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ORIGINAL ARTICLE

Simple Synthesis of 4A Zeolite with the Addition of Al_2O_3 and Na_2EDTA Compounds

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ABSTRACT – 4A zeolite complex derived from coal has been successfully synthesized through the preparation of fractionated samples, analyzed using atomic absorption spectrophotometry (AAS), resulting in a chemical composition of silica (SiO_2) 24.78% and aluminum oxide (Al_2O_3) 29.60%. The fly ash produced from this fractionation is used as the base material for the synthesis of 4A zeolite. The fly ash is reacted with sodium hydroxide (NaOH) at room temperature, yielding a gel that is subsequently crystallized into 4A zeolite through a reflux process. The resulting zeolite crystals are then supplemented with Al_2O_3 and disodium dihydrogen ethylenediaminetetraacetate (Na_2EDTA) as sources of aluminum to achieve a molar ratio of Si/Al = 1.42. Optimal quality 4A zeolite crystals were obtained from the synthesis of 5.9351 g of medium fraction fly ash, along with 1 g Al_2O_3, 4 g NaOH, and 0.569 g Na_2EDTA. Infrared (IR) characterization results indicate that the optimal 4A zeolite from medium fraction fly ash is characterized by crystals with the addition of 1.5 g of Al_2O_3. Wide absorption bandwidths are typically caused by large spectral line widths, which can occur if a significant amount of energy is absorbed by various vibrational modes, assuming that excess Al_2O_3 leads to the formation of functional groups that contribute to the same band. A peak at a wavelength of 564 cm^{-1} indicates double ring stretching vibrations, while a peak at 661 cm^{-1} indicates symmetric stretching vibrations of the zeolite framework. Meanwhile, peaks at wavelengths of 3460.86 cm^{-1} and 974.71 cm^{-1} indicate detected O-H absorption.

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INTRODUCTION

The operation of steam power plants (pembangkit listrik tenaga udara, PLTU) that use coal as fuel results in significant waste in the form of fly ash left over from burning coal. The fly ash from PLTU-Suralaya has been successfully analyzed to determine its chemical composition. Characterization results based on diffractogram data show that coal fly ash from PLTU-Suralaya contains primary components such as silica (SiO_2), aluminosilicate, and amorphous/glassy phases [1]. Additionally, other research indicates that the main component of Suralaya coal fly ash is the mineral quartz [2]. The high levels of silica and alumina in the fly ash suggest its potential use as a basic material for zeolite synthesis.

Zeolite is a chemical compound of hydrous aluminosilicate containing sodium, potassium, and barium cations [3]. The synthesis and characterization of pure phase 4A zeolite from coal fly ash have been successfully conducted, with analysis demonstrating that it can be used to produce low-silicate type zeolites, specifically 4A zeolite, due to its Si/Al molar ratio of approximately 2 [4]. The synthesis of zeolite from fly ash using the hydrothermal method has been effectively carried out, resulting in high purity 4A zeolite using NaOH and Na_2CO_3 to activate the synthesized fly ash. The use of Na_2CO_3 in zeolite synthesis is crucial for controlling the synthesis process to achieve the desired zeolite characteristics, including size, shape, and crystal structure [5]. However, the source materials, such as coal fly ash, contain mineral components that must be separated first. The mineral components in basic fly ash have been successfully analyzed; for instance, Suralaya coal fly ash, before preparation, contains several minerals, including aluminum oxide (Al_2O_3), SiO_2, calcium oxide (CaO), and iron (III) oxide (Fe_2O_3), with concentrations of 14.29%, 36.88%, 17.62%, and 24.88%, respectively, along with other minerals in lower concentrations [6]. Coal fly ash has been analyzed to determine its basic mineral content before treatment, revealing minerals such as Al_2O_3, SiO_2, CaO, and Fe_2O_3 with concentrations of 9.80%, 33.50%, 21.40%, and 30.18%, respectively [7].

The presence of other mineral components in high concentrations within the zeolite structure can interfere with its quality as an adsorbent and affect its cation exchange properties. Zeolite generally consists of aluminosilicate structures. The presence of other minerals, particularly in large amounts, can lead to suboptimal

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synthetic products. Therefore, it is essential to separate the Fe and Ca components present in significant quantities during zeolite synthesis. Zeolite has been successfully synthesized under acidic conditions [6], [8]. Additionally, zeolite has been synthesized using various sodium hydroxide (NaOH) activators, with results indicating that increasing the concentration of NaOH enhances the yield of silica products obtained [9]. Separation of Fe and Ca minerals using hydrochloric acid (HCl) and NaOH has also been performed during the activation of synthetic zeolite [10].

The synthesis of 4A zeolite has been successfully achieved using the hydrothermal method under optimal conditions. This 4A zeolite was synthesized using calcined kaolinite-type pyrite flotation tailings (CKPFT) as sources of silicon and aluminum [11]. Research has shown that pure zeolite A can be synthesized from coal fly ash. In this process, 200 g of fly ash was crushed and filtered through a 100-mesh sieve to ensure uniform particle size. One hundred grams of prepared fly ash was washed with 200 mL of 1M HCl at room temperature for 30 minutes to remove metal oxides such as Fe_2O_3, CaO, and other impurities, as these can dissolve in acid. The resulting fly ash was then activated with NaOH. The study found that the highest crystallinity of zeolite A was achieved at a Si/Al molar ratio of 1.24, yielding a crystallinity of 96.80 [12].

4A zeolite is a synthetic zeolite that can be used as an adsorbent material in petroleum and gas refining applications due to its ability to exchange calcium (Ca^{2+}) cations [13] and its cation exchange capacity for absorbing CO_2 compounds [14]. Another study produced a zeolite adsorbent from bottom ash coal, synthesized using a NaOH activator to reduce free fatty acid levels in crude palm oil (CPO). The type of synthetic zeolite produced was faujasite, with a particle size of 2 micrometers as determined by scanning electron microscope (SEM) analysis [10]. The adsorptivity of fly ash synthetic zeolite synthesized via the hydrothermal method is highly effective as an adsorbent for lead (Pb), achieving an efficiency level of 99.04%. This zeolite synthesis includes sodalite-type zeolites and several aluminosilicate minerals such as eucryptite and aluminum oxide [15].

Sudarno's research results demonstrate the influence of NaOH composition on the conversion of coal fly ash into zeolite A [16]. In this study, pure zeolite A was successfully synthesized using alkaline and hydrothermal treatment with NaOH. The gel solution was prepared with a SiO_2/Al_2O_3 ratio 1.64 by adding $NaAlO_2$ as an aluminum source and an H_2O/Al_2O_3 ratio of 552.07-278.77. Crystallization occurred at a temperature of 100°C for 24 hours. The synthesized zeolite product was characterized using X-ray diffraction (XRD) and infrared (IR) spectroscopy techniques. The best crystallinity of zeolite A was achieved at a molar composition of the initial gel solution: 1.64 SiO_2, 1 Al_2O_3, 11.29 Na_2O, and 552.07 H_2O.

Various methods were used in zeolite synthesis, focusing on the specific role of aluminum sources. The impact of Al_2O_3 as an aluminum source on the catalytic and adsorptive properties of zeolite X was evaluated, exploring how different aluminum sources affect the crystallization process, morphology, and overall properties of the synthesized zeolite [17]. The study offers insights into optimizing zeolite synthesis for various applications, particularly catalysis and adsorption. The inclusion of chelating agents can enhance the properties of zeolites for specific applications in these fields [18]. The characteristics of the resulting zeolite were examined using disodium dihydrogen ethylenediaminetetraacetate (Na_2EDTA) and similar agents during the synthesis process. This investigation provides a comprehensive analysis of zeolite synthesis using various chelating agents, including Na_2EDTA, highlighting how these agents influence the crystallization process, phase stability, and structural properties of the resulting zeolites. It emphasizes the interactions between chelating agents and metal ions, particularly regarding aluminum sources used in synthesis.

Based on this information, researchers are interested in conducting a study on the synthesis of 4A zeolite with variations in the addition of Al_2O_3 and Na_2EDTA compounds. Al_2O_3 serves as a source of alumina in zeolite synthesis, while the addition of Na_2EDTA is intended to reduce or eliminate the interference of calcium and iron metal ions in the zeolite formation process.

EXPERIMENTAL METHOD

Materials and Instruments

The tools used in this research include atomic absorption spectrophotometry (AAS) for chemical composition analysis and infrared (IR) spectroscopy for characterizing the compounds or molecules formed. The materials used are coal fly ash from steam power plants (pembangkit listrik tenaga udara, PLTU)-Suralaya, Banten; sodium hydroxide (NaOH) (E. Merck NaOH pellets); aluminum oxide (Al_2O_3) compound (Mesh 24 Grade A); and disodium dihydrogen ethylenediaminetetraacetate (Na_2EDTA) compound (For Analysis, Merck, 10 grams).

Method and Procedure

Magnetic separation of fly ash

Magnetic separation of fly ash is a process used to remove magnetic impurities from the ash, enhancing its quality for this application. This method involves using magnetic fields to attract and separate ferromagnetic materials, allowing for the recovery of valuable components and improving the overall purity of the fly ash. By efficiently removing these impurities, magnetic separation can facilitate the utilization of fly ash in the synthesis of zeolite.

Magnetic separation was performed in stages, starting with a 500 ml glass beaker containing 20 g of fly ash. Distilled water was added until the volume reached 100 ml. A bar magnet measuring 5 × 0.7 cm was then inserted into the beaker, and the mixture was stirred using a stirrer. After 30 seconds, stirring was stopped, and using tongs, the bar magnet was removed, along with the fly ash attached to it, which was rinsed off with distilled water from a spray bottle. The fly ash particles that adhere to the bar magnet are referred to as magnetic fly ash, while the particles that remain in the distilled water are called non-magnetic fly ash. The two samples, magnetic and non-magnetic fly ash, obtained from the separation process were then dried at a temperature of 120°C for 3 hours. After drying and cooling, the fly ash samples underwent re-separation through a fractionation process.

Separation of fly ash sample through a fractionation process

The separation of non-magnetic fly ash through the fractionation process is conducted in the following stages. A fractionation tube measuring 60 cm in length and 1.5 cm in diameter, equipped with 2 mm diameter outlet taps, is filled with a mixture of 5 g of fly ash samples and distilled water until the tube is full. The mixture is stirred by inverting the tube until the contents appear homogeneous. After allowing it to settle for 15 seconds, the solution is collected in fractions starting from the top (Figure 1): (1) the top 20 cm of the tube appears transparent and is called fraction I (light fraction); (2) the middle 20 cm appears slightly cloudy and is referred to as fraction II (medium fraction); and (3) the bottom 20 cm is very turbid (dark) and is called fraction III (heavy fraction). Each fraction of non-magnetic fly ash is removed through the three taps at the same time intervals into separate reservoirs, collected in small glass beakers, filtered, and dried. After cooling, the three fly ash fractions are ready to be used as sources of silica and alumina for zeolite synthesis. The medium fraction of fly ash samples will be used for the synthesis of 4A zeolite.

This selection is based on the assumption that the light fraction contains only a small amount of material from the fly ash source, while the heavy fraction may still contain heavy metals with densities greater than that of water. Therefore, the medium fraction is considered the best choice for zeolite synthesis. This separation process aims to avoid any minerals that may still be present in the fly ash sample. A very short settling time is chosen to prevent all minerals from accumulating at the bottom of the fractionation tube. It can be assumed that the materials that fall quickly to the bottom are undesired minerals, such as Fe compounds.

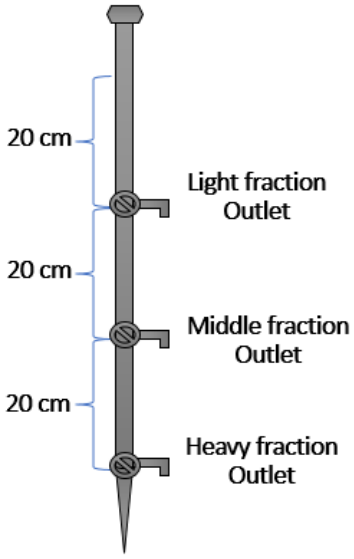

Figure 1. Fractionation tube

Synthesis of 4A Zeolite

The synthesis of 4A zeolite was carried out using a medium fraction of fractionated fly ash sample mixed with a NaOH solution in distilled water. The process involved reacting 5 g of medium fraction non-magnetic fly ash with 4 g of NaOH and varying amounts of Al2O3 (0.5, 1.0, and 1.5 g) until the total volume reached 50 ml. After stirring the reactant mixture overnight at a speed of 600 rpm, gel formation was achieved by heating the mixture to 70°C for 3 hours. Next, the crystallization process was performed by refluxing the gel mixture with the addition of 0.569 g of Na_2EDTA at a temperature of 100°C for 8 hours. The resulting mixture was then filtered and washed with distilled water until a neutral pH was achieved in the washing water. The zeolite collected on filter paper was dried in an oven at 120°C for 3 hours. The final product is then characterized as 4A zeolite crystals using Fourier-transform infrared (FTIR) spectroscopy and atomic absorption spectrometry (AAS).

RESULT AND DISCUSSION

Magnetic Separation of Fly Ash

A total of 20 g of fly ash was separated magnetically to produce non-magnetic and magnetic fly ash. The separation results from nine treatments are shown in Table 1. In the original fly ash, it is estimated that there are magnetic components. Most of these magnetic components, such as minerals containing Fe and Ti ions, are impurities that can interfere with the zeolite synthesis process and may cause the synthesized zeolite to appear less white. Therefore, magnetic separation is necessary. Fly ash that adheres to a bar magnet, thought to be a magnetic impurity component, is referred to as magnetic fly ash, while the fly ash remaining in the water is called non-magnetic fly ash. The amounts of magnetic and non-magnetic fly ash obtained from each separation process are presented in Table 1. This separation successfully removed 15.8% of magnetic impurities. However, this does not imply that non-magnetic fly ash is free of minerals containing Fe or Ti ions. It is possible that some Fe and Ti exist in the form of weakly magnetic minerals, which the bar magnet cannot attract, or as non-magnetic minerals.

Table 1. Results of magnetic fly ash separation

N	Original Fly Ash Weight (g)	Weight of Fly Ash (g)				% Error Weight
		Magnetic		Non-Magnetic		
		X1 (g)	ΔX1 (g)	X2 (g)	ΔX2 (g)	Y (%)
1	20	3.81	0.07	16.13	0.07	0.3
2	20	2.93	0.03	17.01	0.02	0.3
3	20	3.51	0.04	16.45	0.04	0.2
4	20	3.39	0.03	16.59	0.02	0.1
5	20	3.65	0.04	16.33	0.05	0.1
6	20	2.16	0.11	17.82	0.11	0.2
7	20	3.05	0.01	16.93	0.01	0.1
8	20	3.01	0.02	16.97	0.02	0.1
9	20	2.96	0.02	17.01	0.02	0.15
Total		28.47	0.37	151.24	0.36	1.55
Average		3.16	0.04	16.80	0.04	0.17
$\ddot{X} \pm \Delta\ddot{X}$		3.16 ± 0.04		16.80 ± 0.04		

X1, X2: the weight of magnetic and non-magnetic fly ash
ΔX1, ΔX2: the standard deviation of the average
Y: the weight percent error

The presence of magnetic minerals, such as magnetite (Fe_3O_4), in fly ash can adversely affect the quality of the produced zeolite. Magnetic minerals can influence the zeolite synthesis process by interacting with other components in the mixture, potentially altering the nature of the reaction, slowing or changing zeolite crystallization, and affecting process efficiency. Magnetite may mix with zeolite during synthesis, leading to contamination that alters the physical and chemical properties of the zeolites, such as ion exchange capacity, pore size, and adsorption ability. The presence of magnetic minerals can also affect the crystal structure of zeolites, which is crucial for their performance in applications like catalysis or adsorption. Disrupted crystal structures can reduce the effectiveness of zeolites. Therefore, it is important to remove magnetic minerals prior to the zeolite synthesis process to ensure that the final product achieves optimal quality and performance.

In this separation, the weights of magnetic and non-magnetic fly ash do not equal the weight of the initial fly ash because some fly ash adheres to the filter paper during washing and drying. In this treatment, the average percent error is 0.17%.

Fly Ash Sample Fractionation

To separate non-magnetic fly ash based on fractions, a fractionation process was carried out 23 times in a fractionation tube. The results for each fraction obtained are shown in Table 2. The presence of non-magnetic fly ash at the top (fraction 1), middle (fraction 2), and bottom (fraction 3) of the fractionation tube indicates that the non-magnetic fly ash contains components with different specific gravities. The amounts of fly ash samples in fractions 1, 2, and 3 are 1.0 g, 1.2 g, and 1.4 g, respectively. This shows that most of the fly ash sample components have a specific gravity greater than that of water.

Table 2. Results of fly ash sample separation by fractionation

N	Original Fly Ash Weight (g)	Weight of Fly Ash (g)						Comparison of average weights (g)
		Fraction 1		Fraction 2		Fraction 3		
		X1 (g)	ΔX1 (g)	X2 (g)	ΔX2 (g)	X3 (g)	ΔX3 (g)	
1	5	0.83	0.004	1.53	0.026	2.61	0.010	1 : 1,2 : 1,4
2	5	0.91	0.012	1.07	0.076	2.19	0.094	

3	5	1.01	0.032	0.95	0.100	3.01	0.070
4	5	0.72	0.026	1.61	0.032	2.61	0.010
5	5	0.88	0.006	1.05	0.080	3.04	0.076
6	5	0.91	0.012	1.56	0.022	2.51	0.030
7	5	0.97	0.024	1.71	0.052	2.31	0.070
8	5	0.87	0.004	1.50	0.010	2.60	0.012
9	5	1.12	0.054	0.91	0.092	2.90	0.048
10	5	0.85	0.000	1.39	0.012	2.70	0.008
11	5	0.92	0.014	1.67	0.044	2.39	0.054
12	5	1.05	0.040	0.88	0.114	3.02	0.072
13	5	0.75	0.020	1.42	0.006	2.81	0.030
14	5	0.81	0.008	1.51	0.012	2.66	0.000
15	5	0.83	0.004	1.21	0.005	2.91	0.050
16	5	0.91	0.012	1.59	0.028	2.47	0.038
17	5	0.77	0.026	1.47	0.320	2.70	0.008
18	5	0.88	0.006	1.61	0.032	2.49	0.034
19	5	0.69	0.032	1.55	0.020	2.73	0.014
20	5	0.72	0.026	1.67	0.044	2.59	0.014
21	5	0.68	0.034	1.78	0.066	2.52	0.028
22	5	0.59	0.052	1.01	0.088	2.50	0.032
23	5	0.89	0.008	1.11	0.068	2.97	0.062
Total		19.55	0.498	33.35	1.339	61.18	0.864
Average		0.85	0.022	1.45	0.058	2.66	0.037
$\ddot{X} \pm \Delta\ddot{X}$		0.85 ± 0.27		1.45 ± 0.33		2.66 ± 0.38	

X1, X2, X3: the weight of non-magnetic fly ash fraction 1, fraction 2, and fraction 3
ΔX1, ΔX2, ΔX3: the average weight of non-magnetic fly ash fraction 1, fraction 2, and fraction 3

Fly ash sample is thought to consist mainly of silica and alumina, such as quartz and mullite, along with other inorganic compounds that contain small amounts of Fe and Ti. To maximize the amounts of amorphous silica and alumina while minimizing impurities (Fe and Ti metals), a further fractionation process based on differences in settling rates in water was conducted.

Table 2 presents the data on the separation of non-magnetic fly ash, showing weights of 19.55 g, 33.35 g, and 61.18 g for the light, medium, and heavy fractions, respectively. In this fractionation, the weights of non-magnetic fly ash from each fraction do not equal the weight of the initial fly ash. This discrepancy may be due to instability in the balance caused by fluctuations in electrical voltage. Consequently, the percent error in this treatment is 0.4%.

Analysis of Fly Ash Samples with AAS

The fly ash samples resulting from fractionation, referred to as medium fraction non-magnetic fly ash, are analyzed using atomic absorption spectrometry (AAS) to determine their chemical composition. The results of the AAS analysis are presented in Table 3. The data in Table 3 shows that the chemical composition of each fraction differs, indicating that the separation through fractionation affects the chemical composition of the fly ash. In the light fraction, the Si/Al molar ratio is 1.29; in the medium fraction, it is 2.55; and in the heavy fraction, it is 2.86. This demonstrates that the aluminum content decreases relative to the differences in specific gravity among the fly ash sample fractions.

Table 3. Chemical composition of fly ash sample result of ASS analysis

Types of fly ash samples	% by weight of the constituent oxide elements				Si/Al molar ratio
	SiO_2	Al_2O_3	CaO	Fe_2O_3	
Light fraction fly ash	23.50	9.00	2.01	1.58	1.29
Medium fraction fly ash	22.50	15.12	2.81	2.45	2.55
Heavy fraction fly ash	25.99	15.43	2.57	7.09	2.86

Synthesis of 4A Zeolite from Medium Fraction Fly Ash Sample

Medium fraction non-magnetic fly ash was reacted with NaOH in aquabides, with variations in the addition of aluminum oxide (Al_2O_3): 0.5 g for sample A, 1.0 g for sample B, and 1.5 g for sample C. The purpose of adding Al_2O_3 is to provide a source of aluminum to achieve a Si/Al ratio close to 1. Al_2O_3 serves as a source of alumina in zeolite synthesis, which is a key component in the structure of zeolites, typically composed of alumina and

silica. In this synthesis process, Al_2O_3 supplies aluminum ions that become part of the zeolite's structural framework.

The crystallization of 4A zeolite is carried out by refluxing the gel mixture with the addition of disodium dihydrogen ethylenediaminetetraacetate (Na_2EDTA). The role of Na_2EDTA is to reduce or eliminate the interference of calcium and iron metal ions in the zeolite formation process. Consequently, 0.569 g of Na_2EDTA was added during the synthesis. The results of the synthesis of 4A zeolite, incorporating NaOH, Al_2O_3, and Na_2EDTA, are presented in Table 4.

Table 4. Weight of synthesized zeolite 4A solids

Sample	Non-magnetic fly ash (g)	Addition of NaOH (g)	Variations in adding Al_2O_3 (g)	Addition of Na_2EDTA (g)	4A Zeolite Crystals (g)
A	5	4	0.5	0.569	5.6342
B	5	4	1.0	0.569	5.9351
C	5	4	1.5	0.569	6.8550

From Table 4, it can be concluded that variations in the addition of Al_2O_3 influence the formation of 4A zeolite crystals. The weights of the 4A zeolite crystals from the successive syntheses are as follows: A = 5.6342 g, B = 5.9351 g, and C = 6.8550 g. Optimal formation of 4A zeolite crystals occurred with the addition of 1.5 g of Al_2O_3. This indicates that increasing the amount of Al_2O_3 in the synthesis enhances the weight of the 4A zeolite crystals. Aluminum functions to connect the silica units in the zeolite structure, aiding in the formation of the three-dimensional framework typical of zeolites.

Table 5 illustrates the differences in the Si/Al ratio based on the chemical composition of the synthesis results, showing a significant change in the ratio. However, in sample A, the chemical composition of the Si/Al ratio is further from 1 compared to the ratio before the addition of the Al_2O_3 compound. This may indicate that changes in the structure and framework of the zeolite only occur under specific conditions. Thus, it can be concluded that the optimum conditions for this study are found in sample B.

Table 5. Chemical composition of synthesized zeolite 4A

Sample	% by weight of the constituent oxide elements				Si/Al molar ratio
	SiO_2	Al_2O_3	CaO	Fe_2O_3	
A	33.12	31.59	2.11	0.32	1.77
B	24.78	29.60	1.68	0.48	1.42
C	25.99	29.99	2.01	0.44	1.46

Meanwhile, the effect of adding Na_2EDTA plays a complementary role in the synthesis process, acting as a chelating agent that binds metal ions. The chemical composition analysis shows a significant reduction in the Fe_2O_3 content before and after the addition of Al_2O_3 and Na_2EDTA. In this case, Na_2EDTA binds Fe ions in solution or as contaminants, resulting in a drastic decrease in the mass percent of the Fe_2O_3 content from each sample. This demonstrates that Na_2EDTA prevents these metals from interacting with the main reactants or disrupting the synthesis process, allowing them to be removed in solution. This improves product quality and helps ensure the formed zeolite structure has better quality and more consistent composition.

Chemical Composition of Synthesized 4A Zeolite

The synthesized 4A zeolite was analyzed using atomic AAS to determine its chemical composition. The results of this analysis are presented in Table 5. The table demonstrates that the addition of Al_2O_3 not only affects the weight of the produced 4A zeolite but also influences its chemical composition. Sample B, with a Si/Al molar ratio 1.42, exhibits better quality than the synthetic zeolites A and C. This indicates that the addition of the appropriate amount of Al_2O_3 plays a crucial role in the synthesis of 4A zeolite.

In sample A, the addition of Al_2O_3 results in a high molar ratio value, suggesting that the alumina supply is still not optimal. Similarly, in sample C, the high ratio indicates that the alumina supply exceeds the optimal limit in solution. This condition shows that to achieve an ideal molar ratio, the alumina source must be appropriately adjusted.

The effect of removing other oxide elements, such as CaO and Fe_2O_3, is also noteworthy. The addition of Al_2O_3 results in a significant decrease in the percent content of Fe_2O_3; however, the decrease in CaO content is significant only when the appropriate amount of Al_2O_3 is added.

Characterization of Synthesized 4A Zeolite Crystals

The synthesized 4A zeolite was characterized using an infrared (IR) spectrophotometer in the wavelength range of 500–4000 cm^{-1} to determine the structure of the 4A zeolite framework. The IR spectra of the three synthesized zeolite solids are presented in Figure 2.

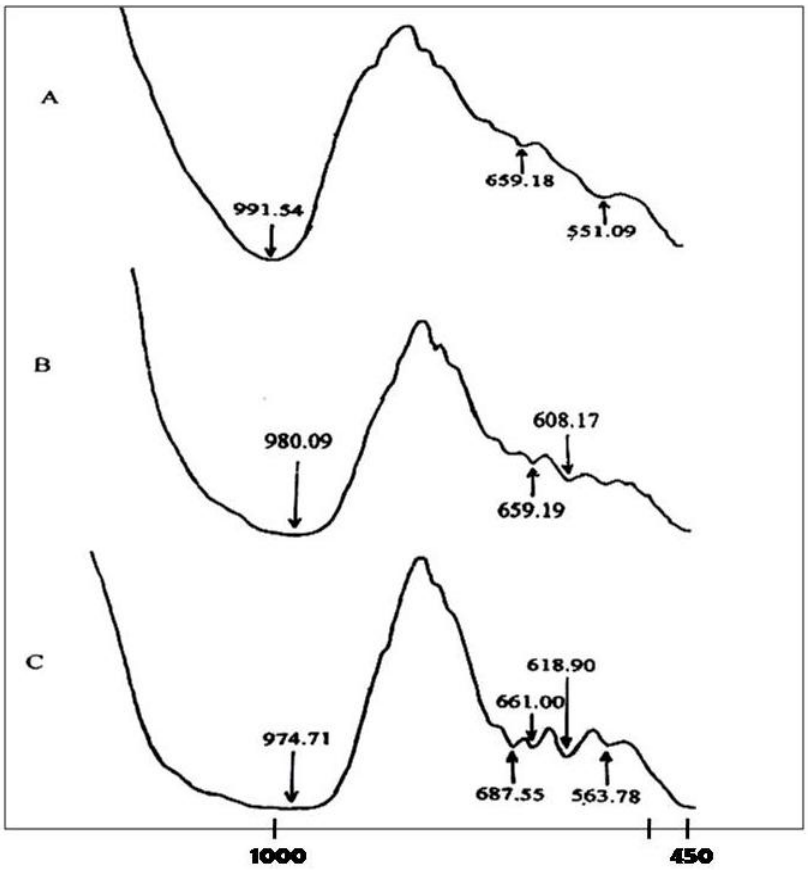

Figure 2. IR spectra of 4A zeolite synthesis results with the addition of Al_2O_3: A) 0.5 g, B) 1.0 g, and C) 1.5 g

Figure 2 shows the absorption bands that mark the double 4-ring characteristic of 4A zeolite in the spectrograms of zeolites synthesized from the medium fraction as the base material, with the addition of 0.5 g and 1.0 g of Al_2O_3, appearing at wave numbers 551.09 cm^{-1} cm^{-1} and 608.17 cm^{-1}, respectively. Meanwhile, the medium fraction with the addition of 1.5 g of Al_2O_3 showed absorption at wave numbers 618.90 cm^{-1} and 563.78 cm^{-1}, with greater absorption intensity. Wide absorption bandwidths are typically caused by large spectral line widths, which can occur when significant energy is absorbed by various vibrational modes. This suggests that the presence of excess Al_2O_3 may lead to the formation of functional groups contributing to the same band.

Similarly, the absorption bands marking the asymmetric stretching vibration of TO_4 (T stands for Si or Al atom in the zeolite framework) in the spectrograms for the zeolites synthesized with the medium fraction and varying amounts of Al_2O_3 (0.5 g, 1.0 g, and 1.5 g) appear at 991.54 cm^{-1}, 980.09 cm^{-1}, and 974.71 cm^{-1}, respectively. Based on these wave number values, it can be inferred that the T–O bonds in the double 4-ring and tetrahedral TO_4 framework of 4A zeolite, synthesized using the medium fraction with the addition of 1.5 g of Al_2O_3, are stronger than those in the zeolites synthesized with 0.5 g and 1.0 g of Al_2O_3. This indicates that the addition of Al_2O_3 influences the quality of the produced 4A zeolite. The 4A zeolite with a Si/Al molar ratio of 1.46 demonstrates better quality than those with ratios of 1.77 and 1.42.

CONCLUSION

4A zeolite has been successfully synthesized from Suralaya coal fly ash. The fly ash, containing silica and aluminosilicate minerals, serves as the base material for zeolite synthesis. Impurities from other elements have been effectively separated at low levels using a magnetic stirrer and fractionation. Optimal quality 4A zeolite crystals were obtained from the synthesis of 5.9351 g of medium fraction fly ash, along with 1 g of aluminum oxide (Al_2O_3), 4 g of sodium hydroxide (NaOH), and 0.569 g of disodium dihydrogen ethylenediaminetetraacetate (Na_2EDTA). Infrared (IR) characterization results indicate that the optimal 4A zeolite from medium fraction fly ash is characterized by crystals with the addition of 1.5 g of Al_2O_3. Variations in the addition of Al_2O_3 compounds

significantly influence the quality of the synthesized 4A zeolite. Based on IR spectrogram data, the optimum 4A zeolite framework structure is indicated by a wave number of 564 cm^{-1}, which confirms the presence of double vibrations, and 661 cm^{-1}, which signifies symmetric stretching vibrations. Additionally, the presence of H_2O hydrate is suggested by O-H absorption peaks at wave numbers 3460.86 cm^{-1} and 974.71 cm^{-1}, indicating asymmetric stretching vibrations linked to the external connections of the zeolite framework structure.

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