

## Variation of Alumina Sources on the Synthesis of High-Silica Mordenite from Lapindo Mud without Organic Template

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**ABSTRACT:** Mordenite with high-silica content was successfully synthesized without organic template with variations in alumina sources. Silica was extracted from Lapindo mud using NaOH and the filtrate was titrated with HCl. The alumina sources studied in this paper includes natural zeolite, aluminum foil and sodium aluminate. The synthesis of zeolite using natural zeolite, aluminum foil and sodium aluminate was conducted under the following reaction conditions  $6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:30\text{SiO}_2:780\text{H}_2\text{O}$  at 190 °C for 24 hours;  $3.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:20\text{SiO}_2:219\text{H}_2\text{O}$  at 165 °C for 48 hours; and  $8\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:50\text{SiO}_2:960\text{H}_2\text{O}$  at 170 °C for 24 hours respectively. The synthesized zeolite and high-silica commercial mordenite was then characterized by XRD, FTIR and XRF. The results showed that high-silica mordenite was successfully formed from sodium aluminate, while other sources formed high crystalline analcime. The results suggested the significance of the effect from impurities in the alumina sources during the synthesis of zeolites.

**Keywords:** Free template, Lapindo mud, Mordenite, Synthesis.

### I. INTRODUCTION

Mudflow from the drilling locations of Lapindo Brantas Inc. on May 29, 2006, has resulted in tremendous losses and is expected to continue up to 31 years from the present time. The increasing volume of mud has become a serious problem in the environment. Many researchers have put effort to solve the problem and because of the silica content of Lapindo mud is quite high, a research by Munasir had successfully synthesized silica gel with 97.8% purity [1]. Therefore, Lapindo mud is potential to be used as a silica source in the synthesis of mordenite.

By utilizing synthetic mordenite, the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  could be tuned according to the intended application. Due to its high thermal and acid stability, mordenite has been used as catalysts for important reactions such as hydrocracking, alkylation, reforming, dewaxing, hydroisomerization and the production of dimethylamines [2-9]. Mordenite has also been used in the adsorptive separation of gas or liquid mixtures [2, 10]. In addition, mordenite has been considered to be used for applications in semiconductors, chemical sensors, and nonlinear optics [11].

Mordenite zeolites are commonly prepared by the hydrothermal method of the gel containing precursors of silica, alumina, nonbridging metal cations, and organic template as structure directing agents. 1,8-diamino-p-menthane [12] and o-phenylenediamine [13] were used as SDA for the synthesis of mordenite; however, different amines instead of 1,8-diamino-p-menthane or o-phenylenediamine have also been used as structure directing agents (SDAs) [14-17]. The use of organic templates can cause many adverse problems such as high production cost, contamination to waste water, air pollution arising from thermal decomposition, and coke deposits due to incomplete decomposition. Therefore, to overcome such detrimental effects, many researchers have made great effort to synthesize mordenite in the absence of organic templates [18, 19].

In this communication, we have synthesized mordenite zeolite powders using Lapindo mud as a silica source and other low cost water-based precursors, in the absence of any organic template, following a single step hydrothermal process at relatively low temperature under static condition; to our knowledge, it has not yet been reported before. As the present method for the preparation of mordenite zeolite powders starts with abundantly available Lapindo mud, and avoids the use of any organic precursors, it will have the advantage as a low cost and environmental friendly process.

One of the important factors that influence the quality of the resulting zeolite is the presence of metal impurities in the reaction system that can interfere with the formation of zeolite [20]. This paper aims to study the effects of metal impurities contained in the alumina source towards the type of synthesized zeolite. This

research can invite and challenge any scientist to develop innovative chemical process to renew the conventional chemical processes become more friendly to the environment and humans without abandoning the principles of optimization in the production process.

## II. EXPERIMENTAL

### 1. Preparation of silica source

Lapindo mud in the form of hard solid was obtained from Sidoarjo, East Java. Lapindo mud was sifted and then stirred in 6 M NaOH solutions for 5 hours at 90 °C. The filtrate was titrated with HCl until pH 8 to produce silica gel. It was then used as the silica source in the synthesis of zeolite.

### 2. Synthesize of high-silica mordenite

Zeolite was synthesized through hydrothermal reaction in an autoclave by mixing the alumina source, silica source and sodium hydroxide. The alumina sources utilized in this experiment were natural zeolite, aluminum foil and sodium aluminate. The molar composition of reagents and reaction conditions during the synthesis of zeolite varied for each alumina sources. For natural zeolite, aluminum foil and sodium aluminate were  $6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:30\text{SiO}_2:780\text{H}_2\text{O}$  at 190 °C for 24 hours (ZS-1);  $3.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:20\text{SiO}_2:219\text{H}_2\text{O}$  at 165 °C for 48 hours (ZS-2); and  $8\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:50\text{SiO}_2:960\text{H}_2\text{O}$  at 170 °C for 24 hours (ZS-3) respectively. All of the synthesized zeolites were calcined at 550 °C. Commercial mordenite (HSZ-640HOA,  $\text{SiO}_2/\text{Al}_2\text{O}_3=13$ , DTA= 998 °C, BET= 650 m<sup>2</sup>/g, % Crystallinity= 73) was used as the reference materials for the synthesized zeolite.

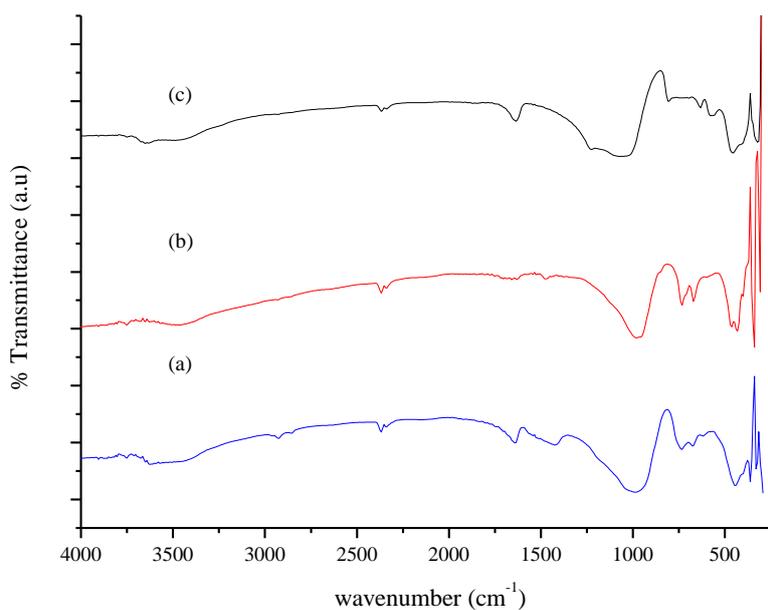
### 3. Material characterization

The crystalline phases present in the zeolites were determined using X-ray Diffractometer (XRD Shimadzu 6000) using Cu filter ( $\lambda=0.15$  nm) with operating condition of 40 kV and 30 mA. Fourier Transform Infrared Spectrometer (FTIR Shimadzu 8201 PC) was used to characterize the framework structure of the zeolites; the samples were dissolved in KBr pellets and were measured in the wavenumber 400-4000 cm<sup>-1</sup>. X-ray Fluorescence Spectrometer (XRF PANalytical MiniPal 4) was used to determine the chemical compositions of the zeolites in operating conditions of 7 kV and under air and helium atmosphere.

## III. RESULTS AND DISCUSSION

### 1. Infrared spectra

Fig. 3.1 showed that the internal asymmetric stretching vibration frequency of ZS-3 is larger than ZS-1 and ZS-2. This phenomenon indicated that the ZS-3 has a Si/Al ratio greater than that of ZS-1 and ZS-2. This fact was further reinforced by the presence of a hump in 1226 cm<sup>-1</sup> region in the ZS-3 absorption. The double ring absorption of ZS-1 appears at 617.22 cm<sup>-1</sup> whereas the ZS-2 at 601.79 cm<sup>-1</sup>. This showed the vibration frequency of a 6 membered rings and 4 membered rings of analcime respectively. Double rings absorption of ZS-3 appeared at 563.21 cm<sup>-1</sup> and 632.65 cm<sup>-1</sup>. Both absorptions indicated that mordenite has been successfully formed in ZS-3 product. Table 1 showed the IR absorption wavelength of ZS-3 and commercial mordenite. The results showed that the ZS-3 IR absorption wavelength was almost identical with that of the commercial mordenite.

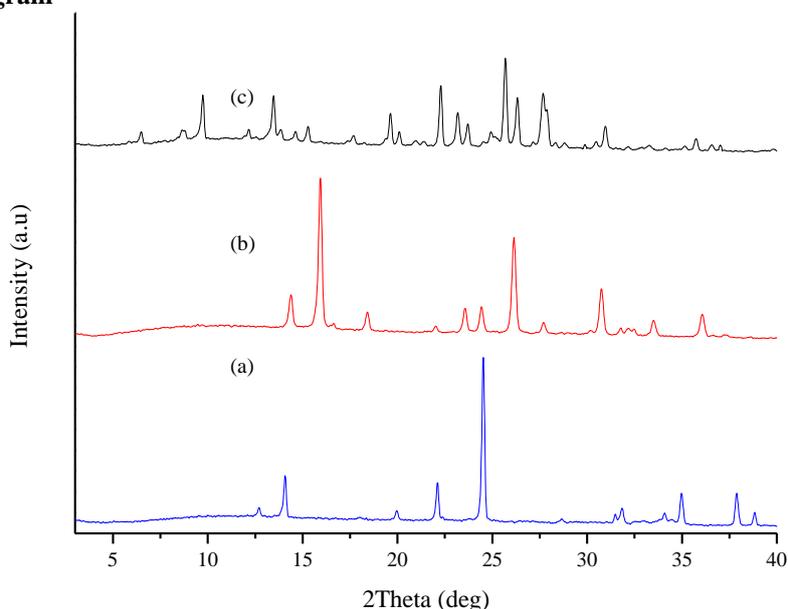


**Fig. 3.1.** Infrared spectra of (a) ZS-1, (b) ZS-2 and (c) ZS-3

**Table 1.** Infrared adsorption of mordenite commercial and ZS-3

Vibration	Commercial	ZS-3
$\nu_{as}$ external	1219 $\text{cm}^{-1}$	1226 $\text{cm}^{-1}$
$\nu_{as}$ internal	1080 $\text{cm}^{-1}$	1064 $\text{cm}^{-1}$
$\nu_s$ external	763 $\text{cm}^{-1}$	810 $\text{cm}^{-1}$
Double ring	640;578 $\text{cm}^{-1}$	632;563 $\text{cm}^{-1}$
Bend T-O	462 $\text{cm}^{-1}$	455 $\text{cm}^{-1}$

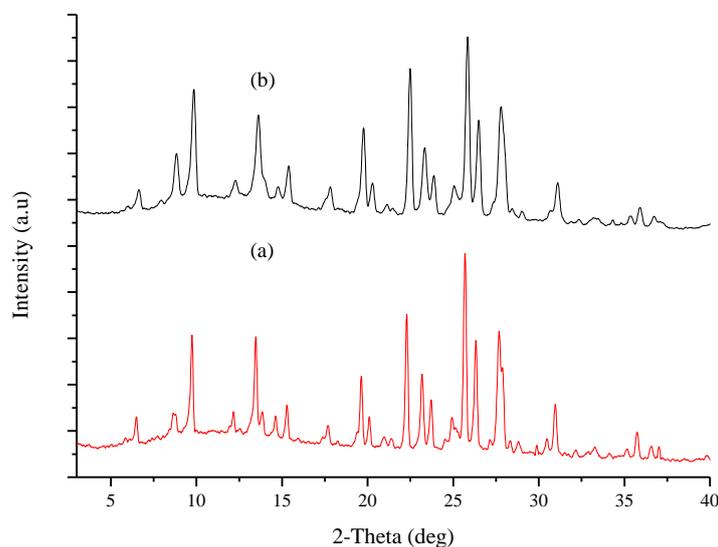
## 2. X-ray diffractogram



**Fig. 3.2.** X-ray diffractogram of (a) ZS-1, (b) ZS-2 and (c) ZS-3

Fig 3.2 showed the diffractograms of ZS-1 and ZS-2. Both of them have the characteristic  $2\theta$  peaks of analcime. The highest intensity peaks indicated that most of the minerals formed in the ZS-1 was in fact analcime. This could be explained by in the amorphous silica, silicon that exists as silanol is about 20-40% and from this number, silanols that could be accounted for the formation of zeolite framework was only 9%wt [21]

and by the presence of impurities in the reaction system resulted in lesser number of amorphous silanol that underwent silylation. Therefore by having lesser number of silylated silicon, the molar composition of Na<sub>2</sub>O rised and shifted the reaction pathway from mordenite formation to analcime [22]. Based on fig. 3.3, it was shown that the diffraction pattern of ZS-3 was similar to that of the commercial mordenite. It was consistent with the IR spectrum. Table 2 showed that not all silica was converted into the zeolite framework.



**Fig. 3.3.** X-ray diffratogram of (a) ZS-3 and (b) commercial mordenite

**Table 2.** Chemical composition of zeolite synthesized (% wt)

Sample	ZS-1	ZS-2	ZS-3
SiO <sub>2</sub>	49.0	72.3	89.4
Al <sub>2</sub> O <sub>3</sub>	13.0	22.3	6.7
Fe <sub>2</sub> O <sub>3</sub>	15.8	2.20	1.30
CaO	18.9	1.49	0.89

#### IV. CONCLUSION

Mordenite with high silica content has been successfully synthesized using sodium aluminate as an alumina source. The synthesized mordenite has a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 21.29. The presence of metal impurities could interfere with the nucleation and crystallization process. This was evident in a shift of the product formation pathways from mordenite to analcime.

#### V. ACKNOWLEDGMENT

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