

Facile synthesis of zeolite NaX using rice husk ash without pretreatment by Shella Santoso

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zeolite NaX using rice husk ash without pretreatment Phuong Lan Tran-Nguyena,* , Kim-Phung Lyb, Luong Huynh Vu Thanhb, Artik Elisa Angkawijayac, Shella Permatasari Santosod, Nguyen-Phuong-Dung Trane, Meng-Lin Tsaie, Yi-Hsu Juc, f a Department of Mechanical Engineering, Can Tho University, Campus II, 3/2 street, Can Tho city 900100, Vietnam b Department of Chemical Engineering, Can Tho University, Campus II, 3/2 street, Can Tho city 900100, Vietnam c Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, #43, Sec. 4, Keelung Rd., Taipei 10607, Taiwan d Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya

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ARTICLE INFO Article History: Received 19 February 2021 Revised 29 April 2021 Accepted 9 May 2021 Available online 25 May 2021 Keywords: Rice husk ash Zeolite NaX Aging time Energy and time saving integrated process ABSTRACT Rice husk ash (RHA) is an abundant agricultural waste in Mekong Delta, Vietnam. The utilization of RHA for zeolites production has been widely studied by pretreating RHA before reaction. In this study, zeolite NaX was synthesized directly using RHA without any pretreatment. Key parameters including

16 molar ratios of SiO₂ to Al₂O₃ and Na₂O to Al₂O₃, reaction time, and aging time were

investigated. The results showed

13 that the optimal conditions for the synthesis of zeolite

NaX are: molar ratio of SiO₂/Al₂O₃ = 4, molar ratio of Na₂O/ Al₂O₃ = 10, reaction time = 4 h, and without aging. Zeolite NaX

9 with a specific surface area of 388 m²/g and a pore diameter of

12.37 Å was obtained, which were comparable to the published data. The method developed in this work is an energy and time saving, integrated, and environmental friendly process. It has the potential to be applied for synthesizing other types of zeolite. ©

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1. Introduction Zeolites are inorganic materials with regular microporous structure which have been widely developed and used in many applications [1,2]. The structure of zeolite consists of the network of tetrahedral [

12 SiO₄ and [AlO₄] [1]. These tetrahedrons are linked through oxygen

-spherical bonds to form an open structure with empty holes [2]. Many types of zeolite such as zeolite X, A, P1, Y or ZSM-5 have been successfully synthesized from commercial silica sources or wastes with high silica content [1,3,76]. Zeolite X which belongs to the faujasite (FAU) family with large pore size (about 8 Å) [1] possessed special properties in the adsorption of heavy metals, gas or organic wastes [1,7,28]. Zeolite X has been synthesized using silica sources such as kaolin [2], bauxite [1], diatomite [9], bagasse fly ash [10],

coal fly ash [11], and RHA [4, 12]. RHA, an agricultural waste, can cause serious environmental pollution [13]. Mekong Delta is the major agricultural center of Vietnam which produces tens of million ton of rice annually [14]. Rice husks are often used as fuel, partially replacing coal and gas [13]. A small portion of RHA, the residue of burning rice husk, is used as organic fertilizer, light concrete, or activated carbon [15]. However, * Corresponding author. E-mail address: tnplan@ctu.edu.vn (P.L. Tran-Nguyen). the amount of rice husk is huge and the main treatment is usually burning or landfilling [13]. These treatment methods cause greenhouse gas emissions, air pollution, and consume large areas for landfilling [13]. Meanwhile, RHA is well-known as a rich source of silica (about 90%) [16] and is an excellent source for the synthesis of zeolite, silica and cordierite [4, 17, 18]. Zeolite synthesis from RHA [11, 13] opens a new route in alleviating environmental pollution caused by RHA. In previous studies for producing zeolite NaX, RHA required calcination or chemical pretreatment before reaction [4, 12, 19]. Meanwhile, the processes involved were complicated, energy and time consuming and low economic efficiency [4, 5, 12, 20]. There were some reports on the synthesis of zeolite NaX using untreated RHA but the reaction time required was quite long [21, 22]. In addition, previous studies have not given the full evaluation on the important factors that affected the synthesis of zeolite NaX from the RHA without calcination. In this study, the effects molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, reaction time and aging time on the final zeolite product were carefully investigated under mild conditions and shorter reaction time. The mechanism of the formation of NaX was also proposed. RHA and zeolite products

5were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), dynamic light scattering (DLS), Brunauer - Emmett - Teller (BET), and X-ray fluorescence (XRF)

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22. Experimental 2.1. Raw materials RHA was collected from

Nam Tien Joint Stock Company, Tra Noc Industrial Park, Can Tho City, Vietnam. The collected ash was directly used for the zeolite synthesis. Other chemicals such as sodium hydroxide pellets and aluminum powder (purity 99%, Union Chemical Industry Company Ltd.) were obtained from commercial sources.

152.2. Synthesis of zeolite NaX The synthesis procedure of

zeolite NaX, based on previous studies with some modifications, is depicted in Fig. 1 [2, 22]. RHA and NaOH solution (5 M) were placed in a round bottom flask and stirred at 300 rpm and 90°C for 3 h with a certain solid/liquid ratio [23]. A refluxed condenser was applied during the reaction. After the reaction, the products were collected and filtered to separate the aqueous fraction, mainly sodium silicate, from the solid fraction. NaAlO₂ solution

4was prepared by dissolving aluminum powder in NaOH solution

according to the required molar ratio. Then, the prepared NaAlO₂ solution was gradually added to the aqueous fraction at 50°C and vigorously stirred for 2 h. After obtaining a homogeneous gel mixture, the mixture was heated to 90°C and kept for certain time T₁ (h). Then, the supernatant was aged at T₂ (h). The precipitate was then collected by filtration, centrifuged and dried at 100°C until constant weight to obtain the

zeolite NaX powder. Each data was the results of triplicate experiments. 2.3. Characterization The zeolite NaX products

1 were characterized by using XRD, BET, FE-SEM, DLS and XRF while the composition of

RHA was analyzed by using XRF and TGA. XRD was performed on a D8 Advance instrument (Bruker), with an X-ray diffractometer using CuK radiation ($\lambda = 1.54056 \text{ \AA}$) scanned at 7.0000 degree/min, an applied current of 30 mA and an accelerating voltage of 40 kV. FE-SEM measurement was taken with a Hitachi S-4800 scanning electron microscope. DLS from SZ-100 (Horiba)

4 was used to determine the size distribution profile of

NaX. The analysis of major and trace elements in RHA and the synthesized NaX was processed by using XRF (S8 TIGER Series 2, Bruker). TGA was also performed by using a thermogravimetric analyzer (Pyris Diamond TG-DTA, PerkinElmer Instrument, USA). BET was applied for determining

12 the specific surface area and the pore diameter of the synthesized NaX. The sample

was dried for 16 h at 105°C before being analyzed with a Nova 2000 (Quantachrome Instruments, USA). 3. Results and discussion XRD was used to determine the polymorphism of SiO₂ in the untreated RHA [5]. Fig. 2a shows that only a broad peak of SiO₂ appeared at $2\theta = 22^\circ$, indicating amorphous form of silica [5]. The amorphous SiO₂ dominated in the untreated RHA, so it was a potential material for zeolite synthesis [15]. Moreover, XRF result showed that silica accounts for > 95% of the RHA (Table 1). The total weight loss from room temperature to 800°C was about 1.5% (Fig. 2b). Very Fig. 1. Flowchart of zeolite NaX synthesis process. 340 P.L. Tran-Nguyen

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123 (2021) 338-345 Fig. 2. XRD pattern of silica from RHA and thermogravimetric curve of RHA. Table 1 Chemical composition of RHA used in this study. Elements Content (%) SiO₂ 96.11 K₂O 1.47 Al₂O₃ 1.16 CaO 0.48 P₂O₅ 0.2 MnO 0.19 Fe₂O₃ 0.15 Na₂O 0.11 SO₃ 0.03 Sb₂O₃ 0.03 CdO 0.02 SnO₂ 0.02 ZnO 0.02 BaO 0.01 SrO 0.01 Ta₂O₅ 0.01 little weight loss between 100 and 200°C was observed due to the removal of adsorbed water on the surface of particles. Some organic matter may be retained in RHA [24]. From 200 to 600°C, a more rapid weight loss was observed owing to decomposition of organic matter which was also reported by Fernandes et al. [25]. It was reported that 90°C is the suitable reaction temperature for zeolite X synthesis [2,12,26-29], so 90°C was used in this study. To better understand the formation of zeolite X [30,31], a reaction mechanism was proposed in Fig. 3. The mechanism could be described as follows: the precursor sources are firstly dissolved to form silica and alumina tetrahedra. The two tetrahedral are combined to form gel aluminosilicate, followed by formation of secondary structures such as sodalite cages and double six member-rings (D6R) in the presence of OH⁻. The secondary structures then combine to create crystal Fig. 3. The proposed mechanism of zeolite NaX formation. seeds, which enter the growth phase influenced by reaction time and temperature. Finally, the complete crystals of zeolite X are found. 3.1. Effect of SiO₂/Al₂O₃ Zeolites were synthesized at SiO₂/Al₂O₃ molar ratios from 2.0 to 4.5 with the other

reaction conditions fixed (Fig. 4). The main peaks in XRD patterns of the synthesized zeolite were compared with the standard peaks of NaA, NaX and NaP1 (JCPDS card No. 38-0237,

14 **JCPDS card No. 43-0142** and **JCPDS card No. 39-0219**, respectively). In

Fig. 4a, a single phase zeolite NaA was formed at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.0$. When this ratio was increased to 2.5 (Fig. 4b), all

14 **peaks of zeolite NaA decreased and**

peaks of zeolite NaX appeared with low intensity. Al- Jubouri et al. successfully synthesized pure zeolite NaA at $\text{SiO}_2/\text{Al}_2\text{O}_3$ between 1.0 and 2.0 and obtained formation of zeolite X at a ratio > 2.0 [32]. In fact, as this ratio was increased from 3.0 to 4.0 (Fig. 4c- 4h), a significant increase of zeolite NaX peaks intensity and decrease peaks intensity of zeolite NaA, which completely disappeared at a ratio of 4.0. At ratios of 3.0 and 3.125, alternating formation of zeolite NaA and NaX was observed. More zeolite NaA was formed at a ratio of 3.0 while the main peak of zeolite NaX was found at a ratio of 3.125 with the coexistence of zeolite NaA. This result agrees with those reported in Fig. 4. XRD patterns at different

16 **molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the standard of**

zeolite NaA, NaX and NaP1. (a) 2.

20, (b) 2.5, (c) 3.0, (d) 3.125, (e) 3.25, (f

) 3.5, (g) 3.75, (h) 4.0, and (i) 4.5. literature when the ratio used was above 2.5 [28,33,34]. An increase of this ratio resulted in a decrease of NaA and the appearance of NaX [28]. Between the ratio of 3.25 - 4.0, the peak of NaA almost completely disappeared because the significant decrease in the solubility of Si^{4+} ions as Al^{3+} ion concentration was increased. The low concentrations of Si^{4+} ions favored the formation of structure such as double four member-ring (D4R); thus, zeolite A usually appeared at low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [4,28]. It was reported that $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for the synthesis of zeolite NaA should be < 3.0 [32,35]. Alternating peaks of zeolite NaX and NaP1 were observed at a ratio of 3.25 and NaX with high intensity can be found at ratio > 3.5 . Besides the predominant formation of zeo- lite NaX, the sample still contained a little zeolite NaP1. Similar results of NaX at a ratio of 4.0 using different feedstock were reported [3,36]. The tendency to form zeolite NaP1 when increasing this ratio was also mentioned previously [29,37]. At a ratio of 4.3, NaX was the dominant zeolite [37]. At ratio between 3.0 and 4.8, the products contained NaA, NaX and NaP1 [38]. As $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was increased to 4.5 (Fig. 4i), zeolite NaP1 peaks started to appear. Similar trend was reported by Hildebrando et al. (2014) [39]. The formation of NaP1 was more significant when changing this molar ratio and a decrease of Al used favored the for- mation of zeolite NaP1 [36,40]. The

2 **control of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio**

was crucial to achieve single-phase zeolite NaX. A ratio of 4.0 was chosen to achieve NaX zeolite crystallized with high intensity. 3.2. Effect of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ Previous studies reported different results in the synthesis of zeo- lite X when changing $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio [33,41,42]. In this study, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios from 2.0 to 12 were investigated (Fig. 5). At a ratio of 2.0, only amorphous phase was found. When this ratio was increased

to 8.0, the peaks of zeolite NaX and NaP1 appeared with NaX as the dominant phase. To eliminate zeolite NaP1, Na2O/Al2O3 = 12.0 was applied based on previous studies which reported that an increase of alkalinity of the reaction mixture inhibited zeolite NaP1 formation [3,34,43]. However, more alkaline added resulted in a decrease of peaks intensity of zeolite NaX (Fig. 5e). An increase of NaOH would decrease NaX owing to poor stability of zeolite in high alkaline solution [42]. Fig. 5d shows similar crystallization to that of Na2O/Al2O3 = 12 and the peaks of zeolite NaX were weaker than that of Na2O/Al2O3 = 8.0.

4 The characteristic peaks of zeolite NaX indicated high crystallinity

at a ratio of 10.0 (Fig. 5c). Zeolite NaX only existed with high intensity when optimal alkalinity of the reaction mixture was employed [44]. OH⁻ group was the stimulator in forming primary structures and helped forming the bonds between the SiO₄ and AlO₄⁻ tetrahedra. If alkalinity of the mixture was low, the OH⁻ group was not enough to form bonds of tetrahedra. When the alkaline concentration reached the required level, tetrahedral bonds were easily formed to facilitate the crystallization of zeolite X. At too high alkalinity, the tetrahedra would be partially dissolved, resulting in a decrease of the crystallinity [45]. At Na2O/Al2O3 = 10.0, the product was of high crystallinity intensity with almost no interference. 3.3. Effect of reaction time Fig. 6 shows the effect of reaction time on the synthesis of zeolite NaX. At 2 h, the characteristic peaks of zeolite NaX appeared with low intensity. The optimal reaction time with high crystallinity was between 3 and 6 h [28]. In this study, a reaction time of 4 h was employed to obtain NaX with high crystallinity (Fig. 6b). A decrease in characteristic peaks intensity of zeolite NaX and the formation of zeolite NaP1 with low intensity were observed at 6 h. At prolonged reaction time, the peak intensity of the desired products started to decrease [46]. Only zeolite NaX crystallized well at a specific reaction time [9,47]. At 8 h, the result was not much different from that of 6 h. However,

13 when the reaction time was increased from 4 h to 6 h

, crystallization intensity rapidly increased and formed relatively uniform crystals [48]. This trend was also mentioned before [28,49]. Fig. 7 indicates that the crystals were not uniformly formed and some non-crystallized aluminosilicate gel regions existed at 2 h. At 4 h, the crystals formed complete structure with almost no visible amorphous region. The morphology of NaX crystals in this work was similar to those of Garcia et al. (2016) and Zhang et al. (2019) [36,50]. Zeolite X had higher crystallinity at 4 h than that at longer time in other studies using RHA [4,12]. Microwave assistance and ultrasonic treatment could be used to speed up dissolution of precursors, help formation of bonds, and promote rapid growth of crystals [27,51]. The

2 effect of aging time on the nucleation and crystallization of zeolite crystal was

reported before [34,52], and investigated in this study. Fig. 8 shows that aging time from 0 to 24 h had no effect. This can be explained because the prolonged aging time would support the formation of GIS family zeolites like zeolite P instead of zeolite A and X. Similar results were reported by Ghasemi and Younesi (2012) and Thuadaj and Nuntiya (2012) [19,53]. In this work, the alkalinity of solution was investigated because it also affected on the nucleation and crystallization of zeolite crystals. Instead of using microwave and ultrasound assistance to help shortening nucleation and reaction time of zeolite [27,51], this study employed the increase of solution alkalinity to improve the reaction rate. The morphology of samples obtained at aging time of 0 h and 6 h was examined (Fig. 8). No significant difference between 0 h and 6 h

was observed; thus, aging was unnecessary in this work. 3.4. Comparison of the current method with published methods Many different feedstocks were used for zeolite synthesis such as commercial/natural mineral sources, wastes from industrial and agri- cultural production such as diatomite, fly ash and RHA. Generally, Fig. 6 . XRD patterns at different reaction time and the standard of zeolite NaA, NaX and NaP1. (a) 2

7h, (b) 4 h, (c) 6 h, and (d) 8 h

. when using waste and natural mineral precursors, most required pre- treatment like fusing at high temperatures or extracting silica which needs long time before subjecting to zeolite synthesis. Thuadaj et al. (2012) prepared zeolite X from fly ash and amorphous silica RHA by fusion at 550°C [53] while Muriithi et al. (2020) used fly ash as the precursor with a reaction time of 9 h [11]. Wang et al. (2018) carried out the synthesis in 24 h to extract Na₂SiO₃ from RHA [20]. Ghasemi and Younesi pretreated (2012) RHA with HCl, then calcinated at 700° C for 6 h before proceeded to the synthesis of zeolite X [19]. The sur- face area (m²/g) and pore diameter (A) of their synthesized NaX was 89.96 and 92, respectively compared to a surface area of 388.4 and a pore volume of 12.37 of this study. In terms of reaction time, this study required is much shorter (4 h) than the 48 h required in their study [19]. The research of Katsuki et al. (2009) used a procedure sim- ilar to this study, and obtained NaX zeolite

9with a surface area of 553 m²/g at a longer reaction time of

6 h. However, rice husk had to be burned in nitrogen gas at 600-1000°C before used as the raw material for the synthesis [22]. Although Zhang et al. (2013) synthesized NaX using commercial silica source and a specific surface area of 526 m²/g was obtained; however, the reaction time needed was 15 h [26], which was much longer than that of this work (4 h). This study could directly synthesize zeolite X using RHA without calcination and the optimal conditions were

8SiO₂/Al₂O₃ molar ratio of 4.0, Na₂O/Al₂O₃ molar ratio of

10.0, reaction time of 4 h and without aging. The ratio of SiO₂/Al₂O₃ of 4 was comparable with that from other publications; nevertheless, the Na₂O/Al₂O₃ molar ratio of 10 Fig. 7. FESEM images of the NaX at different reaction time. (a) 2 h, (b) 4 h, (c) 6 h, and (d) 8 h. was much higher than that of other studies. The higher molar ratio of Na₂O/Al₂O₃ would help the formation of high purity and crystallinity NaX as mentioned. Although this study used agricultural by-product as the feedstock, the specific surface area of the synthesized NaX was quite high (388 m²/g). Additionally, DLS result showed that the aver- age particles size of the synthesized NaX was 484.1 nm. The total reaction time, including extraction of silica, stirring to obtain homogenous mixture and synthesis of zeolite, was estimated to be about 10 h while calcination or fusion was not required, thus the process was carried out at mild conditions. Therefore, this work could provide an integrated and promising process to obtain valuable materials with low energy consumption and low cost. The low pore diameter of the synthesized NaX (12.37 A) was due to the use of RHA Table 2 Comparison of zeolite synthesized in this study with those in other studies. without calcination. This precursor source may contain organic mat- ters which partially blocked the pores of the products, resulting in lower specific surface area and pore diameter of NaX than those of some studies, as shown in Table 2. In general, this study was performed to evaluate the impact of fac- tors affecting the formation of zeolite NaX from RHA without pre- treatment. The final product was the highly crystallized zeolite NaX with a relatively large surface area compared to similar studies using other waste sources. Materials with a large surface area have been mentioned in previous studies with good adsorption capacity of CO₂, or dyes [9,13,54,55]. Our preliminary results on the adsorption of methylene blue by zeolite NaX showed that the removal

capacity of the dye can be more than 80% (data not shown). In addition, the Raw materials Reaction conditions Surface area (m²/g) Pore diameter References Ratio of SiO₂/Al₂O₃ Ratio of Na₂O/Al₂O₃ Reaction time (h) Aging time (h) (A) SiO₂ commercial Diatomite Fly ash and amorphous silica (Fused 550°C ? 1 h) Coal fly ash (Fused 550°C ? 1.5 h with NaOH) RHA (extracted Na₂SiO₃ by NaOH in 70°C and 24 h) RHA (pretreated HCl and calcined at 700°C in 6 h) Rice husk (carbonized at 600-1000°C for 1h and extracted Na₂SiO₃ by NaOH 2N at 90° C) RHA (without calcined) 3.5 3.5 - - 3.71 - 3.63 4.9 4.0 5.5 4.0 - 1.9 - 15 - 5 0.5 24 18b 9 0 24 0 48 0 6 0 526 - 53 - 232.73 - 257 122 644 18.8 89.96 92 553 - [26] [9] [53] [11] [20] [19] [22] 4.0 10.0 4 0 388.41 12.37 This study a silica was extracted from RHA b aging before reaction 344 P.L. Tran-Nguyen et al. / Journal of the Taiwan Institute of Chemical Engineers 123 (2021) 338?345 Moreover, the optimal condition of zeolite NaX synthesis such as reaction

15time of 4 h, reaction temperature of 90 °C

8SiO₂/Al₂O₃ molar ratio of 4, Na₂O/Al₂O₃ molar ratio of

10 and without aging were comparable to other works which employed RHA as the feedstock. The obtained NaX with a specific surface area of 388 m²/g suggests its potential application in environmental remedy.

1Declaration of Competing Interest The authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

. CRediT authorship contribution statement Phuong Lan Tran-Nguyen: Conceptualization, Methodology, Investigation, Resources, Writing ? original draft. Kim-Phung Ly: Conceptualization, Methodology, Writing ? original draft. Luong Huynh Vu Thanh: Writing ? review & editing. Artik Elisa Angkawi- jaya: Writing ? review & editing. Shella Permatasari Santoso: Writing ? review & editing. Nguyen-Phuong-Dung Tran: Writing ? review & editing. Meng-Lin Tsai: Writing ? review & editing. Acknowledgment

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. Fig. 8. XRD patterns at different aging time and the standard of zeolite NaA, NaX and NaP1. (

7a) 0 h, (b) 6 h, (c) 12 h, and (d) 24 h. FESEM images of

NaX at different aging time. (a) 0 h, and (b) 6 h. combination of materials synthesized from waste with other materials to create composite materials with outstanding properties at low cost is also a remarkable trend [8,56?58]. Furthermore, the synthetic method in this work can also be used for synthesizing other types of zeolites such as zeolite NaA and NaP1. 4. Conclusions In this study, zeolite NaX was successfully synthesized by directly using RHA without any pretreatment. The synthesis process was simple, environmental friendly, time-saving and energy-saving. References [1] Qiang Z, Shen X, Guo M, Cheng F, Zhang M. A simple hydrothermal synthesis of zeolite X from bauxite tailings for highly efficient adsorbing

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