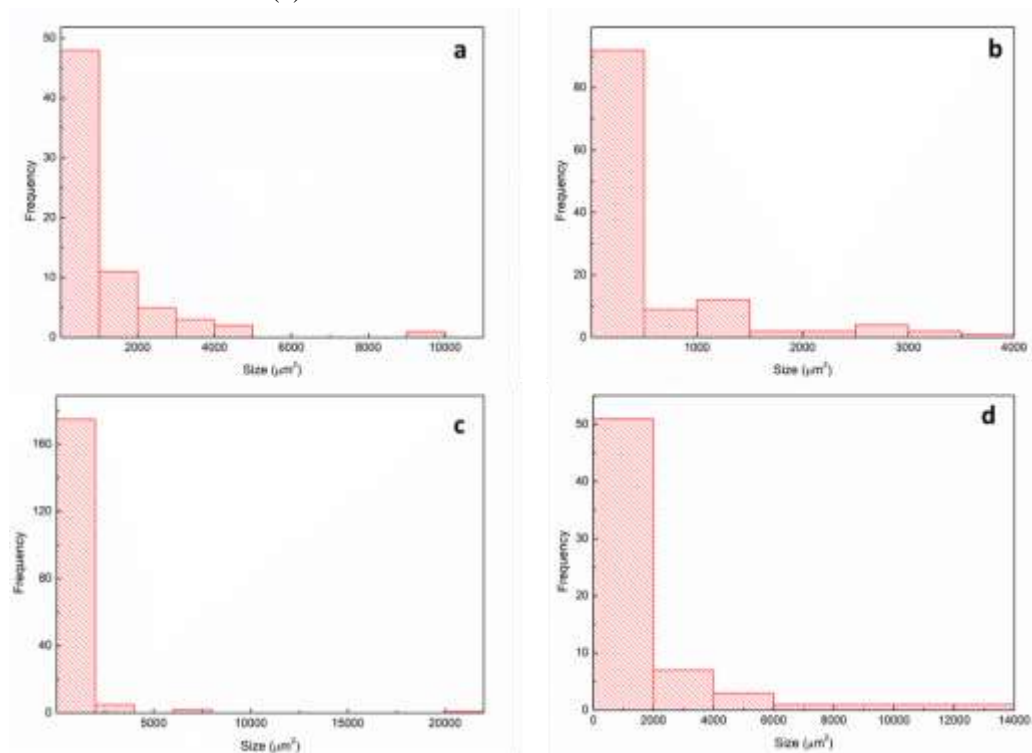


Figure 5. Particle size distribution of (a) ANZ (b) ZB 0.2 M (c) ZB 0.5 M and (d) ZB 2 M

Conclusions

Natural zeolite activation process with NaOH or desilicalization is able to improve crystallinity and the ratio of Si/Al in catalysts at a low concentration such as 0.2 M. Meanwhile at high concentration, such as 0.5 M, the crystallinity of catalyst decreases as reinforced by FTIR characterization with the changes of silanol bonds to become silicate and aluminate. Surface morphology is homogenous at low concentration while lumpy/rough at high concentration. The use of base at low concentration is more effective than in high concentration.

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References

- Dewi, E. M., Suryaningtyas, D.T., & Anwar, S. (2017). Utilization of natural zeolites as Cu (II) and Zn (II) adsorbent. *Journal of Tropical Soils*, 21(3), 153-160. <http://dx.doi.org/10.5400/jts.2016.v21i3.153-160>
- Elysabeth, T., Zulnovri, Ramayanti, G., Setiadi, & Slamet (2019). Modification of Lampung and Bayah natural zeolite to enhance the efficiency of removal of ammonia from wastewater. *Asian Journal of Chemistry*, 31(4), 873-878. <https://doi.org/10.14233/ajchem.2019.21810>
- Erlynata, A., Amalia, S., Adi, T.K., & Khalifah, S.N. (2014). Pemanfaatan zeolit alam, H-Zeolit alam dan Ti-H-Zeolite alam Malang sebagai katalis reaksi isomerisasi glukosa. *Alchemy*, 31-38. <http://dx.doi.org/10.18860/al.v0i0.2898>
- Fathi, S., Sohrabi, M., Falamaki, C., (2014), Improvement of HZSM-5 performance by alkaline treatment: Comparative catalytic study in the MTG reactions, *Fuel*, 116, 529-537.
- Gatta, G. D., & Lee, Y. (2014). Zeolites at high pressure: A review. *Mineralogical Magazine*, 78(2), 267-291. <https://doi.org/10.1180/minmag.2014.078.2.04>
- Hartono, R., Wijanarko, A., & Hermansyah, H. (2019). Modification of bayah banten natural zeolite as heterogeneous catalyst in biodiesel production. *Journal of Applied Engineering Science*, 17(3), 431-438. <https://doi.org/10.5937/jaes17-20399>
- Hasanudin, H., & Rachmat, A. (2015). Isoterm Adsorpsi-Desorpsi dan Porositas Katalis Ag-TiO₂/Zeolit. *Sainmatika: Jurnal Ilmiah Matematika dan Ilmu Pengetahuan Alam*, 7(2). <http://dx.doi.org/10.31851/sainmatika.v7i2.10>
- Hernawan., Wahono, S.K., Maryana, R., & Pratiwi, D. (2015). Modification of Gunungkidul Natural Zeolite as Bioethanol Dehydrating Agents. *Energy Procedia*, 65(2015), 116-120. Elsevier. <https://doi.org/10.1016/j.egypro.2015.01.042>

- Jumaeri, J., Sutarno, S., Kunarti, E. S., & Santosa, S. J. (2009). The Effect of NaOH Concentration and Temperature on Zeolite Synthetis From Fly Ash by Hidrothermal Alkali. *Jurnal Zeolit Indonesia*, 8(1), 22-32.
- Kaelbe, E, F. (1997). *Handbook of X-Ray*, McGraw Hill, New York, 21-512,10
- Lari, G. M., Desai, K., Mondelli, C., & Pérez-Ramírez, J. (2016). Selective dehydrogenation of bioethanol to acetaldehyde over basic USY zeolites. *Catalysis Science & Technology*, 6(8), 2706-2714. <https://doi.org/10.1039/C5CY02020D>
- Noelaka, Y.A.B., Kalla, E.B.S., Malelak, G.A., & Rukman, N.K. (2018). Adsorption of methylene blue using acid activated green color natural zeolite from Ende-Flores, Indonesia. *Rasayyan J.Chem*, 11(2), 494-504. <http://dx.doi.org/10.7324/RJC.2018.1121994>
- Pa,C,F., & Chik,A. (2018). Effect of NaOH Concentration and Reaction Time on zeolite synthesized from treated Oil palm Ash, *Journal AIP Conference Proceeding*.
- Palomo, A., Blanco-Varela, M. T., Granizo, M. L., Puertas, F., Vazquez, T., & Grutzeck, M. W. (1999). Chemical stability of cementitious materials based on metakaolin. *Cement and Concrete Research*, 29(7), 997-1004. [https://doi.org/10.1016/S0008-8846\(99\)00074-5](https://doi.org/10.1016/S0008-8846(99)00074-5)
- Panagiotopoulou, C., Kontori, E., Perraki, T., & Kakali, G. (2007). Dissolution of aluminosilicate minerals and by-products in alkaline media. *Journal of Materials Science*, 42(9), 2967-2973. <https://doi.org/10.1007/s10853-006-0531-8>
- Park, S. S., and Kang, H. Y. (2008). Characterization of fly ash-pastes synthesized at different activator conditions. *Korean Journal of Chemical Engineering*, 25(1), 78-83. <https://doi.org/10.1007/s11814-008-0013-6>
- Rahmayani, R, F, I., Arryanto and Y, M Kartini, I I., (2020), The Effect of Alkaline activation on the Zeolite binding properties toward dissolved irons, IOP Conf. Series: *Journal of Physics*, DOI: 10.1088/174-6596/1460/1/012084
- Rownaghi, AA., Rezaei F., Hedlund J., (2011), Yield of gasoline-range hydrocarbons as a function of uniform ZSM-5 crystal size, *Catal Commun*, 14: 37-41
- Sadowska, K., Góra-Marek, K., Drozdek, M., Kuśtrowski, P., Datka, J., Triguero, J. M., & Rey, F. (2013). Desilication of highly siliceous zeolite ZSM-5 with NaOH and NaOH/tetrabutylamine hydroxide. *Microporous and mesoporous materials*, 168, 195-205. <https://doi.org/10.1016/j.micromeso.2012.09.033>
- Schmidt F., Lohe MR., Buchner B., Giordani F., Bunino F., Kaskel S., (2013), Improved catalytic performance of hierarchial ZSM-5 syntesized by desilication with surfactans, *Microporous Mesoporous Mater*, 165, 148-57.

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- Sihombing, J. L., Pulungan, A. N., Herlinawati, H., Yusuf, M., Gea, S., Agusnar, & Hutapea, Y. A. (2020). Characteristic and Catalytic Performance of Co and Co-Mo Metal Impregnated in Sarulla Natural Zeolite Catalyst for Hydrocracking of MEFA Rubber Seed Oil into Biogasoline Fraction. *Catalysts*, *10*(1), 121. <https://doi.org/10.3390/catal10010121>
- Sihombing, J.L., Gea, S., Pulungan, A.N., Agusnar, H., Wirjosentoso, B., & Hutapea, Y, A. (2018). The Characterization of Sarulla natural zeolite crystal and its Morphology Structure, *AIP Conference Proceedings*.
- Yuan, W., Wu, H., Zheng, B., Zheng, X., Jiang, Z., Hao, X., & Wang, B. (2007). Sorbitol-plasticized chitosan/zeolite hybrid membrane for direct methanol fuel cell. *Journal of power sources*, *172*(2), 604-612. <https://doi.org/10.1016/j.jpowsour.2007.05.040>
- Wei, R., Li C., Yang C., Shan H., (2011), Effect of ammonium exchange and Si/Al ratio on the conversion of methanol to propylene over a novel and large partical size ZSM-5, *J. Nat Gas Chem*, *20*: 261-5
- Zhong, J., Han, J., Wei, Y., Tian, P., Guo, X., Song, C., & Liu, Z. (2017). Recent advances of the nano-hierarchical SAPO-34 in the methanol-to-olefin (MTO) reaction and other applications. *Catalysis Science & Technology*, *7*(21), 4905-4923. <https://doi.org/10.1039/C7CY01466J>