Dealumination and Na activation of natural zeolite for CO_2 adsorption on biogas

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Abstract:- In this study, natural zeolites from the Philippines were modified using NaOH heat treatment and NaCl hydrothermal process. Pre-treatment using ferro-filtering and dealumination using different concentrations of HCl acid leaching were prepared prior to sodium activation. Heat treatment was performed using 5M NaOH at 80 °C for 72 hrs while 3 cycle hydrothermal process was performed using 5M NaCl at 10 psi for 1 hr. Diffraction pattern from XRD showed Heulandite (HEU) – Clinoptilolite (CLI) and Mordenite (MOR) framework for raw and acid pre-treated zeolites. There was a shift in HEU characteristic peak from 9.9084° and 8.91 Å to 9.6901° and 9.12 Å which can be attributed to the decrease of contribution of HEU type zeolite. The decrease in contribution enabled the peak to move towards 9.10 Å, value expected for MOR. However, it was found that presence of amorphous phase widens MOR structure on d-spacing 13.45 Å that created humps. Reduction of intensity peaks on HEU – CLI on 9.85°, 9.88° and 22.22° regions were observed attributed to acid leaching. The decline on this characteristic peaks implies severe degradation of crystal framework after heavy acid treatment although the framework was stable. Acid treated modified zeolites intensify Si/Al ratio due to dealumination. Sodium uptake along with higher Si/Al ratio was preferred for CO_2 adsorption in a mixed gas system of CO_2/CH_4. Both NaOH heat treatment and NaCl hydrothermal process increase Na uptake as confirmed by EDS but the latter is preferred due to higher Si/Al ratio..

Keywords:- Dealumination, Na activation, Zeolite, Si/Al ratio, CO_2 adsorption

I. INTRODUCTION

Natural and synthetic zeolites are long been used in various industrial applications [1-10]. Zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores, channels and cavities of molecular dimensions [11]. Zeolite is made of negatively charged alumino-silicate building blocks that are stabilized by cations such as calcium and sodium [12-20]. Different classifications of zeolites exists, as a general rule, it is grouped in different frameworks based on the arrangement of T-atoms [21]. The structure of zeolites contains aluminum, silicon, and oxygen in regular frameworks with cations and water in the pores.

Zeolites as the physical adsorbents for CO_2 capture have been reviewed and explored by numerous researchers [22-26]. Since the gas adsorption reactions initially take place at the surfaces, the elements at the surface play an important role in the initial adsorption process [27-28]. Literatures on zeolite and its preparation with synthesis and modifications have been widely published to improve the adsorption characteristics of zeolites [29-34].

Hydrothermal treatment of zeolites involves the application of high pressure to effectively exchange native calcium cations into sodium [35-37]. This process is widely used to produce high quality modified zeolites. In this study, hydrothermal treatment was used and compared to reflux heat treatment and effects of acid pre-treatment. To date, limited published articles are seen on engineered Philippine natural zeolites.

II. METHODOLOGY

Natural local zeolites were acquired from Industrial Technology Development Institute under the Department of Science and Technology, Government of the Philippines, thru the Materials Science Division. These zeolites were prepared by continuous washing and passing thru a magnetic separator for ferro-filtering to remove ferrous substance then air-dried at 25 °C for 1 week. Effective separation of zeolite and fine iron particles from slurries passing by gravity flow is needed prior to modification since natural zeolites have high iron content embedded into their cavities which move into extra framework of zeolites upon high temperature calcination or steaming. Three (3) bags of 300 grams each were used for acid pre-treatment using hydrochloric acid with different molarity of 0M, 1M, 3M and 5M of HCl respectively that lasted for 48 hours at 25 °C. These

acid pre-treated zeolites were washed using distilled water until pH is equal to 7. Upon washing, acid pre-treated zeolites were dried at 80 °C for 72 hours. Dried acid-treated zeolites were manually crushed and pounded until it passed thru Tyler mesh no. 100. Particle sizes were below 149 microns prior to sodium activation. There were three conditions considered in the sodium activation of zeolites. First condition was the heat-treatment process where acid pre-treated zeolites underwent NaOH reflux for 72 hours at 80 °C hot plate. Second condition was the hydrothermal condition where raw and acid pre-treated zeolites with 5M NaOH were subjected to a 3 cycle pressurized cooker of 10 psi for 1 hour. Third condition was 3 cycle hydrothermal modification using 1M and 5M NaCl for 1 hour in a pressure cooker of 10 psi.

About 30 grams of 1M, 3M and 5M HCl acid pre-treated zeolites were subjected to 3M and 5M NaOH heat-treatment for 72 hours at 80 °C. Also, about 30 grams each of 3M and 5M HCl pre-treated zeolite were prepared for a 3 cycle 5M NaOH hydrothermal process where 10 psi for 1 hr process time is used each cycle. Washed until pH was equal to 7 and dried for 72 hrs at 80 °C, modified zeolites were pounded until particle sizes of less than 149 microns were acquired using Tyler mesh no. 100.

Hydrothermal synthesis was performed after preparation of 1M and 5M NaCl in a beaker over 400 rpm magnetic stirrer for 2 hrs. About 20 grams of acid treated zeolites were mixed in autoclave bottles with 200 mL of 1M and 5M of NaCl separately in a pressure cooker of 10 psi for 1 hr. After 3 cycle hydrothermal modification, zeolite were washed until pH was equal to 7 and then dried for 72 hrs at 80 °C.

III.   RESULTS AND DISCUSSIONS

Elemental spectra were acquired using Energy dispersive x-ray spectrometer (EDS) by Oxford Instruments attached to the Nano Helios Focused Ion Beam – Field Emission Scanning Electron Microscopy (FIB-FESEM) by FEI. Using less than 4 mm working distance and 20 – 25 kV beam voltage, spectra and mapping were captured to evaluate elemental composition of each acid pre-treated zeolite as presented in Fig. 1. EDS was used to acquire elemental composition of different types of zeolites. Using Helios FIB-FESEM coupled with EDS, elemental spectra were acquired and studied. Summary of elemental data for different treated zeolite from pre-treatment HCl acid pre-treatment, NaOH heat treatment, and NaCl hydrothermal process were presented in Fig. 2 and 3 showing elemental composition and Si/Al ratio respectively.
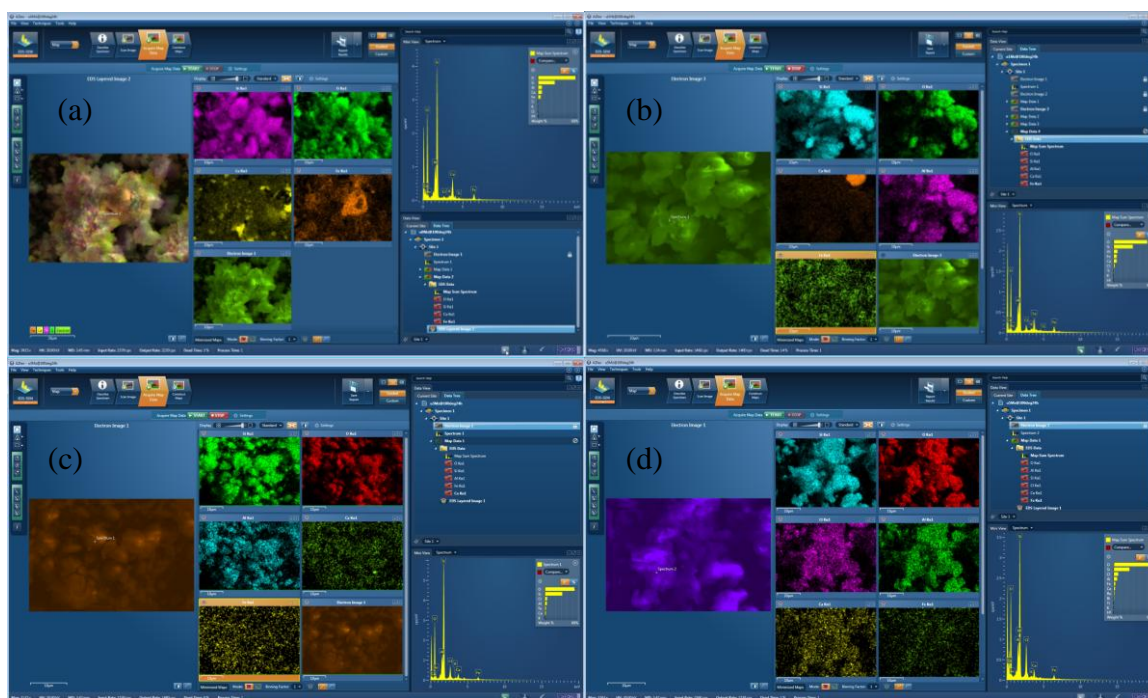

Fig. 1 EDS complete elemental data mapping of acid pre-treatment for: (a) raw zeolite, (b) 1M HCl pre-treatment, (c) 3M HCl pre-treatment, (d) 5M HCl pre-treatment

Using SHIMADZU X-Ray diffractometer LAB X, crystal structures of raw and treated zeolites were studied. Dried zeolite powdered samples about 3 μm thick were mounted in the XRD sample holder. The diffractometer model XRD-6000 using Cu K-alpha target was running at 40 kV and 30 mA. At a continuous scan mode and rate of 1 deg/min, scan range from 2 – 60° were evaluated using divergence slit of 1°, scattering slit of 1°, and receiving slit of 0.3 mm at 0.01° sampling pitch. Pre-treated zeolite using HCl were subjected to XRD for elemental analysis. Heulandite (HEU) – Clinoptilolite (CLI) and Mordenite (MOR) framework were

detected based on diffractograms of ferro-filtered zeolite and different acid pre-treated zeolites as shown in different XRD patterns.

After 1M and 5M NaCl hydrothermal synthesis was performed for 0M, 1M, 3M and 5M HCl pre-treated zeolites, samples were washed until pH was equal to 7 and then dried for 72 hours at 80 °C. Dried samples about 3 μm thick were mounted in the XRD sample holder where crystal structures were studied as well.
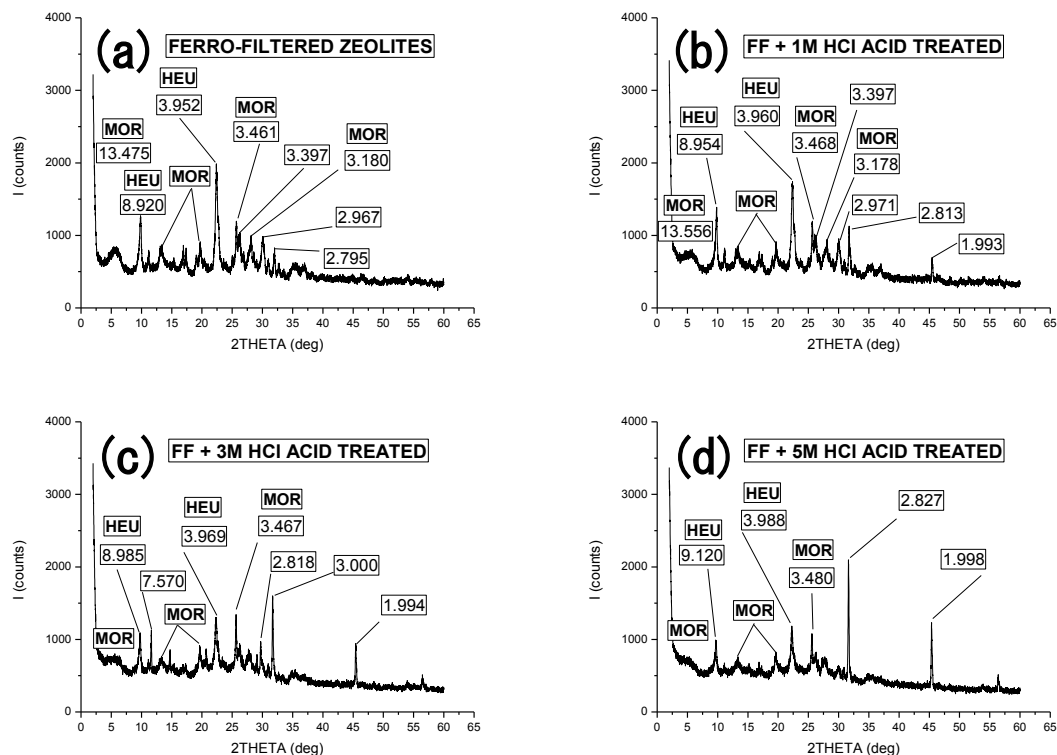

Fig. 2 Diffractogram of different concentration of acid pre-treatment for: (a) raw zeolite, (b) 1M HCl pre-treatment, (c) 3M HCl pre-treatment, (d) 5M HCl pre-treatment
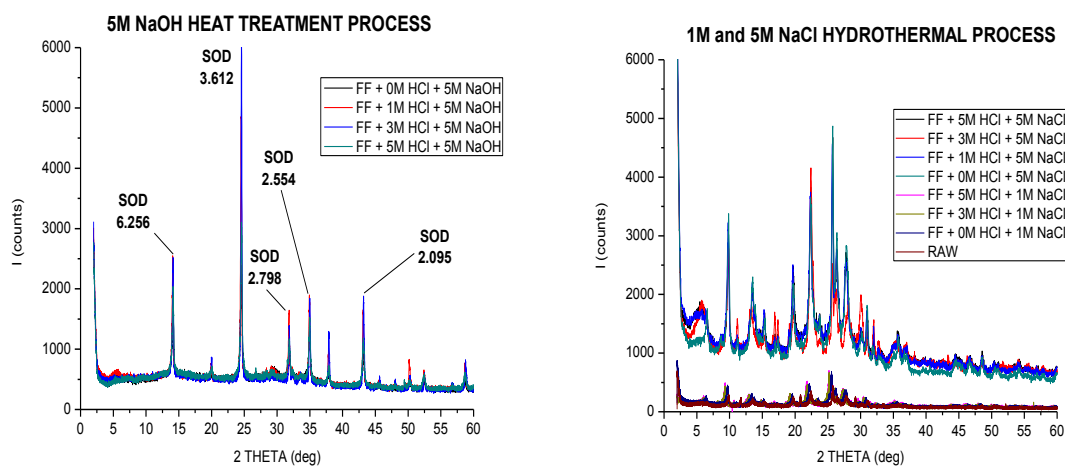

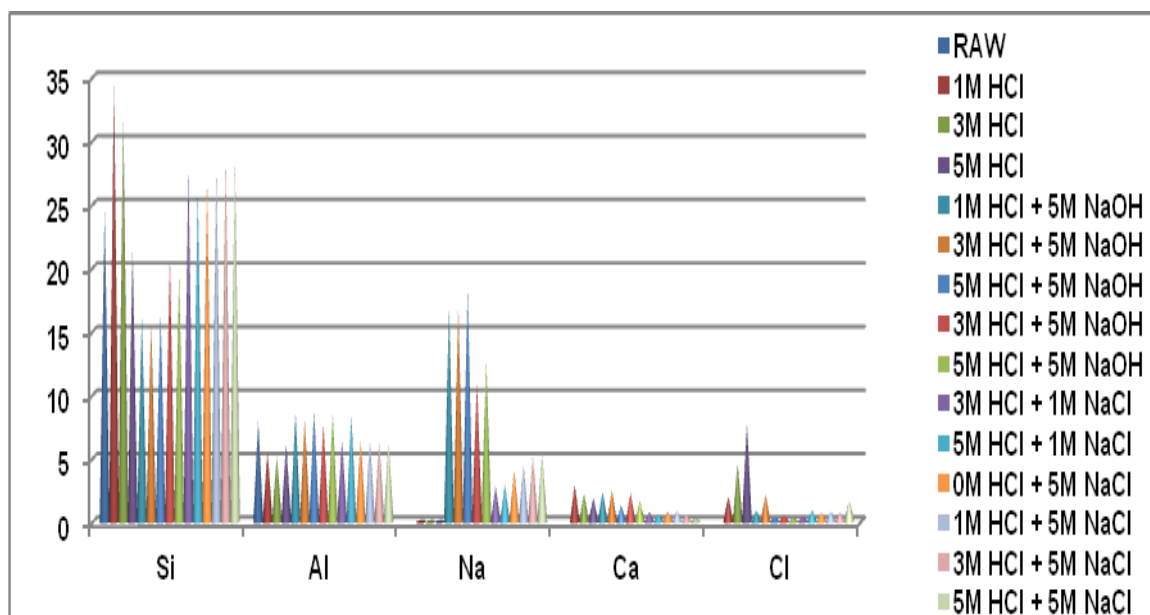**Fig. 3 Diffractograms of modified zeolites**

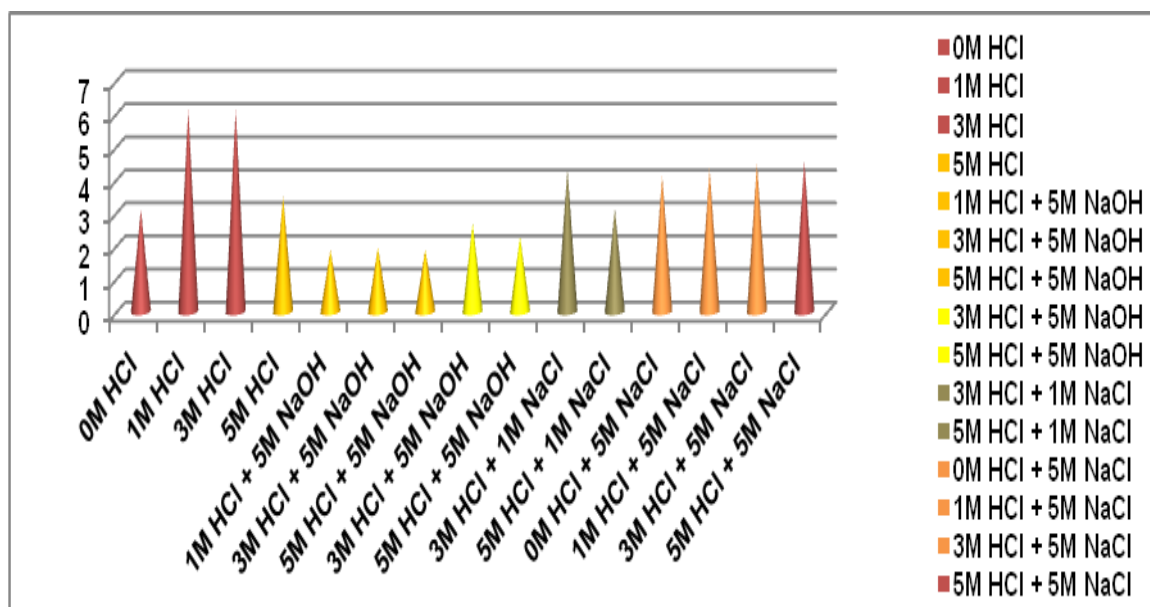**Fig. 4 Cone bar graph of elemental composition of zeolites**

Fig. 5 Cone bar graph of Si/Al Ratio for different types of zeolite processing

Diffraction pattern from XRD showed Heulandite (HEU) – Clinoptilolite (CLI) and Mordenite (MOR) framework for raw and acid pre-treated zeolites. Upon HCl acid pre-treatment, same structure were acquired. There was a shift in HEU characteristic peak from 9.9084° and 8.91 Å to 9.6901° and 9.12 Å which can be attributed to the decrease of contribution of HEU type zeolite. The decrease in contribution enabled the peak to move towards 9.10 Å, value expected for MOR. However, it was found that presence of amorphous phase widens MOR structure on d-spacing 13.45 Å that created humps.

Also, reduction of intensity peaks on HEU – CLI on 9.85°, 9.88° and 22.22° regions were observed attributed to acid leaching. The decline on this characteristic peaks implies severe degradation of crystal framework after heavy acid treatment. Meanwhile, heat treatment using 5M NaOH showed different zeolite framework compared to raw and other modification. Comparison of interplanar spacing (d-spacing) and relative intensities similar to Kotashane et al. in 1986 proves an effective approach in defining zeolite frameworks. Characteristic peaks with diffraction pattern revealed sodalite octahydrate (SOD) type zeolite for 5M NaOH heat treatment modification, same structure formed by Baccouche et al. in 1998 for preparing sodalite octahydrate from 5M NaOH. A sodalite octahydrate framework was produced with literature value of window pore size 0.27 nm which is applicable for water separation. In general, zeolites with low Si/Al ratio (Si/Al < 5),

for example, zeolites A (LTA), X (FAU), and hydroxysodalite (SOD), are prepared from reaction mixtures with low Si/Al ratio and strong alkalinity. Sodalite has been theoretically suitable for hydrogen storage, water selective material and H2/CH4 separation because of low Si/Al ratio. Produced sodalite is an assembly of β-cages, the building blocks of many other zeolites which could be used for future study. The increase of alkalinity affects the induction and nucleation periods and speed up the crystallization of zeolites, forming new framework.

The Si/Al ratio in the reaction system plays an important role in determining the structure and composition of the crystallized product. Alkaline solution contributes in dispersing the Si/Al ratio (T-atoms) during growth. Meanwhile, the effects of higher NaCl concentration on hydrothermal modification were seen in stacked pattern diffractogram of 1M and 5M NaCl. In 5M NaCl hydrothermal process, peak height significantly increases compared to 1M NaCl owing to higher intensity counts. Although strongest peaks did not alter much, reduction in characteristic HEU peaks was expected during hydrothermal process at 10 psi due to the severe pressure experienced by zeolite. With minimal shifts on MOR diffraction peaks for both acid pre-treatment and hydrothermal processes, MOR phase was far more resistant to chemical and thermal treatment than HEU type. The interferences of predominant peaks of other crystalline phase lead to minimal peak shifting but slight shrinking of zeolite cells.

IV.   CONCLUSIONS

Sodium activation was successfully performed using heat treatment and hydrothermal treatment. Both NaCl hydrothermal process and NaOH heat treatment increase Na content of modified zeolites based on EDS spectra. Too much sodium and basic in nature, NaOH treated zeolites transformed into a new framework of sodalite type as confirmed by XRD peaks. Sodium as major cation present in modified zeolites performs the higher CO_2 adsorption capacity compared to lower sodium but molecular sieving would be eliminated in the transport mechanism if sodalite type zeolite would be used for CO_2/CH_4 gas separation. In terms of sodium composition of zeolite and higher Si/Al ratio, NaCl hydrothermal process was preferred for CO_2/CH_4 gas separation experiment although sodium acquired during NaCl hydrothermal process was far less active than the NaOH heat treatment process. Moreover, dealuminated zeolite reduces the acidity of zeolite surface which is preferred since the zeolite must have basic surface in order for the CO_2, as Lewis acid, to act on zeolite base sites. CO_2 adsorption would be more effective in a basic surface of zeolite with higher Si/Al ratio for the adsorption of non-polar compounds such as CO_2.

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