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Research Paper

Characterization of Natural Zeolite Synthesized by Dealumination and Desilication Method

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Abstract

Delamination and desilication are two methods used in the hierarchical synthesis of zeolites. This process is important for industrial applications, particularly in synthesizing natural zeolites due to their abundance. For instance, Lampung, Indonesia, has abundant natural zeolites. The synthesis process of natural zeolite can be simplified using the solvent swelling mechanism. The swelling solvent mechanism combines the dealumination and desilication methods into one process, making it advantageous to use natural zeolites as raw materials for manufacturing hierarchical zeolites on an industrial scale. The sample used in this study was Natural Zeolite Lampung (NZL), and the resulting product was characterized as NZL_Swelling. In this study, only two characterization analyses were selected to test the reliability of the dealumination and desilication methods simultaneously in one process, namely XRD and BET.

Keywords *Dealumination, Desilication, Hierarchical Zeolites, Synthesis of Zeolites, Swelling*

INTRODUCTION

Several techniques have been developed to produce hierarchical zeolites, such as dealumination, desilication, and templating (Li et al., 2017; Jia et al., 2019; Li et al., 2021). Among these techniques, high-temperature steam treatment is used (Reichinger et al., 2012; Ibáñez et al., 2017; Saito et al., 2018) and alkali/acid solution treatment (Valdiviés-Cruz et al., 2017; Zhang et al., 2017; Gackowski et al., 2018), these are the most practical for use in large-scale industries. The most popular post-treatment technique to raise the silica-alumina ratio and create mesopores is acid treatment, also known as dealumination, particularly for Y zeolites with a low SiO_2/Al_2O_3 molar ratio (Qin et al., 2013; Vasconcelos et al., 2023).

Processing parameters, including temperature, reaction time, and acid supply and concentration, influence hierarchical zeolite's porosity and textural characteristics. Although inorganic acids with strong acidities, like hydrochloric and nitric acid, can be used to etch aluminium formwork, the dealumination process frequently results in the loss of zeolite structure and a reduction in crystallinity (Silaghi et al., 2014; Nascimento et al., 2024). Although organic acids, such as oxalic acid, are less acidic than inorganic acids, they nevertheless have a considerable dealumination impact because of their acid ions' strong complexation with aluminium (Feng et al., 2019). The mesoporosity of crude clinoptilolite was increased by NaOH desilication (Aziz et al., 2023). Adding regulated mesoporosity to crude clinoptilolite can enhance its performance. The findings demonstrate that alkali-treated clinoptilolite, as opposed to crude clinoptilolite with a high silicon concentration, is noticeably more effective at removing methylene blue from aqueous solution. Thus, we can deduce that mesoporosity is increased by alkali treatment, which improves methylene blue adsorption. Another reason for the enhanced adsorption capacity of desilicated clinoptilolite is the decrease in the Si/Al ratio, which results in a more significant number of

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negatively charged sites per unit mass. Desilication is a successful modification technique that increases the ability of natural zeolites like clinoptilolite and zeolite to remove methylene blue (Akgül & Karabakan, 2011; Aziz et al., 2023).

Similar to this, various techniques for creating hierarchical zeolites rely on alterations to the crystallization process (a bottom-up strategy), typically by adding mesoporogen-acting additives to the synthesis gel (Jia et al., 2019). Most of the research has been conducted as removal or elution studies or in a segregated or nonintegrated fashion (Rodríguez-Iznaga et al., 2018). The study integrated the synthesis of natural zeolite hierarchy through a solvent swelling mechanism between Natural Zeolite and $C_{15}H_{35}$ solvent without separating the dealumination and desilication processes.

LITERATURE REVIEW

However, zeolite micropores impose diffusion restrictions on large molecules, significantly reducing catalytic efficiency (Xiao et al., 2023). An increasingly popular technique for getting beyond the diffusion constraints of traditional zeolites is the utilization of hierarchical porous structures. In hierarchical zeolite synthesis, two types of mesopores can form: intra-crystalline mesopores, which are mesopores in the zeolite pore wall, and inter-crystalline mesopores, which are meso-sized voids between nano-zeolite aggregates (Khatrin et al., 2024). The primary goal of creating hierarchical zeolites is to shorten the diffusion path for molecules that can fit into these tiny pores and to enable the transformation of giant molecules that cannot fit into zeolites' micropores. Thus, in order to increase the catalyst lifespan, hierarchical materials have been utilized to maximize the intercrystalline diffusion rate, decrease the deactivation rate, and increase the external surface area (Yan et al., 2015; Jia et al., 2019). It is still difficult to use the majority of hierarchical zeolites on an industrial scale despite all of their potential uses and characteristics. While a recent assessment defined hierarchical zeolites as an industrial reality, one of the primary obstacles preventing these materials from being produced on a wide scale may be the time-consuming and expensive synthesis process (Li et al., 2014; Hartmann et al., 2016).

Zeolite hydrogen forms (Brønsted acid sites) are created when zeolite cations exchange protons under low acid concentrations. The coordination tetrahedral aluminium moves to the three-coordination exchange position when the acid concentration rises, forming the aluminium form (Lewis Center). However, the strong acidity of zeolites usually causes substantial breaking and liquid fuel loss (Briones et al., 2024). Brønsted acid sites significantly influence medium-strong Cracking and hydroisomerization reactions. This fact has significant ramifications for catalysis (Socci et al., 2019). The desiccation process significantly affected the zeolite's acidity, as seen by the Zeolite-$Al(OH)_3$ sample that had the lowest Si/Al ratio. Desilication is the process of extracting silicon and adding additional framework aluminum, which denotes re-alumination (Philia et al., 2023). It is significant to remember that clinoptilolite's crystal structure may be weakened if more than 50% of the aluminium oxide is removed.

Increasing hydrochloric acid treatments causes dealumination and the amorphous phases to develop in clinoptilolite (Dziedzicka et al., 2016; Pavlovic et al., 2019). Dealumination, applied to comparatively diluted treatments, causes acidic clinoptilolite to decationize and produce hydrogen forms. Dealumination happens concurrently, causing the zeolite to be partially amorphized (Dziedzicka et al., 2016). Under the right circumstances, zeolite samples can be modified with inorganic acids to improve their sorption capacity and catalytic qualities (in terms of silicate modulus). Iron oxide from zeolites cannot be eliminated by this method, though.

Regarding oxide composition, the dissolution of organic acids results in a decrease in the relative amount of oxides in clinoptilolite. Natural zeolites have slightly fewer alkali metal oxides than alkaline earth metal oxides, which are nearly entirely eliminated. The iron oxide level decreased as well, leaving only 4.0–5.0 percent. It has been discovered that, in comparison to inorganic acids, the influence of organic acids on the chemical composition and characteristics of natural zeolite is minimal (Kadirbekov et al., 2017).

The aluminosilicate crystal structure of clinoptilolite contains two-dimensional partially interconnected pore systems; two varieties of eight-membered and one variety of ten-membered oxygen ring pores are present in the sample. The window diameters of the clinoptilolite are roughly 0.4-0.76 nm, 0.33-0.46 nm, and 0.26-0.47 nm (Chmielewská and Chmielewská, 2019). It can be difficult to exchange ammonium ions for cations in the clinoptilolite's channels and windows. In order to replace the cations with Brønsted acid protons H^+, the initial material is often treated with mineral acids. The method yields HCLIN, an acidic version of natural clinoptilolite zeolite. Clinoptilolite dissolution may result in partial starting material loss and environmental contamination. It is also difficult to get the mineral acids out of the catalyst. In order to solve this problem, ammonium ions from zeolite cations were swapped out for clinoptilolite's acidic form, which resulted in the NH_4CLIN form. The ammonium ions were then calcined in air until they broke down, producing the HCLIN catalyst (Chmielewská & Chmielewská, 2019).

Indonesia's zeolite reserves amount to 400 million tons, but so far, they have only been exported in raw form. Today, Indonesians are less aware and utilize natural resources with various potentials to improve the nation's economy. Most of Indonesia's territory has many volcanoes that have the potential to be a source of diverse rocks, one of which is zeolite (Fajriani et al., 2022; Philia et al., 2023). Natural zeolites in Indonesia are generally divided into two types, namely mordernite and clinoptilolite (Ramadhan et al., 2019; Philia et al., 2023).

RESEARCH METHOD

NZL 10 g mesh 100 was dissolved in a 40% polar and 60% non-polar solvent (100 ml) using a mechanical propeller stirrer at a low rotation of 150 rpm. The mixture was stirred for 30 minutes at an operating temperature of 80°C. After each process, it was filtered and dried in an oven for 12 hours at 150°C. Furthermore, XRD and BET analyses were conducted to determine the effect of the swelling mechanism.

FINDINGS AND DISCUSSION

The lack of previous research studies on the topic in this study, especially previous studies that provide information that the dealumination and desilication processes are no longer a hierarchical synthesis method on separate zeolites, has the potential for limitations in this study therefore, this study to test the reliability of the dealumination and desilication methods at the same time in one process, only two characterization analyses were selected, namely XRD and BET.

Qualitative X-ray diffraction (XRD) analysis can be performed to identify the crystal type by comparing diffraction peaks with standard diffractogram data. The XRD analysis was conducted at the Technical Implementation Unit (UPT) of Undip Indonesia Integrated Laboratory. The characterization of the modified NZL revealed several peaks with diffraction angles of 2ϴ (refer to Figure 1). The peak data at 2θ angles 10.160, 22.180, 28.110, 30.580, and 35.150 in the Swelling solvent treatment were compared with the ICSD standard using the Match! Application.

The ICSD standard includes peak data at 2θ angles 22.330, 22.630, 11.070, 25.920, 22.350, 22.620, 11.100, 21.890, 22.650, 29.960, 22.310, 25.890, and 11.050, which indicates the identity peak of clinoptilolite. The identity peaks of $C_{48}H_{96}Al_{21}Na_{21}(O_2)_{16}Si_{75}$ are 10.160, 22.180, 28.110, 30.580, and 35.150, which indicate the result of swelling. Figure 1 shows the XRD analysis results of Natural Zeolite Lampung (NZL) samples in this study using the Match! Application. The NZL content consists of Clinoptilolite-Na (63.1%), Milarite (26.5%), and Analcime (10.4%). The XRD analysis of the NZL Swelling sample also shows the same results through the Match! Application.

The application indicates that NZL Swelling is composed of 92.7% Clinoptilolite-Na and 10.4% Analcime compounds. As the percentage of Clinoptilolite-Na increases, the purity of NZL also increases, suggesting a cleaning or washing process. This process also indicates dealumination and desilication.

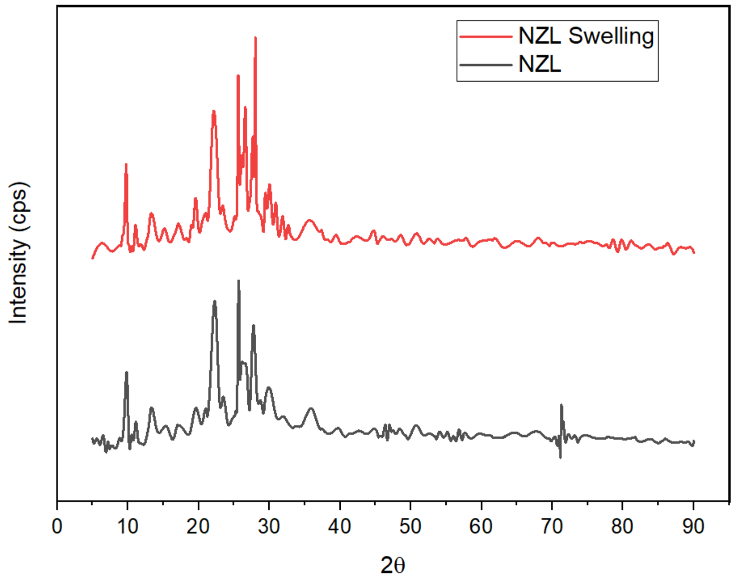

Figure 1. XRD Analysis of NZL and NZL Swelling

Table 1 shows the results of BET (Brunauer-Emmett-Teller) testing using the gas sorption data acquisition and reduction were conducted using Quantachrome® ASiQwin™, version 3.01 of Quantachrome Instruments, by the UNDIP operator, in the year range of 1994-2013. The table includes NZL BJH Adsorption Data and NZL Swelling. According to the surface area data presented in Table 1, the swelling treatment applied to NZL increased pore size from 15.269 Å to 19.115 Å. This indicates that swelling has occurred on NZL. Additionally, there is a decrease in specific pore volume after the swelling process due to the formation of secondary porosity. This suggests that there is a greater mass addition than volume addition, as the increase in pore diameter is followed by a decrease in pore depth due to swelling on NZL.

Figure 2 shows the typical nitrogen sorption isotherms of NZL and NZL Swelling composite materials. The material exhibits micro and mesoporous features, as demonstrated in Figure 3. The transition from monolayer to multilayer coverage starts at point B in Figure 3. Type IV isotherms are common in solids with micro- and mesopores, where gas molecules interact with the adsorbent mesopore surface, resulting in capillary condensation (Prokešová et al., 2003; Prokesova-Fojtikova et al., 2007; Bardestani et al., 2019; Jia et al., 2019). The swelling mechanism has caused the hierarchical synthesis of NZL, resulting in an increase in the size of its pores to include both micropores and mesopores. The sorption increased at $P/Po < 0.05$ can be attributed to the volume of micropores filled within the zeolite structure. At a relative pressure of $P/Po = 0.3\text{-}0.4$, the increase in the amount of adsorption suggests the existence of mesopores formed by the concurrent reaction of the precursor solution mesopores and the Lampung natural zeolite-containing solution. All isotherms show the presence of a hysteresis circle at $P/Po > 0.6$, which is associated with capillary condensation in the inter-particle (Neimark et al., 2003). The initial linear segment of the αs plot, associated with P/Po values between 0.05 and 0.3, is attributed to nitrogen sorption on the mesoporous and particle surfaces. Keep in mind that the volume of a mesopore is filled at a relative

P/Po pressure of 0.3-0.4 (Arumugam et al., 2022). The second linear part at P/Po = 0.4-0.7 is due to nitrogen absorption on the outer surface (Zhang et al., 2016).

Table 1. BJH Adsorption Data NZL dan NZL Swelling

	Surface Area	**Pore Volume**	**Pore Size**
Quantachrome® ASiQwin™ is a software program for automated gas sorption data acquisition and reduction. It was developed by Quantachrome Instruments, and the copyright dates from 1994 to 2013. The current version is 3.01.	(m^2/g)	(cm^3/gr)	(Å)
NZL	19.635	9,7 x 10^{-2}	15.269
NZL Swelling	17.071	9,5 x 10^{-2}	19.115

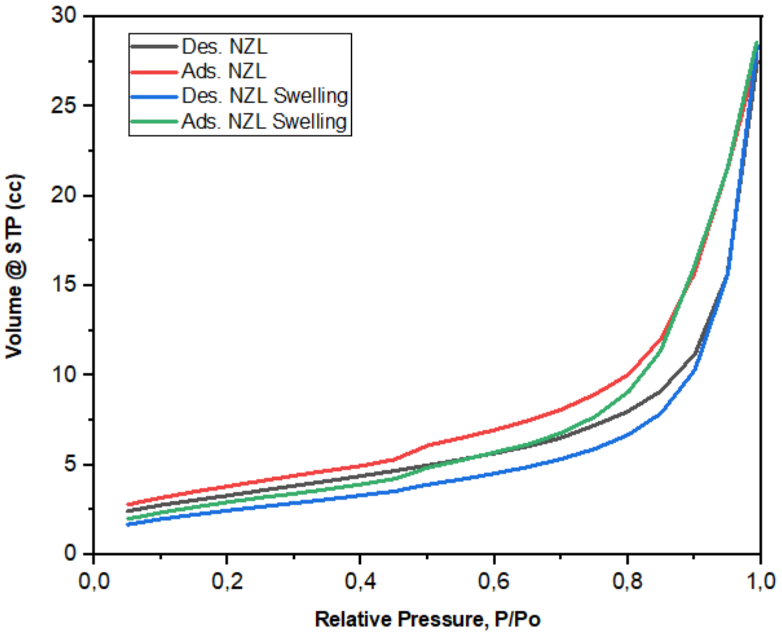

Figure 2. Nitrogen adsorption-desorption isotherms of NZL and NZL Swelling incorporating micro and mesoporous features

The H-form and the steam sample that has been acid-treated exhibit the nitrogen adsorption-desorption isotherms in Figure 2. The IUPAC categorization Type IV includes the H-form isotherm, which has a prominent hysteresis loop. The loop exhibits two distinct sections: one that opens at high pressure (p/p0 ~ 0.9) and another that shuts at p/p0 ~ 0.4. The first region is more prominent in the p/p0 range of 0.9 – 0.65, while the second zone is located between 0.65 and 0.4. Figure 2 displays mesopores with an irregular structure ranging in size from 5 to nearly 20 nm.

The results of the XRD and BET analyses demonstrate that the Dealumination and Desilication Method can effectively combine the dealumination and desilication processes into one step in synthesizing natural zeolite hierarchy through the swelling mechanism. However, the XRD and BET analysis methods cannot determine the percentage of changes in aluminosilicate content, as well as other materials such as alkali metals and alkaline earth metals, resistance to heat treatment, acidity, changes in functional groups, or microstructure in NZL and NZL Swelling. Therefore, further research is necessary to characterize these aspects.

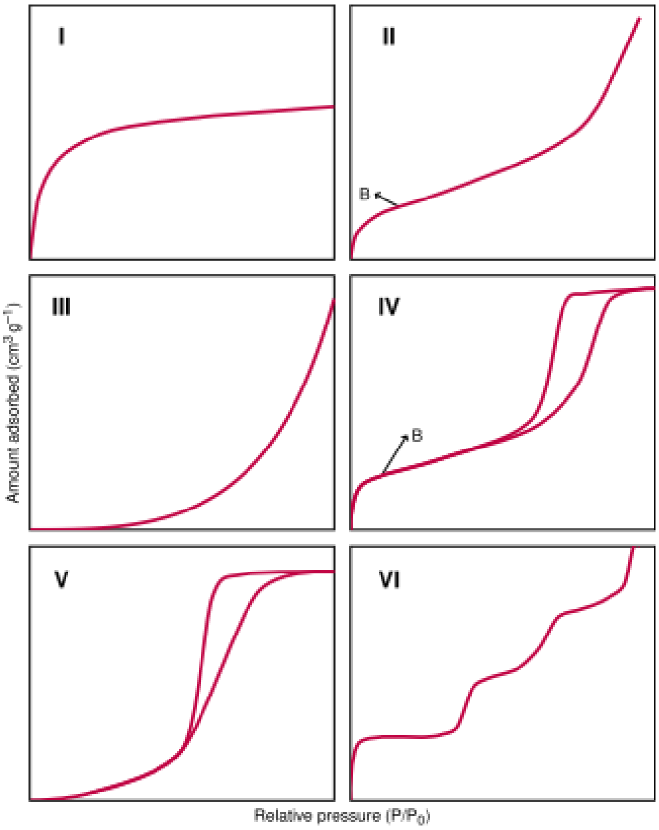

Figure 3. Isotherms of nitrogen adsorption-desorption (Bardestani et al., 2019)

CONCLUSIONS

The XRD results indicate that Lampung Natural Zeolite (NZL) is clinoptilolite. The purity of NZL increases with the increasing percentage of Clinoptilolite-Na after the solvent swelling process is carried out on NZL. This suggests that there has been a cleaning or washing process of NZL and that the dealumination and desilication processes have occurred simultaneously rather than separately. The BET results indicate that the swelling treatment of NZL caused an increase in pore size from 15.269 to 19.115Å. This text describes the occurrence of swelling in NZL and the subsequent decrease in pore volume size due to the formation of secondary porosity. This leads to a greater mass addition compared to volume addition, as the increase in pore diameter is followed by a decrease in pore depth caused by the swelling in NZL. The swelling mechanism in the hierarchical synthesis of natural zeolite can effectively combine the dealumination and desilication processes into a single step.

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