X-ray Diffraction Analysis on Effect of Time Reaction and Alkali Concentration in Merlinoite

Eddy Heraldy¹², Syaiful Ahmad Nur Cahyo¹, Nurul Apri Indri¹, Fitria Rahmawati¹²

¹Department of Chemistry, Mathematics and Natural Sciences Faculty, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan, Surakarta, Indonesia 57126
²Solid State Chemistry & Catalysis Research Group, Chemistry Department, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan, Surakarta, Indonesia 57126

E-mail : eheraldy@mipa.uns.ac.id

Abstract. This research objectives is to determine the effect of time reaction and alkali concentration on the synthesis of merlinoite. The synthesis of merlinoite was performed by hydrothermal method with variation of reaction time in 8, 12, 24 hours and various concentration at 1, 3, 5M. The quantitative X-Ray Diffraction (QXRD) was employed on product using Le Bail refinement method. Characterization XRD shows the highest crystallinity of the product was obtained at 3M of alkali concentration in 8 hours reaction time. The refinement result revealed three other phases such as quartz, mullite, and tobermorite.

Keywords : Fly ash, Le Bail refinement, Merlinoite, X-ray Diffraction

1. Introduction
Merlinoite is one type of zeolite that has small pores and its presence is very rare in nature [1,2,3,4]. According to Sherman [5], merlinoite has a good ability in ion exchange and adsorption capacity. Merlinoite, also known as zeolite W [6,7,8] is a potential material because it has been widely used as an adsorbent removal of pollutant in water [9], ion exchange, and slow-release potassium fertilizer [10]. In addition, merlinoite also can be used as catalyst through a process of dehydration of methanol [11].

Some researchers have developed a synthesis of merlinoite from various sources (raw material). Collela et al. [12] used natural glass for synthesis merlinoite. Strohmaier and Robson [13] reported that merlinoite have been made from alumina, colloidal silica, and potassium hydroxide. While Medina et al. [9] had successfully converted fly ash to merlinoite. Moreover, Schubert and Husing [14] suggested the parameters that affect the synthesis of merlinoite include in time, alkali concentration, temperature, and molar ratio. Alkali concentration and reaction time has very influent in the formation of merlinoite and its crystallinity [11].

Determine of quantitative phase analysis from merlinoite can be used lattice parameter from standard X-ray diffraction (XRD). Quantitative phase analysis using XRD data could be further by approached with Rietveld refinement [15,16] and Le Bail method [17]. The aim of this paper is to discuss the crystal structure with the Le Bail method on the effect of time reaction and KOH concentration on synthesis of merlinoite from fly ash.

2. Material and methods

2.1 Material
Raw material that used in this synthesis is coal fly ash (CFA) which was taken from Tanjung Jati B CFPP, Jepara, Indonesia. The reagents KOH, H₂SO₄ 98%, and aquadest was used as solvent.

2.2 Synthesis of merlinoite
Synthesis merlinoite was performed with alkaline hydrothermal method. To remove the unburned carbon and some impurity compounds, CFA was purified with H₂SO₄ solution. The mixture was soaked for 8 h at 60° C and then filtered, washed with distilled water and dried. After CFA was dried, then it mixed with 3M KOH
solution into 150 mL Teflon liner of stainless-steel autoclave in comparison of composition between KOH : fly ash is 2:1. Furthermore, the activation is done by the time variation of 8, 12, and 24 h at 150°C in the oven. After a varying of time was completed, the autoclave was cooled to the room temperature and the solid phase is separated with their liquid phase. Solid product is washed with distilled water until pH 10-11. The solid was dried at 60°C for one night. The dried solids were characterized using X-Ray Diffraction (XRD) in order to note the optimum condition of the reaction time variations. The variation of alkali concentration can be conducted with the same step of the time reaction variation.

The crystallographic structure of merlinoite was studied using XRD Brucker AXS D8 Advance diffractometer with Cu Kα radiation. The diffraction intensity was determined between 10° and 60°. The crystal size of merlinoite was computed using the Scherrer formula \( D = \frac{0.9\lambda}{\beta\cos\theta} \). The product was proven by powder XRD (ICSD#81895 for merlinoite). Le Bail refinement was performed using the refinement program, i.e. Rietica. Experimental parameter refined were the instrument zero, scale factor, peak shape parameters \( u, v, w, \gamma_0 \) and \( \gamma_1 \) [15,16].

3. Result and Discussion
The characterization of fly ash was characterized by X-ray fluorescence (XRF) to determine the composition of chemical constituents in the form of metal oxides. SiO\(_2\) and Al\(_2\)O\(_3\) in this material can be use as source to form the framework of merlinoite (Table 1).

| Compound | Composition (%) |
|----------|-----------------|
| Si       | 49.86           |
| Al       | 21.71           |
| Ca       | 6.76            |
| Mg       | 5.83            |
| K        | 2.52            |
| Fe       | 2.34            |
| Ti       | 1.33            |

Table 1 shown that Silica and Alumina (Si and Al) are the main component of CFA sample which is shows the similarity with zeolite. Thus it possible to converted CFA into merlinoite due to the CFA components were able to serve as a source of Al and Si.

Crystallinity’s character from merlinoite were analyzed using XRD with a range of \( 2\theta \) 10-60°. Diffractogram pattern from merlinoite at the time variation of 8, 12, and 24 hours is present in Fig. 1.
Figure 1 showed the pattern of merlinoite synthesized from variety of time. As shown in Figure 1, the XRD pattern of merlinoite has sharp peak and typical in the range of $2\theta = 27^\circ$ ($013$); $28^\circ$ ($240$); and $30^\circ$ ($123$) [7]. However, the diffractogram showed that still quite amorphous and crystalline yet entirely. The differences in high or low intensity was expected any differences in the crystal growth of merlinoite.

Furthermore, to determine the conformity of XRD diffraction with the crystal structure based on comparison with ICSD, followed by refinement process using Le Bail method. Result of refinement process showed the conformity with the standard data of merlinoite (ICSD#81895). In addition, it found other phases such as quartz (ICSD#280364), mullite (ICSD#23726). Even, at 24 hours in time variation appear new phase like tobermorite (ICSD#100405). There is still any quartz because that phase is stable. Therefore, it was quite difficult to bind with KOH and affecting the formation of merlinoite [18].

Something that is not different showed in Figure 2 for XRD pattern of merlinoite in the variation of alkali concentration (KOH). In Figure 2 was shown that the higher concentration of alkali emerging a new phase like tobermorite (ICSD#100405). It phase was as same as phase at variation of reaction time in 24 hour.
The refinement had the following order zero, lattice parameter, histogram parameter and instrumental peak shape. For every step were used 30 cycles. Table 2 presented the detail about result of refinement for merlinoite with variety treatment. The reliability index parameters are the pattern factor ($R_p$), the weighted pattern factor ($R_{wp}$), and the goodness of fit ($\chi^2$), which is shown the quality of refinement in this study. The ideal value for $\chi^2$ is 1.0 [19] or 3.0, and all the refinement were acceptable quality [19]. In Table 2, merlinoite with variation in 8h and 3M were shown smallest $R_p$ and $R_{wp}$ than other variations. It is indicated that optimum condition in synthesis of merlinoite. On the other hand, the higher reaction of time and alkali concentration would make the possibility to emerge a new phase [10].

Table 2. The result of Le Bail refinement with various phase

| Variation | merlinoite | Phase composition | tobermorite | $R_p$ | $R_{wp}$ | Value | $\chi^2$ |
|-----------|------------|-------------------|-------------|-------|---------|-------|--------|
| 8h        | 76.85      | quartz            | 7.89        | 15.26 | 0.79    | 1.43  | 0.0573 |
| 12h       | 73.67      | 12.66             | 13.67       | 46.13 | 1.28    | 2.17  | 0.1423 |
| 24h       | 49.72      | 4.16              | 14.23       | 1.94  | 2.73    | 0.1847|
| 1M        | 68.34      | 17.43             | 10.37       | 0.79  | 1.43    | 0.0573|
| 3M        | 81.73      | 7.90              | 44.72       | 1.71  | 2.11    | 0.0955|
| 5M        | 48.58      | 2.68              | 4.01        | 0.0573|

Table 3 showed that the treatment of variation in synthesis of merlinoite made some difference in crystallite size ($D$). The diminished in crystallite size with the increasing of various concentration or time reaction may be explained that a merlinoite structure lead to form a small piece. Furthermore, it can be explained that there was an incomplete dissolution of early formed amorphous of merlinoite which contribute to the aggregation of that material.
4. Conclusion

The end of the result from this investigation proved that merlinoite was successfully synthesized from fly ash. The optimum conditions in synthesis are in 8h of reaction time and 3M of alkali concentration (KOH). The higher reaction time and alkali concentration has decreased the crystallite size of merlinoite. It is showed by crystal growth occurred in slow formation. The higher reaction time and alkali concentration also provided a possibility to emerge a new phase. On X-ray diffraction has got another phase beside merlinoite, such as quartz, mullite, and tobermorite, which is confirmed by analysis of refinement Le Bail.

References

[1] Passaglia E, Pongiluppi D, Rinaldi R and Merlinoite 1977 N. Jb. Miner 355.
[2] Alberti A 1979 J. Appl. Crystallogr.9, 373.
[3] Khomyakov A.P., Kurova, T.A., Muravitskaya, T.N., 1981 Doklady Akademiy Nauk SSSR, 1 172.
[4] Donahoe RJ and Liou JG 1984 Clay. Clay Miner. 32 433.
[5] Sherman J D 1978 American Chemical Society, Washington, 40 30.
[6] Sherman D 1977 Amer. Chem. Sot., Symposium Series 40 30.
[7] Bieniok A, Bornhold K and Brendel U 1996 J. Mater. Chem. 6 (2) 271.
[8] Skofteland, B.M., Ellestad, O.H., Lillerud, K.P., 2001 Micropor. Mesopor. Mat., 43, 61.
[9] Medina A, Gamero P, Almanza J.M, Vargas A, Montoya A, Vargas GM and Izquierdo M 2010 J. Hazard. Mater., 181 91.
[10] Jing L, Zhuang X, Font O, Moreno N, Vallejo VR, Querol X and Tobias A 2014 J. Hazard. Mater. 265 242.
[11] Hou J, Yuan J and Shang R 2012 Powder Technol. 226 222.
[12] Colella C, Caputo D, de Gennaro B and Torracca E 2004 Stud. Surf. Sci. Catal., 154 (2) 1920.
[13] Strohmaier K. and Robson H 2001 Verified Synthesis of Zeolitic Material, second ed., (Netherlands – Elsevier)
[14] Schubert and Husing, 2000 Micropor. Mesopor. Mat., 34 301.
[15] Peterson V.K. 2005 Powder Difr20 14.
[16] Heraldy E, Nugrahaningtyas K D and Heriyanto 2016 JOP Conf. Ser. Mater. Sci. Eng., 176.
[17] Sanches E.A, Carolino ADS, Dos Santos A.L, Fernandes EGR, Triches DM and Mascarenhas YP 2015 Adv. Mater. Sci. Eng.
[18] Wu D 2008 Fuel, 87 2194.
[19] Yakubovich, O V , Massa W, Pekov I V, Kucherinenko T V, 1999 Crystallogr. Rep., 44 (5) 776.