SYNTHESIS OF ZEOLITE NaA AND ACTIVATED CARBON COMPOSITE FROM RICE HUSK

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Abstract

Rice husk charcoal, composed of SiO_2 39%, K_2O 1.18%, and L.O.I. 58.50% weight basis, was prepared by burning rice husks (obtained from Klong 6 Rice Mill, Lumlookka, Patumthani, Thailand) in an incineration furnace below 700°C which was used as an SiO_2 source for the synthesis of zeolite NaA and carbon composite under hydrothermal conditions. The prepared powders were formed into pellets with 25 mm diameters by hydraulic pressing at 40 MPa. The pellets were activated in N_2 atmosphere at 300-700°C for 1 h. Phase analysis, morphology, and specific surface area of the synthesized pellets were characterized using X-ray diffraction, scanning electron microscopy, and the Brunauer-Emmett-Teller technique, respectively.

Keywords: Zeolite NaA, rice husk charcoal, activated carbon, composite

Introduction

Thailand is an important rice paddy producing country in which rice husks are a leftover product of the rice milling industries (Wang *et al*., 1998; Kordatos *et al*., 2008). Burning of rice husks in a low oxygen content atmosphere at 550-700°C can produce rice husk charcoal (RHC) which contains high amounts of amorphous silica (Artkla *et al*., 2008) and carbon. Silica and carbon obtained from the RHC are of interest for use as raw materials in many industries. Zeolites can be found in nature and synthesis. They are microporous crystalline aluminosilicates which are composed of SiO_4 and AlO_4 tetrahedra with oxygen atoms connecting neighboring tetrahedra (Prasetyoko *et al*., 2006; Khemthong *et al*., 2007). Zeolites have been utilized in many fields such as the petroleum industry, detergency (Khabuanchalad *et al*., 2008), water treatment, pharmaceuticals, and cosmetics (Yusof *et al*., 2010). Zeolite A (LTA) is synthesized by a hydrothermal method widely used in detergents to remove Ca^{2+} and Mg^{2+} by selective ion exchange due

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to the small pore diameter and high hydrophilic ability.

Activated carbon has been used for the treatment of wastewater, drinking water, and removing a wide variety of pollutants because it has a high adsorption capacity (Ru-Ling, 2007; Cazetta *et al.*, 2011). Charcoal with a small mineral content can be activated by NaOH to get a high specific surface area (Lillo-Ródenas *et al.*, 2001; Xu *et al.*, 2010).

In this work, RHC was used as a silica and carbon source for synthesizing zeolite NaA and activated carbon composite by the hydrothermal method and activation of carbon in N_2+5% CO_2.

Materials and Methods

Preparation of Rice Husk Charcoal

The RHC composed of 39.00% SiO_2, 1.18% K_2O, and 58.50% loss on ignition was prepared by firing in an incineration furnace at lower than 700°C and then the particle size was reduced by a wet ball mill for 6 h with quartz pebbles as balls and water as a medium. After milling, the slurry was sieved through a #100 mesh and the water removed by filter pressing. Finally, the RHC was dried in an oven at 100°C overnight.

Synthesis of Zeolite NaA and Carbon Composite

Zeolite NaA with Si/Al ratios of 1.0 (Petkowicz *et al.*, 2008) were synthesized from a mixture of RHC, sodium aluminate ($NaAlO_2$ (Riedel-de Haen, Sigma-Aldrich Corp., St. Louis, MO, USA)), sodium hydroxide (NaOH, 99% (Chemmin Corp., Ltd., Vaalpark, South Africa)), and distilled water by magnetic stirring until a sticky gel was formed. The gel was transferred into a stainless cup with a lid and heated to 80-110°C for 2-8 h in an oven. Thereafter, the solution was filtered and dried at 60°C overnight.

Carbon Activation

Zeolite and carbon powders were mixed together with 1 wt% of sodium carboxymethylcellulose (CMC (Ceramics R US Corp., Ltd.,)) and 5-15 wt% of phenolic resin (Kangnam Chemical Co., Ltd., Seoul, South Korea) and were then formed into a pellet shape with a 25 mm diameter by hydraulic pressing at a pressure of 40 MPa. The pellets were fired in a tubular furnace with N_2+5% CO_2 atmosphere at 300-700°C for 1 h.

Characterizations

The crystalline phases of the zeolite and carbon mixed powders were investigated by X-ray diffraction (XRD (D8-Advance, Bruker Corp., Billerica, MA, USA)) with Cu-K_α radiation, and the diffraction data were collected over the 2θ range from 5 to 60° with a step size of 0.02°. The morphology of the

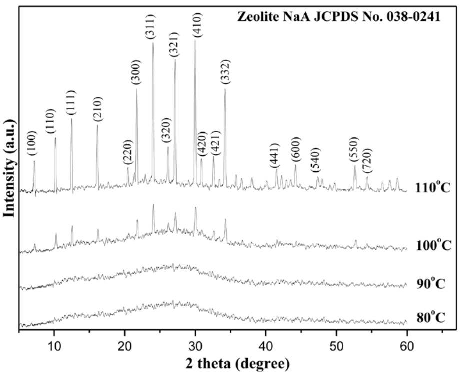

Figure 1. XRD patterns of zeolite NaA and carbon composite synthesized at 80-110°C for 2 h

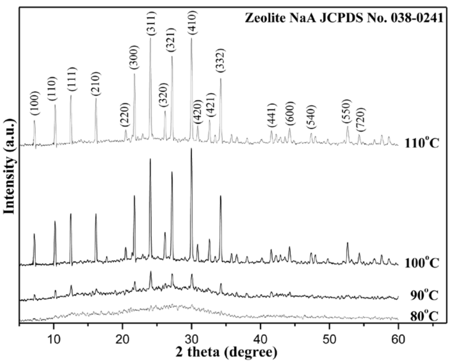

Figure 2. XRD patterns of zeolite NaA and carbon composite synthesized at 80-110°C for 4 h

zeolite NaA was observed by scanning electron microscopy (SEM (JSM 6480 LV, JEOL Ltd., Tokyo, Japan)). The specific surface area was determined by using the Brunauer-Emmett-Teller technique (SA3100, Beckman Coulter Inc., Brea, CA, USA).

Results and Discussion

The XRD patterns of the synthesized zeolite NaA and carbon composite at 80-110°C for 2 h are shown in Figure 1. The peaks of the zeolite NaA were observed at the synthesis temperature of 100°C and the crystallinity increased at 110°C. For the reaction temperature at 80°C and 90°C, only the amorphous phase was found.

Figure 2 shows the XRD patterns of the zeolite NaA and carbon composite synthesized at 80-110°C for 4 h. The zeolite NaA peak could not be observed at the synthesis temperature of 80°C. On the other hand, zeolite NaA peaks were found after synthesis at 90-110°C and the crystallinity gradually increased at 100°C and 110°C, respectively.

Figure 3 and Figure 4 present the XRD patterns of the zeolite NaA and carbon composite synthesized at 80-110°C for 6 h and 8 h, respectively. The zeolite NaA phase was found in all samples. It was found that time and the reaction temperature significantly influenced the synthesis of the zeolite NaA. With increasing the time and reaction temperature, the crystallinity of the zeolite NaA was improved.

In this research, the selected optimal condition for synthesis of the zeolite NaA and carbon composite was at 100°C for 4 h due to the crystallinity of other XRD phases not having a different reaction when the time and temperature were increased.

Figure 5 shows the effect of activation of the temperature on the zeolite NaA and carbon composite synthesized at 100°C for 4 h. The crystallinity of the zeolite NaA was decreased when there was an increased activation temperature and it greatly decreased at 700°C. Moreover, the sodium aluminum silicate phase was formed by the decomposition of the zeolite phase.

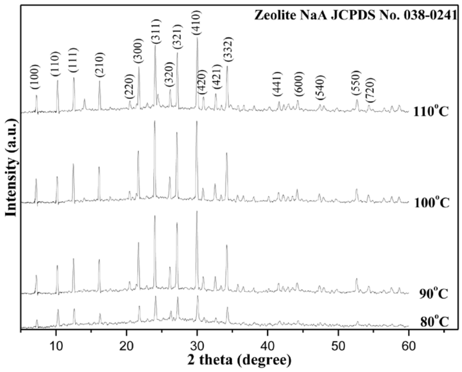

Figure 3. XRD patterns of zeolite NaA and carbon composite synthesized at 80-110°C for 6 h

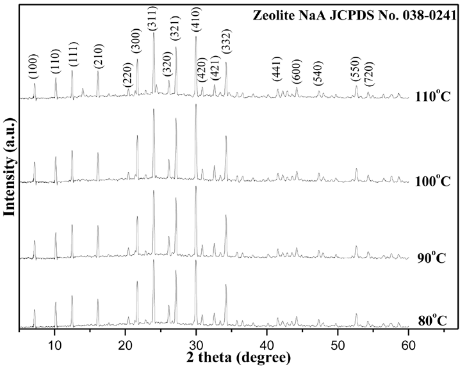

Figure 4. XRD patterns of zeolite NaA and carbon composite synthesized at 80-110°C for 8 h

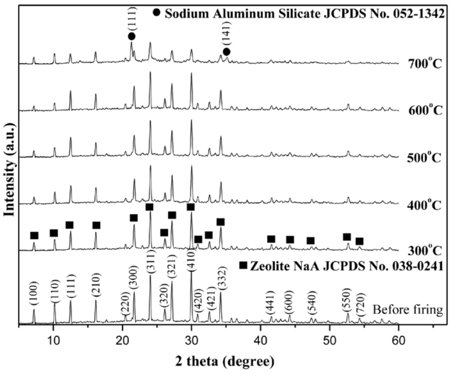

Figure 5. XRD patterns of zeolite NaA and carbon composite synthesized at 100°C for 4 h with various activation temperatures

Table 1 shows the specific surface area of the zeolite NaA and carbon composite synthesized at 100°C for 4 h mixed with 1 wt% of sodium carboxymethylcellulose and various amounts of phenolic resin. The mixer was thermally activated at various activation temperatures from 300-700°C. The specific surface area of the sample added with 1 wt% of CMC decreased when the activation temperature was increased as a result of an agglomeration diminishing the porosity (Della *et al*., 2002). The samples mixed with 1 wt% of CMC and various amounts of phenolic resin (5-15%) were activated at 300°C, 400°C, 500°C, 600°C, and 700°C, respectively. It was indicated that the specific surface area increased with more of a load of phenolic resin at 500°C and 600°C owing to the carbonization of phenolic resin leading to a carbon material product (Zhao *et al*., 2009).

Figure 6 shows SEM micrographs of the zeolite NaA and carbon composite synthesized at 100°C for 4 h. Figure 6(a) shows the sample before being activated. The crystalline shape of the zeolite NaA is cubic with a size of about 5 µm. Figure 6(b) shows the sample mixed with 1 wt% of CMC and activated at 300°C, (c) activated at 400°C, (d) activated at 500°C, (e) activated at 600°C, and (f) activated at 700°C, respectively. From Figure 6(b) to 6(f) it is indicated that the morphology of the zeolite NaA and activated carbon is more agglomerated when the increased activation temperature affects the specific surface area.

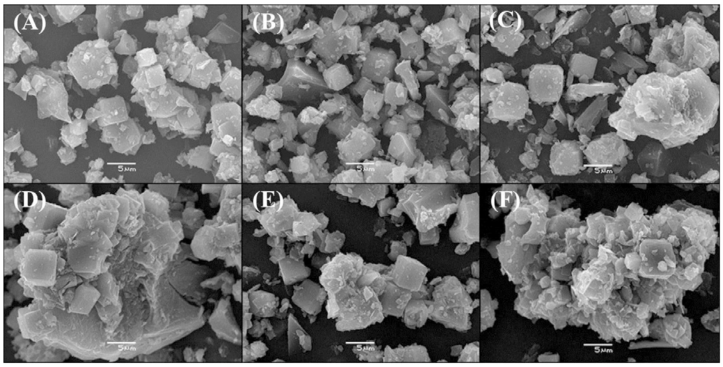

Figure 6. SEM micrographs of zeolite NaA and activated carbon composite as (A) before being activated, (B) mixed with 1 wt% of CMC and activated at 300°C, (C) at 400°C, (D) at 500°C, (E) at 600°C, and (F) at 700°C, for 1 h

Table 1. Specific surface area of zeolite NaA and carbon composite mixed with 1 wt% of CMC and various amounts of phenolic resin

Samples	Specific surface area (m^2/g) Activation temperature				
	300°C	400°C	500°C	600°C	700°C
1%CMC	64.60	56.95	53.85	44.69	33.85
1%CMC 5%phenolic resin	41.10	69.43	58.60	54.45	26.69
1%CMC 10%phenolic resin	44.00	69.14	66.83	58.51	23.66
1%CMC 15%phenolic resin	56.37	68.39	71.57	65.72	26.21

Conclusions

Zeolite NaA and carbon composite are successfully synthesized from RHC by mixing with sodium hydroxide and sodium aluminate under the hydrothermal method at 100°C for 4 h. One percent weight of sodium carboxymethylcellulose was added to assist the sample formation by hydraulic pressing. The specific surface area increased with more of a load of phenolic resin at 500°C and 600°C because phenolic resin is degraded to carbon at 500-600°C.

Acknowledgments

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