

Synthesis of Zeolite A Membrane from Rice Husk Ash

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Abstract

Rice husk is a major by-product of the rice-processing industries. The burning of rice husk in air results in the formation of rice husk ash (RHA) with a content in SiO₂ that varies from 85 to 98% depending on the burning conditions, the furnace type and the rice variety. Numerous studies aimed at using RHA as a cheap alternative source of amorphous silica for the production of silicon based materials with industrial and technological interests. The zeolite gel was prepared with the following batch composition: 3.1Na₂O : Al₂O₃: 1.9SiO₂: 128H₂O synthesized by hydrothermal treatment with various times from 15 min to 4 hrs. Zeolite A crystals have been successfully coated on the substrate surface (Al₂O₃) by direct synthesis method. The silica source was characterized by FTIR and X-ray diffraction (XRD). Zeolite A and zeolite A membrane, the patterns of which showed a unique characteristic of zeolite A respectively were characterized by XRD. They were also examined by Scanning electron microscope (SEM) which at 2 hrs. synthesis time reported the layer thickness of 5.92 μm ± 0.152 and 12.295 μm ± 1.052 at 4 hrs. synthesis time.

Key words: RHA, Zeolite A, Hydrothermal, Direct synthesis

Introduction

In Thailand, the production of electricity from biomass power plants is increasingly significant due to high demand in energy both in the industrial and private sectors. Rice husk is one of the major biomasses in Thailand that can be used as a resource of combustion energy for electricity generation.⁽⁹⁾ The concept of generating energy from rice husk has great potential, particularly in those countries that are primarily dependant on imported oil for their energy needs. Rice husk is high in ash compared to other biomass fuels ashes contain 85-98% silica are highly porous and lightweight, with a very high external surface area.⁽³⁾ RHA is a general term describing all types of ash produced from burning rice husks. RHA can be used as a cheap alternative source of amorphous silica for the production of silicon based materials with industrial and technological interests. Among the various utilizations of RHA, there is a significant interest in its use in the preparation of zeolites due to the widespread industrial use of zeolites in separation processes as sorbents, as well as in catalytic refinery and petrochemical processes.⁽²⁾

The Zeolite membranes are among inorganic membranes which consist of hydrated crystalline aluminosilicates with open three-dimensional framework structures, made up of SiO₄ and AlO₄ tetrahedrons linked by sharing their oxygen atom to form regular intracrystalline cavities and channels of atomic dimensions. Zeolite membranes can be used in several applications such as for separation and catalytic membrane etc.⁽⁶⁾ Zeolite membranes are normally prepared by hydrothermal methods of gel containing silica, alumina, cation, template and water, and which normally are described as silicate and aluminate solution.⁽¹⁰⁾ The membrane usually grown onto porous supports, with or without a previous seeding step. Seeding of the supports leads to a higher reproducibility in synthesis of the zeolite membranes. For zeolite A membranes Pak and Mohammadi (2006) and Boudreau and Tsapatsis (1997), there are several research papers of this membrane. However, there is no report of synthesis of zeolite A using RHA as silica source. Although, there are several research reports on the synthesis of zeolite for RHA.^(8, 4)

In this study, we have attempted the synthesis of silicon dioxide from rice husk ash, and

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then prepared and characterized the zeolite A membrane from rice husk ash by using FTIR, X-ray diffraction (XRD), and SEM. We have investigated the optimum condition of the in situ synthesis of zeolite A membrane with various temperatures and times.

Materials and Experimental Procedures

Preparation of Silica Source From RHA

Organic matters of RHA were eliminated by acid treatment, which was performed by reaction with 0.1M HCl (Carlo Erba) solution, and which was aged for 1 hour at 100°C. After the treatment, RHA was filtered and thoroughly washed with DI water and then dried at 100°C overnight. RHA was converted to silica source by reaction with 10% wt NaOH (Carlo Erba) at a ratio of 2Na: Si solution for 1 hour at 80°C. After 1 hour, the solution was cooled down to room temperature and filtered. The Na₂SiO₃ solution was left for one week in order to generate a clear solution.

Synthesis of Zeolite A Membrane

The zeolite gel was prepared with the following batch composition: 3.1Na₂O : Al₂O₃: 1.9SiO₂: 128H₂O. First, the concentration of Na₂SiO₃ solution was contained in a high-density polyethylene (HDPE) bottle labeled as silicate solution. The composition of aluminate solution that consists of NaOH and Na₂Al₂O₄ (Riedel) dissolved by DI water were then mixed in capped HDPE bottle until clear. The solution of aluminate and silicate were afterwards mixed in capped bottles with Al₂O₃ substrate included until suddenly a thick gel was formed. The mixtures were kept tightly in HDPE bottles and mixed until they became homogenous, which may be done with stirrer or vigorously by hand for 5-10 minutes. After that, the homogeneous solution was heated to 100°C with various synthesis times (15mins, 30 mins, 1 hour, 2 hours and 4 hours). The solution was then removed from the heat source in order to cool it down below 30°C. Then, zeolite A membrane was washed with DI water. Finally, the samples were dried at 100°C overnight.

Characterization

The functional groups of silicon dioxide in RHA and zeolite A were characterized by FTIR (PerkinElmer: spectrum GX). The crystalline phase

and crystallinity of powder samples and membrane were investigated and the preferred orientation and phase of films were determined by using XRD (Siemens: D8 Advance). XRD characterization occurred over a 2theta range of 5° to 60° and a position sensitive detector using a step size of 0.02° and a step time of 2 s. The thickness and morphology of zeolite A membrane was observed by SEM (LEO 1455 VP) working at 18 kV accelerating voltage and magnification 1k and 5k times.

Results and Discussion

Characterization of Silica Source

In Figure 1, FTIR was analyzed and the functional groups of silicon dioxide in RHA were determined. The first functional group was silica or silicate described by the region 1130-1000 and 800-400 cm⁻¹. The bands between 1130-1000 and 800-400 cm⁻¹ were attributed to -O-Si-O- and typical structures of SiO₂, which was an indication of the silica. The second region at 1100-950 cm⁻¹ presented significant interferences from silicates and silica derivatives. As RHA contains carbon compounds, the FTIR result presented functional of polyhalogenated carbon compound inorganic oxide or oxyanion by the regions 1160-1095 cm⁻¹.⁽⁵⁾ Some simple halogenated compounds containing C-H bonds may also be described by this region and the most prominent inorganic compounds which appeared in this region are silicates or silica-based samples and sulphates. The asterisk points on Figure 2 show peaks which probably present distinctive characteristic of cristobalite and tridymite.⁽⁸⁾ The XRD resulted from silicon dioxide obtained from RHA is shown in Figure 3, and the area between 2theta 15° to 2theta 30° reported amorphous SiO₂ with broad and no peaks.

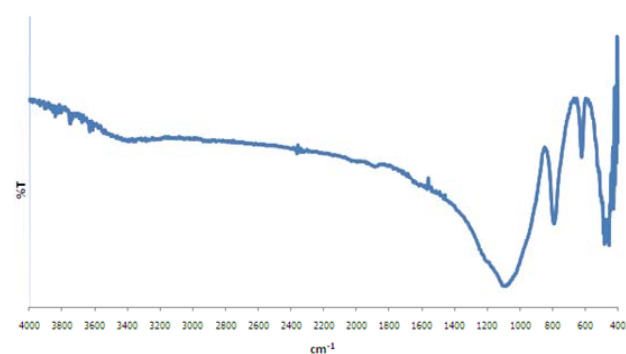


Figure 1. FTIR spectrum of RHA

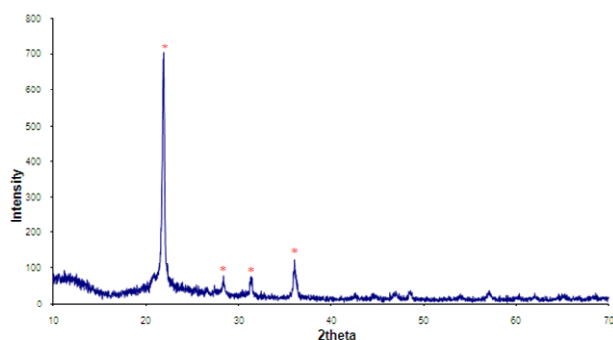


Figure 2. XRD spectrum of RHA

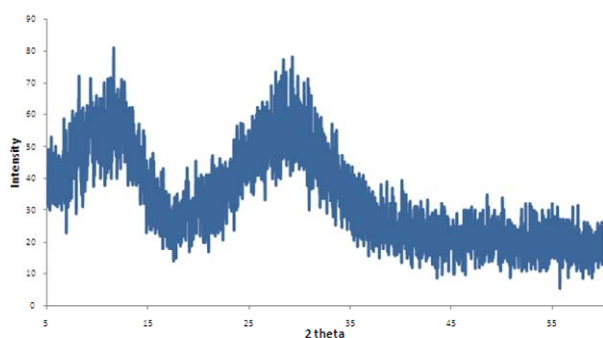


Figure 3. The XRD spectrum of SiO₂

Characterization of Zeolite A membrane

Figure 4 reports significant peaks located at 2theta 25.4°, 2theta 35.02°, 2theta 37.62°, 2theta 43.2°, 2theta 52.4° and 2theta 57.34° illustrated XRD reported that they consist of aluminum oxide (Al₂O₃).

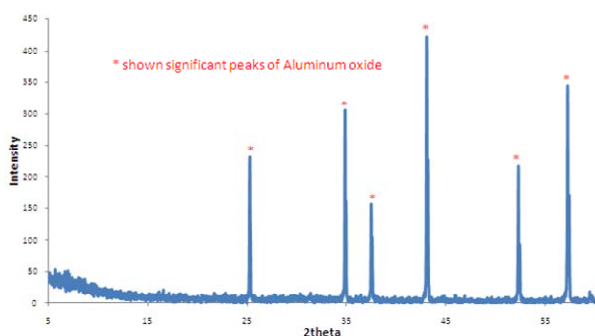


Figure 4. XRD spectrum of substrate (Al₂O₃)

Figure 5 presents a comparison of zeolite A membrane at various synthesis times. At 15 mins, 30 mins and 1 hour synthesis times the XRD results reported significant peaks the same as the substrate (Al₂O₃). This finding corroborates that at

these interval times (15 mins, 30 mins and 1 hour) zeolite A membrane did not grow on the surface of the substrate (Al₂O₃). At 2 hours and 4 hours synthesis times, the XRD results showed significant peaks at 2theta 7.08°, 2theta 10.08°, 2theta 12.36°, 2theta 15.98°, 2theta 21.58°, 2theta 23.9°, 2theta 27.02°, 2theta 29.86 and 2theta 34.06°, which further confirms the formation of zeolite A structure that grew on substrate at 2 hours and 4 hours.⁽⁴⁾ Comparing distinctive characteristics of both synthesis times, the growth of zeolite A membrane at 2 hours synthesis time was not complete because the results revealed an amorphous phase while zeolite A membrane at 4 hours synthesis time showed higher crystallinity than at 2 hours synthesis time.

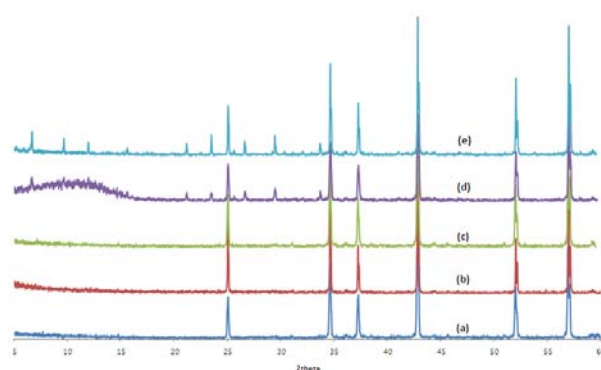
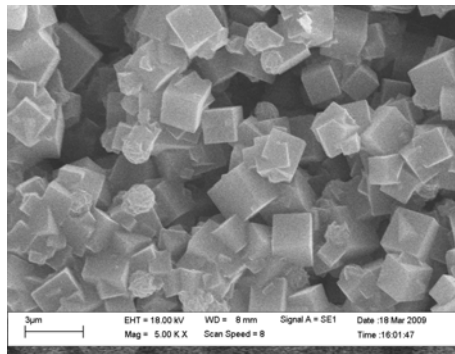
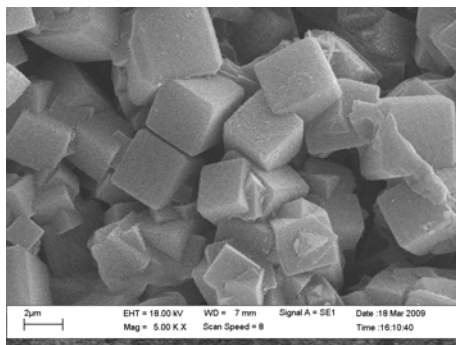


Figure 5. XRD patterns of zeolite A membrane at various synthesis times from 15 min (a), 30 min (b), 1 hour (c), 2 hours (d), 4 hours (e)

The crystalline zeolite A was successfully grown and fully covered the alumina substrate with a particle size of 2.554 μm at 2 hours synthesis time. It was smaller than 3.93 μm at 4 hours synthesis time as shown in Figure 6. At 2 hours synthesis time, the SEM image indicated a smaller size in diameter for zeolite A particles than 4 hours synthesis time. However, in both cases the particles appeared in cubic shape. In Figure 7, the SEM image shows the cross-sectional morphology of crystalline zeolite A on the alumina substrate at 2 hours and 4 hours synthesis time. The membrane has a thickness around 5.92 μm ± 0.152 at 2 hours synthesis time, and 12.295 μm ± 1.052 at 4 hours synthesis time. The SEM image exhibit that zeolite A membrane was thicker at 4 hours synthesis time than 2 hours synthesis time, This is an indication of the zeolite A that was successfully grown on the substrate surface.

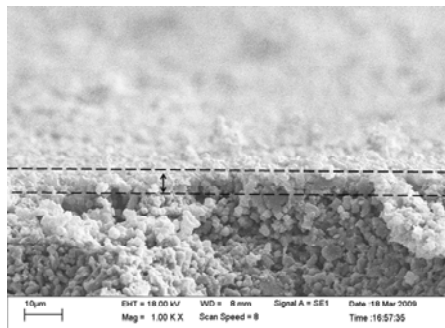


(a)

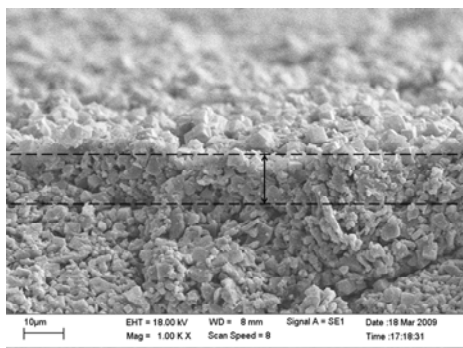


(b)

Figure 6. SEM surface pictures with magnification 5k at 2 hours (a) and 4 hours (b) synthesis time



(a)



(b)

Figure 7. SEM cross sectional area with magnification 1k at 2 hours (a) and 4 hours (b) synthesis time

Conclusion

The rice husk ash was used as raw materials for synthesized zeolite A. It was demonstrated that the SiO_2 can be synthesized directly from RHA. The zeolite A membrane grew on the aluminum oxide substrate by direct synthesis method by which the substrate was transferred directly into the mixture solution of zeolite A using HDPE bottles. The thickness of zeolite A was directly affected by the synthesis time. At 2 hours synthesis time the thickness of zeolite A around $5.92 \mu\text{m} \pm 0.152$ grew on the surface whereas at 4 hours synthesis time a thickness of zeolite A around $12.295 \mu\text{m} \pm 1.052$ grew on the surface.

According to expected results, the layer thickness of zeolite A at 4 hours synthesis time was thicker than for zeolite A at 2 hours synthesis time. SEM surface image at 2 hours synthesis time showed that particles of zeolite A were similar in shaped however, the particle size was smaller than at 4 hours synthesis time.

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