Synthesis and Characterization of Zeolite from Refractory Brick Waste

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Abstract

The synthesis of zeolite from refractory brick waste using hydrothermal technique had been conducted. Two different reactans, NaOH and $Mg(OH)_2$, were separately employed to react with SiO_2 and Al_2O_3 from brick sample to produce metal silicate and metal aluminate which were then reacted to obtain zeolite. XRF results show that the synthesized products using both reactants have Si/Al ratios between 1-1.5 considered as low type of zeolites regardless some remaining impurities. XRD data reveal a typical pattern of zeolite with 2 Ɵ angles of 15.91; 19.52; 25.47; 32.20; 35.54 and 41.54. The IR vibration characteristic of Si-O and Al-O bonds appears in 454 cm^{-1} while the symmetric and asymmetric stretching vibrations of these two bonds absorb around 679.66 – 778.02 cm^{-1} and 2033.96-1092.42 cm^{-1}, respectively. The O-H group from Si-OH associated with the formation of zeolite gives a characteristic feature at 3618 cm^{-1}. SEM analysis also shows similar morphological features with natrolite zeolite. The use of NaOH as reactant gives more zeolite product compared to $Mg(OH)_2$ reactant**.**

Keywords: Brick, zeolite, natrolite, silicate, aluminate, material

Abstrak

Telah dilakukan sintesis zeolit dari limbah batu bata tahan api dengan menggunakan teknik hidrotermal. Dua reaktan yang berbeda, NaOH dan $Mg(OH)_2$, direaksikan secara terpisah dengan SiO_2 dan Al_2O_3 dari sampel guna memperoleh logam silikat dan logam aluminat yang kemudian direaksikan lebih lanjut untuk mendapatkan zeolit. Hasil analisis XRF menunjukkan bahwa produk yang disintesis menggunakan kedua jenis reaktan tersebut memiliki rasio Si/Al antara 1-1,5 sehingga dapat dikategorikan sebagai jenis zeolite rendah meskipun masih mengandung sejumlah pengotor. Data XRD mengindikasikan adanya pola difraktogram khas zeolit dengan sudut 2 Ɵ: 15,91; 19.52; 25.47; 32.20; 35,54 dan 41,54. Karakteristik vibrasi IR ikatan Si-O dan Al-O muncul pada bilangan gelombang 454 cm^{-1} sedangkan vibrasi regangan simetris dan asimetris kedua ikatan tersebut berturut-turut menyerap antara 679,66 – 778,02 cm^{-1} dan 2033,96-1092,42 cm^{-1}. Gugus O-H dari Si-OH yang mengindikasikan adanya pembentukan zeolit menyerap pada 3618 cm^{-1}. Analisis SEM juga menunjukkan adanya kemiripan morfologi dengan zeolite jenis natrolit. Penggunaan NaOH sebagai reaktan menghasilkan produk zeolite dengan jumlah lebih banyak jika dibandingkan dengan reaktan $Mg(OH)_2$

Kata Kunci: Bata, zeolit, natrolit, silikat, aluminat, material

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INTRODUCTION

Indonesia is one of the developing countries that has a significant development in recent years. As a consequence, the demand for infrastructure improvement such as houses, industrial buildings and other public amenities has also increased considerably which requires high quantity of cements for constructions. In the cement production process, brick is essentially needed for furnace protection[1]. To date, brick waste from cement production especially in Semen Kupang Company has not been optimally used in which only a small portion that has been utilized for stone paths.

Bricks typically contain considerable amount of SiO_2 and Al_2O_3 compounds[2,3] indicating that this material is potential as a starting material to produce silica and alumina based materials such as zeolite. Zeolite structure has microporous aluminosilicate in tetrahedral and octahedral formations[4] capable to be utilized for various applications including adsorption, ion exchange and catalysis. For example, Orjioke[5] successfully synthesized and characterized zeolite and used in absorbing nickel metal. Besides, zeolite A was successfully synthesized from coal and employed to adsorb Cu^{2+} in water treatment[6]. Zeolite can also be used to synthesize zeolite/Ni-Cr catalyst as reported by Nurhayati and Wigiani[7]. In the development of solar cell, zeolite is used as a modifier in semiconducting materials to enhance cell performance[8].

With the abundance of brick waste containing substantial amount of silica and alumina, it offers a promising raw material that can be utilized to synthesize zeolite owing to its broader applications. To the best of our knowledge, however, there have been no reports of using refractory brick waste as the raw material in zeolite preparation. Therefore, synthesis and characterization of zeolite from this potential waste becomes our focus of study reported in this paper.

RESULT AND DISCUSSION

Metal silicate and aluminate preparations

The purpose of sample destruction in the initial preparation step is to increase the surface area in order to ease adsorption on its surface leading to rapid chemical reactions[9]. We used water in washing procedure because it is a universal solvent capable to dissolve impurities remaining in the sample followed by drying the sample at 105°C to obtain a dry brick material. The decomposition of organic impurities was achieved by heating the sample using furnace technique at 600°C as reported by Zhao and co-workers[10] to allow the synthesis to proceed efficiently. Reflux technique was employed to remove metal oxide impurities by reacting 10 gram of brick with 10 mL HCl 1 M as suggested by Lestari[11]. This then enables the functional groups being activated by opening the porous sites of the material which in turn increases the reaction rate.

Successful preparation of Na-silicate is chemically initiated by the interaction of OH^- from NaOH with Si from SiO_2 which carries a positive partial charge to form SiO_2OH unstable intermediate. This is followed by releasing hydrogen which then reacts with OH^- to form H_2O and $[SiO_3]^{2-}$. The later anion further interacts with Na^+ ions to form the expected Na-silicate product. Mg-silicate product was also obtained with the same principle.

Characterization of zeolite products

The targeted products were obtained by reacting Na-silicate and Na-aluminate while stirring the mixture (60 rpm) for 60 minutes. The formation of crystals occurred after the mixture was dried in an oven (160°C) for 7 hours which is similar to the study reported previously[12].

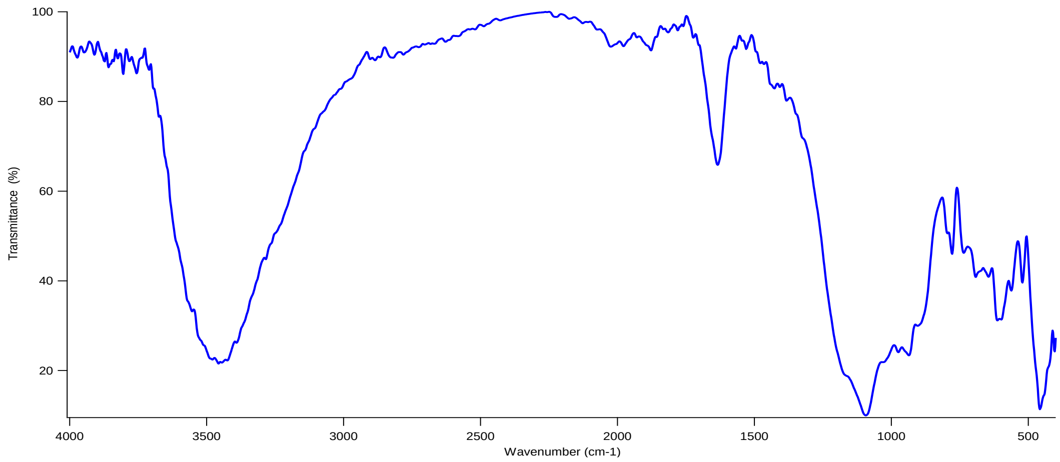

Figure 1. Infra-Red spectra of synthesized zeolite

The IR data of synthesized zeolite in figure 1 shows that the typical vibrations of Si-O and Al-O bonds appears in 454 cm^{-1} while the symmetric stretching vibrations of these two bonds absorb around 679.66 – 778.02 cm^{-1}. The asymmetric Si-O and Al-O bonds stretch at 2033.96-1092.42 cm^{-1}. The O-H group from Si-OH in the zeolite gives a characteristic feature at 3618 cm^{-1}. By comparing zeolite IR spectra with brick spectra as the starting material[2,13], it is clear that there is no O-H vibration at the range of 2800-3800 cm^{-1} in the brick sample while the obtained product shows an intense absorption in this region. This means that the formation of OH group attached to Si and Al is achieved suggesting a successful formation of a compound associated to the targeted product. In addition, the IR spectra of the synthesized compound displays a similar pattern with natural zeolite spectra reported in literature[14,15] confirming a successful formation of the desired product.

We studied the effect of hydrochloric acid concentrations on the amount of zeolite obtained using two different reactants, (NaOH and $Mg(OH)_2$). Both reactants give significant different amount of products in which NaOH as the reactant gives higher amount of obtained zeolite compared to $Mg(OH)_2$. In addition, zeolite with NaOH as the reactant has a rapid neutralization. This is because Na has a low ionization energy causing a loss of one electron to attain a stable configuration resulting Na^+ and OH^-. The anion play a key role in providing O atoms needed to form Na-silicate and Al-silicate[16]. Therefore, zeolite synthesis using NaOH reactant gives higher amount of product compared to $Mg(OH)_2$.

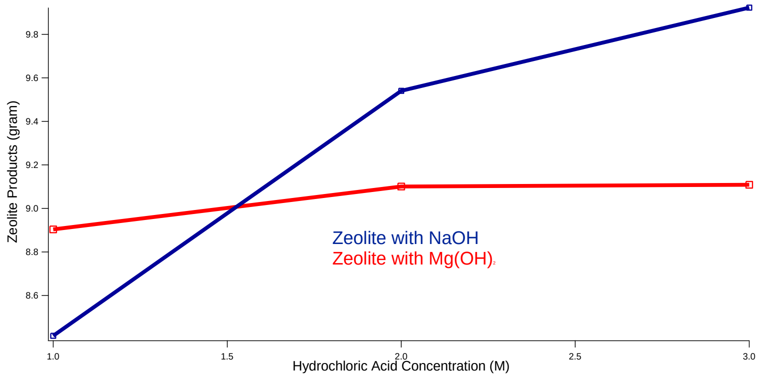

Figure 2. The effect of HCl concentration on yielded zeolite using NaOH and $Mg(OH)_2$ as the reactants

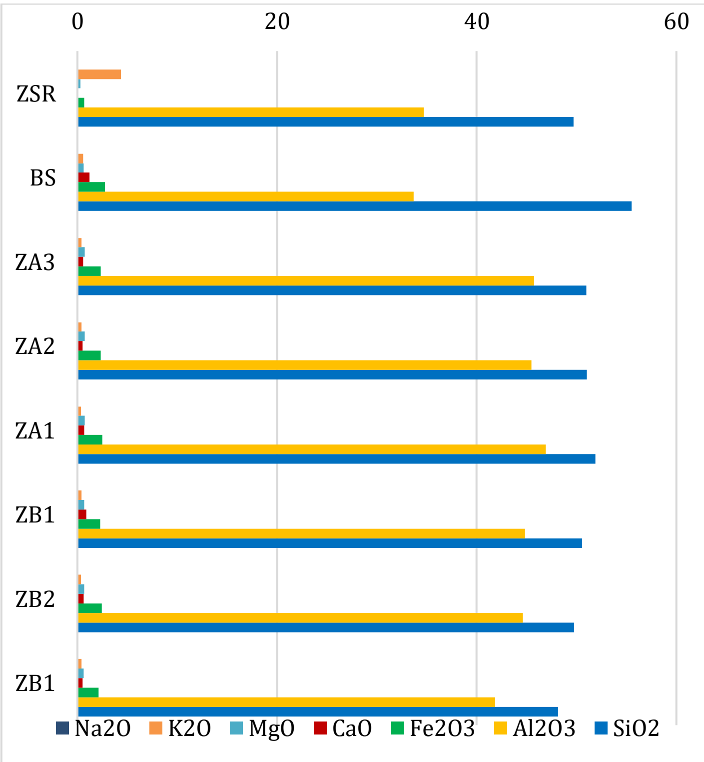

Figure 3. XRF characteristics of zeolite products (x axis = %) using NaOH (ZA) and $Mg(OH)_2$ (ZB) as reactants in various concentration (1, 2, 3 = Molar) in comparison to brick sample (BS) and synthesized zeolite from reference (SZR).

The XRF data of brick waste sample (BS) in figure 3 shows a substantial composition of SiO_2 and Al_2O_3 (55.4 and 33.6%, respectively) underlying the significance of utilizing this material as a starting material for synthesizing zeolite. The analysis using this technique was utilized to measure the zeolite product for all acid concentrations added for both NaOH and $Mg(OH)_2$ reactants (figure 2). This was carried out to ensure the consistency of product obtained as a consequence of acid addition by looking closely at the chemical compositions of the obtained products. The XRF data underpins our interpretations that the yielded product increases as shown in figure 2 with the increase of acid concentration but giving almost the same chemical profiles. This implies that we obtained the same characteristic of products with increasing yields when added with hydrochloric acid.

This XRF data also enable us to calculate the Si/Al ratios of the obtained products which range from 1 – 1.5 for all concentrations of both reactants studied. Previous study reports that the Si/Al ratio of 1 – 1.5 is categorized as low grade of zeolite.[17].

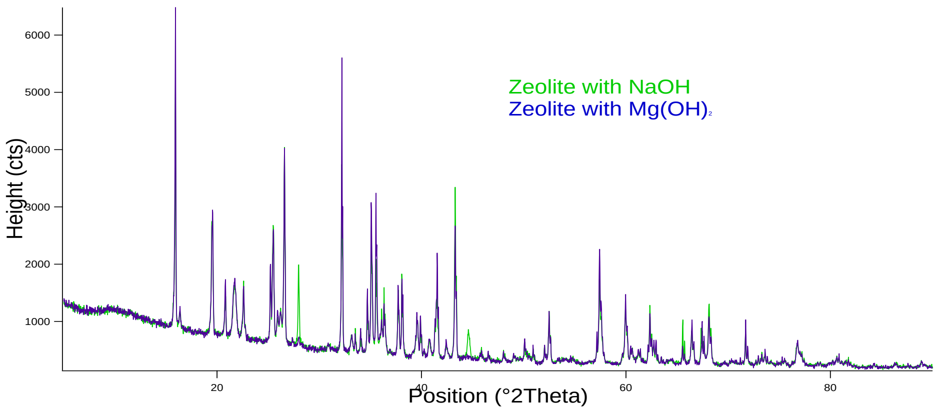

Figure 4. Overlaid XRD diffractogram of zeolite products using two different reactants.

The characterization using XRD shows that there are six main peaks at 2 ɵ angles of 15.91; 19.52; 25.47; 32.20; 35.54 and 41.54 for products with two different reactants. By comparing the XRD data with data from the literature, the XRD pattern of natrolite zeolite, $[Na_{16}(H_2O)_{16}][SiAl_{16}O_{80}]$, seems to have greater similarity of 2 ɵ angles with the synthesized products. By comparing the calculated Si/Al ratio from the synthesized zeolite (~ 1-1.5) with previous study, it aligns with Si/Al ratio of natrolite as reported by Ibrahim[18]. The significant peaks in XRD diffractogram were calculated their hkl values to obtain a specific pattern as shown in this table below.

Table 1. Calculated Miller index of synthesized zeolite

2Ө	Ө	Sin ^{2} Ө	K. Sin ^{2} Ө	$h^2 + l^2 + k^2$	Hkl
15, 9118	7, 9559	0,0191	1,0123	1	100
19, 5210	9, 7605	0,0287	1,5211	2	110
25,4740	12,7370	0,0486	2,5758	3	111
32, 2018	16,1009	0,0769	4,0753	4	200

35, 5492	17,7746	0,0930	4,9290	5	210
41,5408	20,7704	0,1257	6,6620	7	211

Common factor (cf) = 53

As shown in the table above, the hkl values of the studied materials are in a sequential order (1, 2, 3, 4, 5, 7) in which Setiabudi and coworkers[18] categorize it to have a cube unit cell with each cube represents a tetrahedral structure associated to the basic structure of zeolite material.

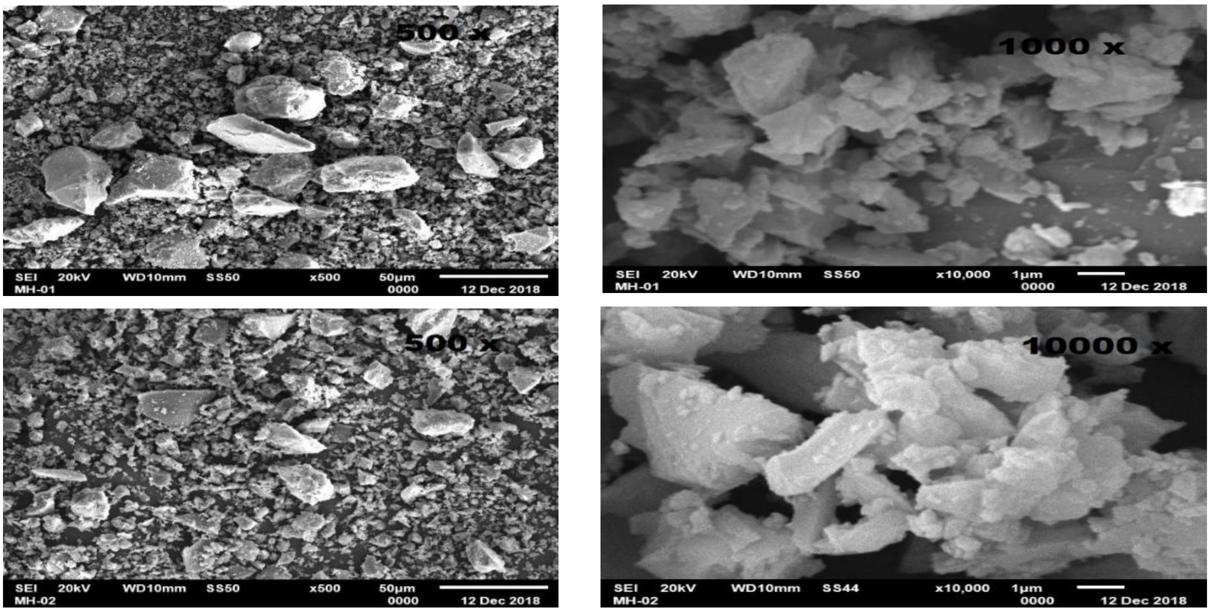

Figure 5. SEM images of zeolite products with different reactants, NaOH (left) and $Mg(OH)_2$ (right)

SEM images of zeolite products with two different reactants as shown in figure 5 have no significant differences in terms of the morphological properties. With magnifications (500 and 10,000 times) the product morphologies display amorphous structure in nature compared to natrolite SEM image from reference[19]. This suggests that there are still some impurities in the obtained product as revealed in the XRF and XRD data and therefore it is challenging to obtain a cubic unit cell crystal as indicated by the calculated Miller index. Therefore, it requires further purification approach to obtain a well-defined rearrangement of its morphological properties associated to this low grade class of zeolite.

CONCLUSION

The formation of zeolite products using brick waste material suggests that it can be utilized as the starting material for synthesizing zeolite where NaOH displays a rapid reaction and neutralization compared to $Mg(OH)_2$. The interpretations of the data propose that the targeted product could be better obtained by using NaOH as the reactant and are potential to be tested in further studies and applications.

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METHODOLOGY

Materials and Instrumentals

Unless otherwise stated, NaOH, $Mg(OH)_2$, and HCl purchased from Merck with pro analysis grades were used without further purifications. Brick sample was collected from PT. Sarana Agra Gemilang (SAG) Kupang. The XRD and SEM analysis was done at Badan Tenaga Nuklir Nasional, Pusat Sains dan Teknologi Bahan Maju Jakarta. IR measurement was conducted at FMIPA – Brawijaya University while XRF data collection was performed at PT. Sarana Agra Gemilang (SAG).

Methods

The experimental work was carried out by referring to previous literatures[20,21].

Sample collection and initial preparations

Brick waste was collected from PT. SAG Kupang followed by destructing, sifting (100 mesh) and washing the sample with water for three times to remove impurities. The sample was then dried using oven (105^{o}C) to remove water. 1500 g of dry sample was weighted and heated at 600^{o}C for 3 hours. The temperature increase is carefully adjusted before it reaches the desired combustion conditions to allow a proper thermal decomposition. It was then collected, characterized and used for further reactions to obtain zeolite.

Na-silicate preparation (A)

The weighted sample was refluxed with HCl 1 M for 60 minutes at 90^{o}C followed by the addition of 1 M NaOH solution with the ratio of 10 ml solution per 10 g sample. The mixture was subsequently heated in the oven for 3 hours at 130^{o}C before cooled down to obtain the desired product.

Na-aluminate preparation (B)

0.0102 g of Al_2O_3 was weighted and mixed with 0.24 g NaOH and 50 mL water. The mixture was stirred using magnetic stirrer with the scale of 6-8. The mixture was then filtered, dried and collected its product. This procedure was similarly applied to prepare Mg-silicate (C) and Mg-aluminate (D) with $Mg(OH)_2$ as the starting material.

Zeolite synthesis

Zeolite was obtained by reacting A and B followed by stirring the mixture for 1 hour. After that, the mixture was placed in an oven at 160^{O}C for 7 hours to obtain the targeted product. Next, the synthesized zeolite was crushed, sieved (100 mesh) and soaked in water before filtered and dried at 110^{o}C for 24 hours. It was then purified using hydrochloric acid in which various hydrochloric acid concentrations were employed to examine the acid addition effects on yielded zeolite.

The experimental procedure was repeated for the synthesis of zeolite using $Mg(OH)_2$ as the starting material to produce C and D followed by reacting C and D to obtained zeolite.