

PAPER • OPEN ACCESS

Effect of kalium hydroxide/fly ash ratio and hydrothermal temperature in Zeolite W formation by X-ray diffraction analysis

To cite this article: Eddy Heraldy *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **509** 012038

View the [article online](#) for updates and enhancements.

Effect of kalium hydroxide/fly ash ratio and hydrothermal temperature in Zeolite W formation by X-ray diffraction analysis

Eddy Herald^{1,2,*}, Fitria Rahmawati^{1,2}, Nurul Apri Indri¹, Syaiful Ahmad Nur Cahyo¹

¹ Department of Chemistry, Mathematics and Natural Sciences Faculty, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan, Surakarta, Indonesia 57126

² Solid State Chemistry & Catalysis Research Group, Chemistry Department, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan, Surakarta, Indonesia 57126

* Corresponding author: eheraldy@mipa.uns.ac.id

Abstract. The Zeolite W synthesized from coal fly ash (CFA) by hydrothermal method using 5 M Kalium hydroxide (KOH), variations of KOH: CFA ratio (1, 2 and 3 L/kg) and hydrothermal temperature (150, 200, and 250°C) for 8 hours had been done. The XRD diffractogram analysis revealed five peaks at 2θ around 10.61°; 12.48°; 27.39°; 28.19°; and 32.92° which correspond to the peaks characteristic of zeolite W. The refinement result showed the other phases such as hematite, quartz, and tobermorite.

Keywords: coal fly ash, hydrothermal, zeolite W, X-ray diffraction

1. Introduction

Zeolite W is one of zeolite type which has small pores and its existence is rare in nature [1-4]. In accordance with Katzer [5], zeolite W has an excellent ability in adsorption capacity as well as ion exchange. Zeolite W, also known as merlinoite [6-8] is a promising material because it has been used as an ion exchange, and slow-release potassium fertilizer [9], and adsorbent removal of pollutant in water [10]. Moreover, zeolite W can also be used in the dehydration of methanol process as catalyst [11].

Several researchers had been manufactured zeolite W synthetic from various raw material. Medina *et al.* [10] had successfully synthesized fly ash become zeolite W. Kühl [12] stated that zeolite W had been made from colloidal silica, alumina and potassium hydroxide. While [13] utilized natural glass for a synthesis of zeolite W. However, little investigators using the brown fly ash to zeolite W synthesis. Furthermore, Thoma and Nenoff [14] shown that the parameters, which affected the synthesis of zeolite W, comprise in molar ratio, temperature, alkali concentration, and reaction time.

Regarding the structure and mineral composition in zeolite W, the quantitative phase analysis may assist to better knowing about zeolite W compound. To find out of the quantitative phase analysis from zeolite W, the parameter from X-ray diffraction (XRD) data can be used. The quantitative phase analysis using XRD data could be approached with Rietveld refinement [15, 16] and Sanches *et al.* [17] to find the individual reflection intensities from powder XRD. The Rietveld method refines user-particular parameters to minimize the difference an experimental pattern (observed data). Herald *et al.* [18] had been performed the XRD analysis on the effect of time reaction and alkali concentration in zeolite W



synthesis. However, not many investigators studied the effect of KOH: CFA and hydrothermal temperature in the zeolite formation by XRD analysis.

The objective of this paper is to discuss the structure of crystal with the Le Bail method on the effect of KOH: CFA ratio variation and hydrothermal temperature on zeolite W synthesis from fly ash.

2. Material and methods

2.1. Material

The raw material used in this synthesis was coal fly ash (CFA) that was taken from Coal Fired Power Plant (CFPP) Tanjung Jati B, Jepara, Central Java, Indonesia. The reagents include KOH and distilled water.

2.2. Synthesis of zeolite W

The zeolite W synthesis was carried out with alkaline hydrothermal method. To remove some impurity compounds, CFA was washed with distilled water and dried in oven at 100°C for 8 h. After dried, then CFA was mixed with 5M KOH solution in Teflon liner of stainless-steel autoclave in various composition between KOH (L): CFA (Kg) of 1:1; 2:1 and 3:1. Furthermore, the activation was performed by the hydrothermal temperature variation of 150, 200, and 250°C for 8 h. After a varying of temperature was completed, the autoclave was cooled to the room temperature and the solid phase was separated from their liquid phase. The solid product was washed with distilled water until pH 10-11, and dried at 60°C for 12 h. The dried solids were characterized using XRD to know the structure of zeolite W.

The zeolite W crystallographic structure was studied using XRD Brucker AXS D8 Advance diffractometer with Cu K α radiation. The diffraction intensity was determined between 10° and 60°. The zeolite W crystal size was computed using the Scherrer formula $D = 0.9\lambda/(\beta \cos \theta)$. The product was proven by powder XRD (ICSD#81895 for zeolite W). Le Bail refinement was conducted by the refinement program, i.e. Rietica. Experimental parameter refined were the instrument zero, scale factor, peak shape parameters u , v , w , γ_0 and γ_1 [15, 16].

3. Result and Discussion

The fly ash analysis was performed by X-ray fluorescence (XRF) to determine the composition of chemical constituents in the form of metal oxides. The result in Table 1 showed a consisted largely of CFA is SiO₂ (44.73%), Fe₂O₃ (19.06%), and Al₂O₃ (17.55%). Due to SiO₂ and Al₂O₃ are the main component of CFA, this material can be used as the starting material for further synthesis of zeolite W.

Table 1. Chemical composition (%) of fly ash by XRF

Compound	Concentration (%)
SiO ₂	44.73
Fe ₂ O ₃	19.06
Al ₂ O ₃	17.55
CaO	6.64
MgO	4.24
K ₂ O	2.63

Identification of the zeolite W synthesis product is based on the comparison with the zeolite W XRD patterns standard (ICSD #81895). The zeolite W diffractogram at the KOH: CFA variation is present in Fig. 1.

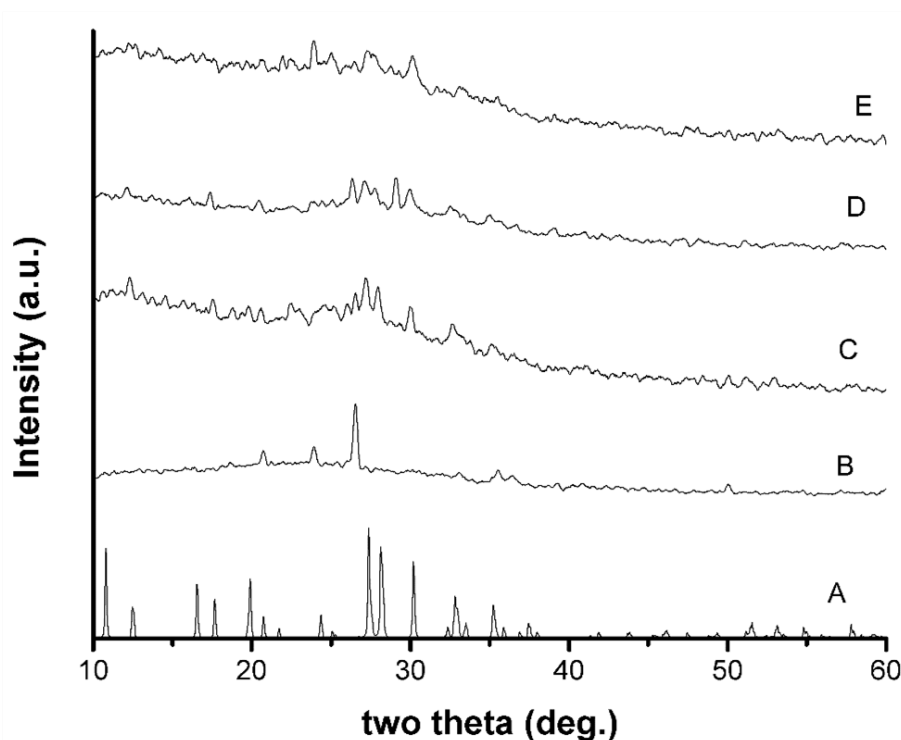


Figure 1. XRD pattern of ICSD#81895 (A), CFA sample (B) comparison with zeolite W synthesized KOH: CFA ratio variation 1 L/Kg (C); 2 L/Kg (D); 3 L/Kg (E) for 8 h reaction time at hydrothermal temperature of 150°C.

As shown in Fig. 1, the XRD pattern obtained has a typical peak in range $2\theta = 10.61\text{--}10.78^\circ$ (d_{011}); $12.29\text{--}12.48^\circ$ (d_{020}); $27.14\text{--}27.39^\circ$ (d_{013}); and $32.64\text{--}32.92^\circ$ (d_{341}). The zeolite W phase was identified as the main crystallite phase. It indicates that synthesis of zeolite W successfully synthesized. Nevertheless, the zeolite W diffractogram show a quite amorphous and yet crystalline entirely. In a given KOH: CFA ratio, the increase in ratio coincides with a decrease in zeolite W phase. The zeolite W obtained with KOH: CFA ratio 1 L/Kg have a peak in $2\theta = 10.61^\circ$ (d_{011}); 12.48° (d_{020}); 27.39° (d_{013}); 28.19° (d_{240}); and 32.92° (d_{341}) with peak intensities higher than others. The presence of the differences intensities may be any differences in the crystal growth of zeolite W.

Moreover, to determine the fitness of XRD pattern with the crystal structure with standard ICSD performed the refinement process by Le Bail method. The refinement result shows that the fitness with the standard data of zeolite W (ICSD#81895). Furthermore, it obtained other phases such as tobermorite (ICSD#100405), hematite (ICSD#100405), and quartz (ICSD#280364). There is still presence the quartz in the zeolite W due to this quartz phase is stable. It was quite difficult, then, to bind with KOH and influencing the zeolite W formation [19].

Regarding the calculation result based on the Le Bail refinement, there are peaks similar both JCPDS standard and sample. The reliability index parameter values i.e. R_p and R_{wp} have low reliability index value (Table 2).

Table 2. Phase composition of zeolite W at various KOH: CFA ratio

KOH/CFA ratio (L/Kg)	Le Bail reliability factors		Molarity percent (%)			
	R_p	R_{wp}	Zeolite W	Quartz	Tobermorite	Hematite
1	1.92	2.35	39.27	6.95	18.34	35.44
2	2.11	2.45	38.92	7.03	17.93	36.12
3	2.11	2.29	39.03	7.02	18.30	35.65

From Table 2, all samples product exhibit zeolite W phase, as well as tobermorite and hematite phase. It is because KOH is used excessively, the other minerals beside silica and alumina in CFA ratio will also dissolve. Since the Fe_2O_3 and CaO content in CFA quite high, it can interfere the conversion process to zeolite. It is possible the Fe_2O_3 and CaO dissolve in KOH to hematite and tobermorite phase formation. The difference of KOH:CFA ratio in zeolite W synthesis influence in the resulting product. Figure 1 shows that diffraction peaks of C (KOH: CFA ratio of 1L/Kg) is well than other ratios. However, the peaks of D (KOH: CFA ratio of 2L/Kg) also a quite high match though the zeolite W crystal formed decreased. Hence, if the ratio increased causes the zeolite W phase decreased. Refinement results indicate that the zeolite W has been formed even though there are still several other phases.

The XRD patterns of hydrothermal temperature variation in zeolite W synthesized were shown in Fig. 2. The diffraction peak 2θ were observed on range 10.78-10.96; 12.46-12.48; 27.12-27.36; 28.10-28.28 and 32.82-32.84°.

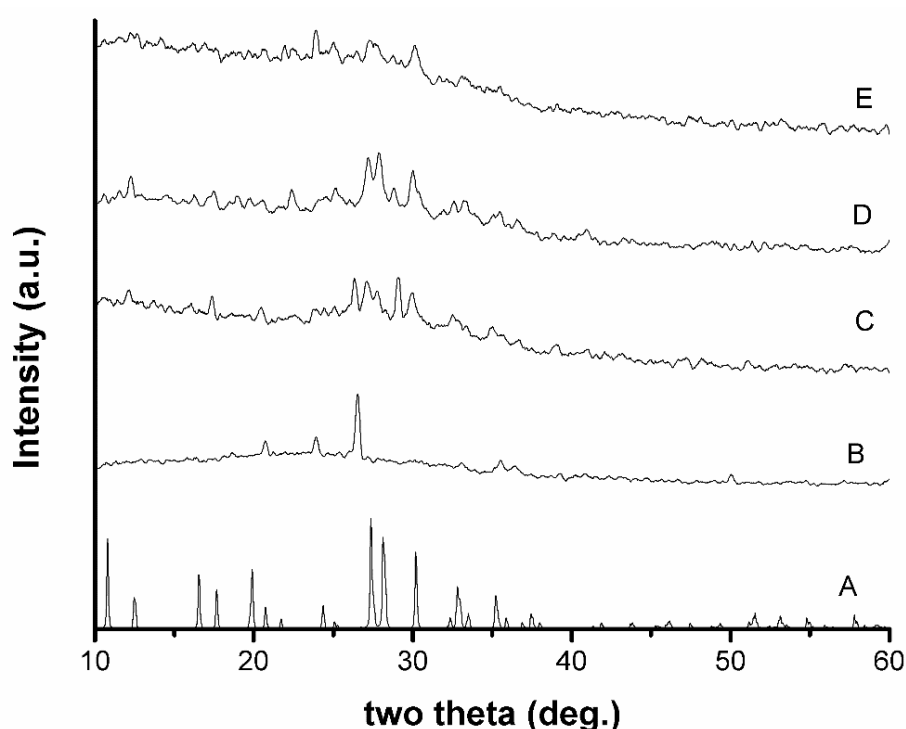


Figure 2. XRD pattern of ICSD#81895 (A), CFA sample (B) comparison with zeolite W synthesized with hydrothermal temperature variation 150°C (C); 200°C (D); 250°C (E)

Based on diffractogram pattern in Fig. 2, it can be noted that as the hydrothermal temperature of synthesis increased, the zeolite W product increased. This was caused the higher the temperature, the

collisions between molecules increased so that the reaction went relatively perfect. At high temperatures, the dissolution of silica and alumina will rise which causes the zeolite conversion also increased. This is in accordance with the research of Medina et al. [10]. However, at a temperature of 250°C the formation of zeolite W phase reduced and increases the formation of tobermorite and perialite. Additionally, the higher hydrothermal temperature cause mullite phase formation is reduced, while the tobermorite, perialite, and silicalite phase increases. This is consistent with research conducted by Medina *et al.* [10].

In Table 3, the reliability index parameter values i.e. R_p and R_{wp} have value <10%.

Table 3. Phase composition of zeolite W at various hydrothermal temperature

Hydrothermal temperature (°C)	Le Bail reliability factors		Molarity percent (%)			
	R_p	R_{wp}	Zeolite W	Quartz	Tobermorite	Hematite
150	2.11	2.45	38.92	7.03	17.93	36.12
200	1.93	2.58	39.43	6.98	18.33	35.26
250	2.42	2.92	39.22	6.95	18.60	35.22

From Table 3 showed that the higher hydrothermal temperature, the higher zeolite W formation but also increases the formation of other phases, namely tobermorite.

4. Conclusion

The zeolite W synthesized with various KOH: CFA and hydrothermal temperature was successfully prepared. The coal fly ash from Coal Fired Power Plant of Tanjung Jati B, Jepara, Central Java, Indonesia may be as a source of zeolite W. The study confirmed that various KOH: CFA ratio and hydrothermal temperature found zeolite W, quartz, tobermorite and hematite phase. The Le Bail refinement value of reliability index parameter has concern limitation value.

Reference

- [1] Passaglia E, Pongiluppi D and Rinaldi R 1977 Merlinoite, a new mineral of the zeolite group *Neues Jb. Miner. Monatsh.* **1977** 355-64
- [2] Alberti A 1976 The use of structure factors in the refinement of unit-cell parameters from powder diffraction data *J. Appl. Crystallogr.* **9** 5 373-4
- [3] Khomyakov A, Kurova T and Muravitskaya T 1981 Merlinoite: the first discovery in the USSR *Dokl. Akad. Nauk SSSR* **256** 172-4
- [4] Donahoe R J and Ltou J 1984 Synthesis and Characterization of Zeolites *Clays Clay Miner.* **32** 6 433-43
- [5] Katzer J R 1977 Molecular Sieves II *the 4th International Zeolite Conference*
- [6] Sherman J D and Katzer J 1977 Identification and characterization of zeolites synthesized in the $K_2O-Al_2O_3-SiO_2-H_2O$ system. I *ACS Symp. Ser.* **40** 30-42
- [7] Bieniok A, Bornholdt K, Brendel U and Baur W H 1996 Synthesis and crystal structure of zeolite W, resembling the mineral merlinoite *J. Mater. Chem.* **6** 2 271-5
- [8] Skofterland B M, Ellestad O H and Lillerud K P 2001 Potassium merlinoite: crystallization, structural and thermal properties *Microporous Mesoporous Mater.* **43** 1 61-71
- [9] Li J, Zhuang X, Font O, Moreno N, Vallejo V R, Querol X and Tobias A 2014 Synthesis of merlinoite from Chinese coal fly ashes and its potential utilization as slow release K-fertilizer *J. Hazard. Mater.* **265** 242-52
- [10] Medina A, Gamero P, Almanza J M, Vargas A, Montoya A, Vargas G and Izquierdo M 2010 Fly ash from a Mexican mineral coal. II. Source of W zeolite and its effectiveness in arsenic (V) adsorption *J. Hazard. Mater.* **181** 1-3 91-104

- [11] Hou J, Yuan J and Shang R 2012 Synthesis and characterization of zeolite W and its ion-exchange properties to K⁺ in seawater *Powder Technol.* **226** 222-4
- [12] Kühl G 2001 *Verified Syntheses of Zeolitic Materials*, ed H Robson and K P Lillerud (Amsterdam: Elsevier Science) pp 19-20
- [13] Colella C, Caputo D, De Gennaro B and Torracca E 2004 *Stud. Surf. Sci. Catal.*: Elsevier) pp 1920-8
- [14] Thoma S G and Nenoff T M 2000 A novel synthesis of zeolite W using organometallic precursors *Microporous Mesoporous Mater.* **34** 3 301-6
- [15] Peterson V 2005 Lattice parameter measurement using Le Bail versus structural (Rietveld) refinement: A caution for complex, low symmetry systems *Powder Diffr.* **20** 1 14-7
- [16] Herald E and Nugrahaningtyas K 2017 X-ray Diffraction Analysis on Post Treatment of Ca-Mg-Al-Layered Double Hydroxide Slurry *IOP Conf. Ser. Mater. Sci. Eng.* **176** 1 012020
- [17] Sanches E A, Carolino A d S, Santos A L d, Fernandes E G, Trichês D M and Mascarenhas Y P 2015 The use of le bail method to analyze the semicrystalline pattern of a nanocomposite based on polyaniline emeraldine-salt form and α -Al₂O₃ *Adv. Mater. Sci. Eng.* **2015**
- [18] Herald E, Cahyo S A N, Indri N A and Rahmawati F 2018 X-ray Diffraction Analysis on Effect of Time Reaction and Alkali Concentration in Merlinoite *J. Phys. Conf. Ser.* **1095** 1 012012
- [19] Wu D, Sui Y, Chen X, He S, Wang X and Kong H 2008 Changes of mineralogical–chemical composition, cation exchange capacity, and phosphate immobilization capacity during the hydrothermal conversion process of coal fly ash into zeolite *Fuel* **87** 10-11 2194-200