Synthesis and characterization of natural zeolite-clay as resistive humidity detection

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Abstract. Zeolite-clay was successfully employed in as resistance type humidity sensor. Zeolite-clay humidity sensor was synthesized by crushing into powder and soaked into 6% H₂SO₄ while stirred for two hours using a magnetic stirrer. The solution was filtered, washed using aquadest and dried at 100°C for 5 hours with the mixture process of zeolite and clay were varied into 10%:0%, 9.5%:0.5%, 9%:1%, 8.5%:1.5%, and 8%:2%. The result pressed with a size of 3x3x1 cm³ using a hydraulic under 3 tons pressure for 10 minutes and heated at temperatures of 800°C. Zeolite-clay was placed in a testing chamber equipped with the electrode that connected to an electrical supply of 3 Volt. The electrical resistance was recorded using Multimeter Hydra Series III Fluke when exposed with humidity in range of 18.5-99% RH. Zeolite 8%-clay 2% sensor exhibits the highest sensitivity properties, which indicate saturated resistance value at 99% RH. Meanwhile, Zeolite 8.5 gr-clay 1.5 gr revealed the highest response value at 54.3 Mega Ohm. Based on SEM and EDX characterization, the ratio of Si/Al and microstructure surface have an effect towards humidity detection process. The results indicate enhancement than previous research on zeolite as a sensor, and therefore Zeolite-Clay has proved the capability to detect humidity.

1. Introduction

Humidity measurement is essential parameters in various fields such as agriculture, industrial processes, and household electronic appliances as well as in the field of medical services [1, 2]. Furthermore, the measurement of humidity is becoming increasingly important to avoid spoilage of chemicals, fuels and pharmaceuticals as well to control storage and manufacturing conditions [3, 4]. Various humidity sensing materials have been developed, such as semiconducting material, polymer material, ceramic material and composite material. However, the demand for good properties such as fast response, high sensitivity and good repeatability towards humidity is required from the material [4-6]. Therefore, it is necessary to discover improved material for sensor performance in order to be used for practical application, especially the commercial field.

The attention of humidity sensing has been well known, and much research has been attracted to the development of humidity sensitive materials, specifically zeolite [7-10]. Natural zeolites are hydrated aluminosilicates containing [SiO₄]⁴⁻ and [AlO₄]⁵⁻ with frameworks structure including of channels, cavities and micropores [11]. The properties of zeolites as sensors depends on different types of zeolite structures which have different pore sizes in the sub-nanometre range [12]. These sizes also
can discriminate the function of zeolite along based on the type of its molecules. Furthermore, the adsorption affinity of the zeolite can be tailored by changing the Si/Al ratio on the zeolites and the nature of the charge compensating cations [8]. Moreover, there are ion conductors within zeolites attributed to intrinsic conductivity properties (unlike silicates) which have a role as mobile cations that hop from one binding site to the others site [13]. Based on that, Schaf et al [14] proposed that there is a possibility of gaseous molecules influenced the conduction process by accessing the zeolite channel system. However, the low response value and sensitivity of zeolites towards sensing humidity is the main problem to overcome. Hence, clay was proposed as an addition to overcoming these problems.

Clay is soil mineral particle which has important properties that naturally trap the analyte that flows by water on the surface or in the ground by the process of adsorbing or the ion exchanging [15, 16]. Another key factor that makes clay used as an additive included the high capability of ion exchange, a stabilization for chemical process, mechanical of matrix and the properties of adsorbent due to the large specific surface [17]. These properties hypotheses have an impact on the repeatability and recovery properties of zeolite. Thus, our research focuses on the synthesis and characterization of natural zeolite-clays a resistive humidity sensor.

2. Materials and Methods
The raw material of this study consisted of natural zeolite lump which mined from Sukamaju Village, Pahae Jae while clay ground was obtained from Wonosari Village, Lubuk Pakam, Deli Serdang, that respectively acquired in Indonesia. Synthesis of natural zeolite-clay was fabricated by crushing zeolite lump and clay ground into powder using mortar with a particle size of 200 mesh. Separately, 6% H₂SO₄ was used as an activator by soaked and stirred natural zeolite and clay powder for two hours using magnetic stirrer until homogenized. The immersion can eliminate impurities and increased the surface area. Then, the solution was filtered and washed using aquades until neutral pH reached, which then dried using an oven at 100°C for 5 hours. The mixture process of zeolite and clay were varied into 10%:0%, 9.5%:0.5%, 9%:1%, 8.5%:1.5%, and 8%:2%. The result poured into solid mould shape with the size of 3x3x1 cm³ which then pressed with a hydraulic under 3 tons pressure for 10 minutes and heated at temperatures of 800°C. Hereafter, the synthesize of natural zeolite-clay resulting solids form that ready to be characterized as a resistive humidity sensor.

The characterization of natural zeolite-clay was performed using an experimental setup in Figure 1. Each natural zeolite-clay was placed in a testing chamber equipped with silver and titanium electrode as positive and negative contact, respectively. The testing chamber has an inlet valve that connected to the outlet valve of a pumped water bottle. The natural zeolite-clay was exposed towards humidity which generated from pumped water bottle within range of 18.5 – 99% Relative Humidity (RH) at room temperature that recorded using Hygrometer. Electrical supply of 3 Volt was series connected to titanium and silver electrode whereas High-Resolution Digital Multimeter Hydra Series III Fluke was used for recording resistance when natural zeolite-clay exposed towards humidity. The characterizations as resistive humidity sensor were included response properties which then analyzed with SEM and EDX characterization of natural zeolite-clay to discover the detection mechanism.

![Figure 1. The experimental setup of natural zeolite-clay when exposed towards relative humidity.](image-url)
3. Result and Discussion

The natural zeolite-clay response towards humidity can be clearly seen in Figure 2. The curve reveals a continuous decrease in resistance from various natural zeolite-clay with an increase in humidity range from 18.5 to 99% RH. The response of zeolite 10 gr shows the lowest saturated resistance at 18.03 Mega Ohm while the highest saturated resistance at 54.3 Mega Ohm was exhibited by Zeolite 8.5%-Clay 1.5% when exposed towards humidity. Moreover, Zeolite 9.5%-Clay 0.5%, Zeolite 9%-Clay 1% and 8%-Clay 2% generating similar trend with saturated resistance values of 22.6, 29.2 and 41.1 Mega Ohm under humidity exposure, respectively. Literally, it means the addition of clay into zeolite increase the response properties, which results in an increment of resistance result when exposed towards humidity. It was found out that results occurred due to the ratio of Si/Al, which affect the resistance value whereby proved by SEM-EDX characterization result.

Furthermore, the saturated resistance of various zeolite-clay occurred at the difference of %RH exposure were regarded as sensitivity properties in detecting humidity. Figure 2 shows the highest sensitivity yielded from Zeolite 8%-Clay 2% while the lowest sensitivity generated from Zeolite 10% during humidity exposure at 99% and 77% RH, respectively. This indicated that Zeolite 10% have the ability to differentiate the humidity from 18.5 to 99% RH, which resulting as resistance value change. Meanwhile, Zeolite 8%-Clay 2% yields properties to distinguish from 18.5 to 77% RH, which literally means humidity higher than 77% RH generated the same resistance values. The results were attributed to aggregates and unevenly distributed particles on the surfaces that affects adsorption mechanism during the sensing process.

![Figure 2. The electrical resistance response of various zeolite and zeolite-clay with relative humidity in range of 18.5 – 99% RH.](image-url)
Figure 3 shows the EDX spectrum of various zeolite and zeolite-clay observed by EDX Oxford instrument. The result indicates the presence of O, Si and Al as the main constituent that corroborates the synthesis of zeolite and zeolite-clay. The lowest Si/Al ratio of 3.53 was produced from Zeolite 10 gr, while the highest value of 3.89 generated from zeolite 8.5%-Clay 1.5%. This result can be attributed to the addition of clay, whereby the decrement weight percent of Al affecting the resistance response in sensing humidity. Nevertheless, the amount of Si and Al for zeolite 8 gr-Clay 2 gr increased, which results in the ratio of Si/Al decreased into 3.75. Hence, the resistance response during humidity exposure was decreased lower than the result of Zeolite 8.5%-Clay 1.5%. This result also implies electron movements were restricted during humidity sensing produces different saturated resistance value[10]. Moreover, the EDX spectrum showed the amount of oxygen was changes depend on the addition of clay which believed have an influence on the surface structure as indicated in SEM Microstructure result.

The relationship between EDX analysis of elements and surface structure is exhibited by SEM images shown in Figure 4. SEM images analysis proved the surface of Zeolite 10% exhibited even
distribution particles and bigger pores. Meanwhile, the addition of Clay into Zeolite changes the distribution particles, and bigger pores become unevenly and smaller on the surfaces. This result implied the sensitivity properties as a sensor which resulting in difference saturated resistance under humidity exposure. It was attributed to the amount of oxygen and the ratio of Si/Al producing smaller size and uniformed holes[8, 16]. The smaller pores were enhancing adsorption ability to differentiate between the higher and lower amount of relative humidity[18]. Therefore, the sensitivity of zeolite and zeolite-clay as a sensor during humidity exposure was influenced by the microstructure surfaces.

![SEM Microstructure Analysis of various zeolite and zeolite-clay.](image)

**Figure 4.** SEM Microstructure Analysis of various zeolite and zeolite-clay.

4. Conclusion
In summary, synthesis, characterization and humidity detection properties of zeolite with the addition of clay are investigated. Zeolite 8%-clay 2% sensor exhibits the best sensitivity properties, while
Zeolite 8.5%-clay 1.5% revealed the best response properties. The best sensitivity properties indicate resistance value change was saturated at 99% RH. Meanwhile, the best response properties stated the highest saturated resistance value at 54.3 Mega Ohm. It was found out that the ratio of Si/Al and microstructure surface have an effect towards humidity detection process. Overall, the results in this study produced improvement than previous research on zeolite as a sensor, and therefore Zeolite-Clay has proved as a resistive humidity sensor.

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