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Utilizing Silica from Rice Hull for the Hydrothermal Synthesis of Zeolite Y

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ABSTRACT

Rice hull, a known agricultural waste product, with 21% silica (SiO_2) content based on elemental analysis, is a promising starting material for zeolite Y synthesis. In this work, silica derived from rice hull samples were extracted via alkaline treatment using 4M NaOH at 130 °C - 150 °C. Further introduction of NaOH and inclusion of aluminium hydroxide were done before subjecting the materials to subsequent ageing and heating at 95 °C to form the zeolite Y crystals. The samples were then analyzed using Fourier transform infrared spectroscopy (FT-IR) and X-ray diffractometry (XRD). Zeolite Y from commercial silica was also synthesized as negative control and together with commercially available zeolite Y, FT-IR and XRD results showed that they possess similar structures with the rice-hull derived material.

Keywords: *rice hull; silica; zeolite Y; XRD; FT-IR*

INTRODUCTION

According to a report by the Philippine Statistics Authority (PSA), the Philippines produced 19.28 million metric tonnes (MT) of rice in 2017. This is 1.65 million MT or 9.36% more than the 17.63 million MT produced in 2016. The higher production resulted in a 2.7 million MT surplus in rice supply which is expected to rise up to 3 million MT (Lomibao, 2008; Special Release, 2012). The increased rice production also results in the increased volume of rice hulls. Rice hulls are agricultural residues abundant in rice-producing countries, such as the Philippines. Rice hulls contain 20% silica, 38% cellulose, 22% lignin, 18% pentose, and 2% other organic components (Adam, *et al.*, 2012). Some of these rice hulls are converted into useful products such as compost, adsorbents and precursor for activated carbons (Adam *et al.*, 2012; Hieu *et al.*, 2015; Basta *et al.*, 2009). However, most of the rice hulls are burnt in open air, causing health and environmental problems by producing aerosol particles that affect air quality (Basta *et al.*, 2009). Furthermore, its potential use as food for livestock is an economic use. The high fibre and silica content also limits its use as food because it is degraded slowly in ruminant animals. Slow degradation of rice hulls affects the energy intake of ruminant animals which can ultimately affect their productivity (Abou-El-Enin *et al.*, 1999; Friedman, 2013). Also, other competitive resources are available for the aforementioned applications, thus, the use of rice hull is still minor (Basta *et al.*, 2009). Therefore, finding other ways to utilize rice hulls are of utmost importance.

Silica, SiO_2, is a primary component of rice hulls, accounting for 20% of its mass. Over the years,

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researchers have utilized rice hulls to prepare zeolites and mesoporous SiO_2 (An *et al.*, 2010). Zeolites are crystalline solids that contain channels and cages of molecular dimensions that allow entry of other molecules (Trinidad *et al.*, 2016). These crystalline solids are composed of three-dimensional networks of silicon and aluminum oxide tetrahedrons (SiO_4 and AlO_4^-) linked by shared oxygen atoms (Garcia *et al.*, 2016). Elements of group IA and IIA such as sodium, potassium, magnesium, and calcium comprise crystalline aluminosilicate zeolites. These cations balance the negative charge that the AlO_4 tetrahedron carries. The empirical formula for zeolites is $M_{2/n}O \cdot Al_2O_3 \cdot y\ SiO_2 \cdot w\ H_2O$, in which n corresponds to the valence electrons of the cations, y's value is 2-200, and w is the water trapped in the channels of zeolite cages (Johnson *et al.*, 2014).

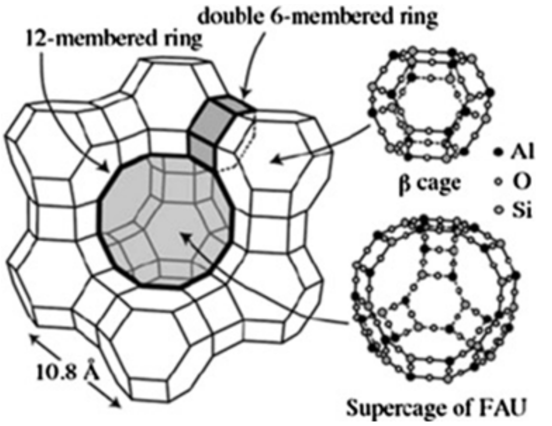

Figure 1. Framework Structure of Faujasite-type Zeolites.

Zeolites X and Y are two zeolites of similar structure and of particular interest. Zeolites X and Y are faujasite type zeolite (FAU) in which the SiO_2/Al_2O_3 for zeolite Y is greater than three (Garcia *et al.*, 2016). Figure 1 shows the framework structure of faujasite zeolites. It consists of two cages: the α-cage (supercage) and the β-cage (sodalite cage). The sodalite cages are linked to one another via hexagonal prisms and the pores of FAU-type zeolites are formed by a 12-membered ring (Johnson *et al.*, 2014). The porous nature of zeolites made them useful in various applications such as ion exchange, adsorption, catalysis, and membrane separation (Garcia *et al.*, 2016). In addition, the presence of aluminum atoms in the framework induces the acidic properties of zeolites, making them good solid-acid catalysts. Petroleum industries utilize zeolites as catalysts for heavy hydrocarbon cracking (Anis *et al.*, 2016). Ninety-five percent of fluid catalytic cracking (FCC) units rely on FAU-type zeolites such as zeolites X and Y (Anis *et al.*, 2016; Vermeiren and Gilson, 2009). Processes such as Methanol to Gasoline (MTG) and Methanol to Olefins (MTO) conversions uses MFI-type and CHA-type zeolite as catalysts, respectively. The catalytic application of zeolites also found their way in the synthesis of pharmaceutical drugs and other fine chemicals (Liu *et al.*, 2016).

In this work, silica was extracted from rice hull and was used as a starting material for the synthesis of zeolite Y via the hydrothermal method. The synthetic zeolite Y was characterized using Fourier-transform infrared spectroscopy (FT-IR) and x-ray diffractometry (XRD).

METHODOLOGY

Materials and Equipment. Aluminum hydroxide (Sigma-Aldrich), sodium hydroxide (Merck), sodium silica solution (Code:001394), zeolite Y (Sigma), and potassium bromide (Sigma-Aldrich) were used as-received. A Memmert oven was used for the ageing and drying processes. An FTS-40A BioRad FT-IR spectrophotometer was used for the spectroscopic analysis. An Xpert Powder X-ray diffractometer was used for the structure analysis of the zeolite.

Extraction of Silica from Rice Hull. Rice hull samples were collected from the Bureau of Animal Industry. Samples of rice hull were sent to SGS Philippines, Inc for elemental analysis. The rice hulls were used without any pre-treatments prior to extraction. Rice hull samples (2.90 g) were added to 30 ml of 4M NaOH solution in a poly (tetrafluoroethylene) bottle. The mixture was subjected to heating at 130-150 °C for 24 hours, accompanied by periodic addition of water to maintain its initial volume. Without cooling, the hot solution was subsequently filtered using a filter paper through a plastic funnel. The filtrate is then cooled to room temperature for zeolite Y synthesis.

Synthesis of Zeolite Y from Rice hull-derived and Commercially Available Silica Sources. Sodium hydroxide (2.16 g) was dissolved in deionized water in a poly (tetrafluoroethylene) bottle. Aluminum hydroxide (1.25 g) was then added and the bottle was shaken until all aluminum hydroxide were dissolved completely. To the resulting solution, 20 g of 30% rice-hull derived silica solution was added, followed by an ageing process for 24 hours at room temperature. Subsequent heating of the solution to 95 °C without stirring was done for 72 hours. The product was filtered, washed with deionized water until the pH of the washings was below 9, cooled to room temperature, and air-dried. The product was then subjected to x-ray diffractometry (XRD) and Fourier-transform infrared spectroscopy (FT-IR). A similar set up was also done but using commercially-available silica instead of the extracted silica.

RESULTS AND DISCUSSION

Extraction of Silica from Rice Hull. Rice hull samples were sent to SGS Philippines, Inc. for elemental analysis. The elemental analysis revealed that the samples contain 21% SiO_2. Alkaline treatment using 4.0 M NaOH at temperature of 130-150 °C for 24 hours was done in order to dissolve and convert SiO_2 into a viscous and transparent solution consisting of Na_2SiO_3 as shown in Equation 1 (Todkar *et al.*, 2016; Yuvakkumar *et al.*, 2014).

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \qquad (1)$$

The resulting silica-rich extract was separated from the crude rice hull samples via hot filtration. This process parts the silica form other water-insoluble materials such as lignin and cellulose that were also present in the crude samples. Lignin solubility in aqueous solution is limited due to its hydrophobicity, but it dissolves to some extent in alkaline solution. However, the periodic addition of water decreased the alkalinity of the solution, causing lignin to precipitate out and be separated in the filtration step (Evstigneev, 2011). Cellulose was found to be soluble in aqueous NaOH only by freezing it to –20 °C followed by thawing to room temperature. The high temperature conditions of the method ensured that cellulose remain undissolved in the extraction step. Thus, it is also separated during the filtration step (Isogai and Atalla, 2011).

Synthesis of Zeolite from Rice Hull-derived and Commercially Available Silica Sources. The resulting Na_2SiO_3 solution was then utilized as the silica-source for the conventional hydrothermal Zeolite Y synthesis. A previous study by (Rahman *et al.*, 2009) also used the hydrothermal technique for Zeolite Y synthesis. The silica solution, together with NaOH, H_2O and alumina (Al_2O_3), are the building blocks for zeolite Y. The Al_2O_3 molecules are converted to aluminate ions which links to oligomeric silica molecules, forming and the excess ions remain in solution. During the ageing process, the gel consumes more aluminate, forming the three-dimensional structure of zeolite Y. The 3D structure is stable at room temperature and the negatively charges inside the zeolite Y prevents further inclusion of other negatively charged ions such as OH^-. Hydroxide ions are further eliminated from the mixture by reducing the pH below 9 (Lutz, 2014).

Fourier-Transform Infrared Spectroscopy (FTIR). FT-IR was used to deduce structural information for the zeolite samples. However, only the mid-infrared region (1300-200 cm^{-1}) was used to investigate the framework of synthetic zeolites. It contains the fundamental vibrations of TO_4 (T=Al, Si) tetrahedra. Two types of vibration can be observed from zeolite structures: internal TO_4 tetrahedrons and vibrations due to linkages (de Araujo *et al.*, 1999). The FT-IR spectra for the commercially available zeolite Y, synthesized zeolite from commercial silica and rice hull-derived silica are shown in Figures 2, 3 and 4.

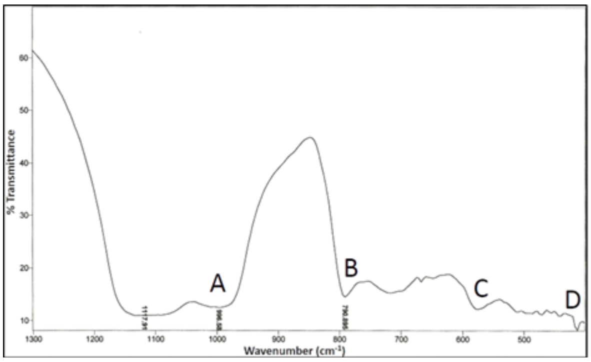

Figure 2. FT-IR Spectra of Commercially Available Zeolite Y.

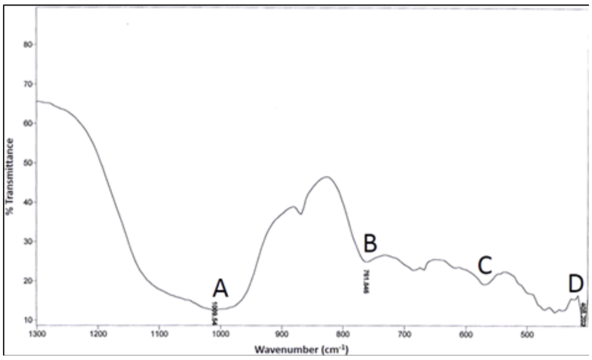

Figure 3. FT-IR Spectra of Zeolite Y from Commercial Silica.

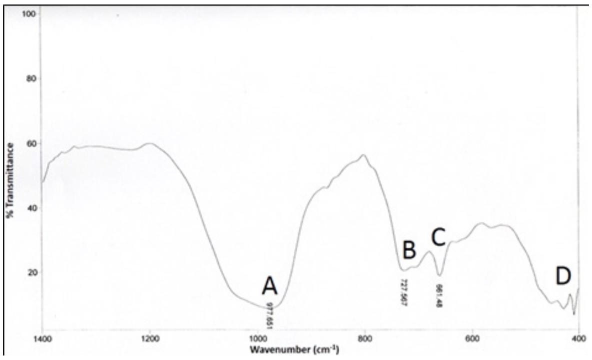

Figure 4. FT-IR Spectra of Zeolite Y from Rice Hull-derived Silica.

From the FT-IR spectra presented in Fig. 2-4, it can be seen that there are four characteristic vibrations common on all three samples analyzed. Peaks A, observed at ~1000 cm^{-1}, is the strongest vibration found in all zeolites. These vibrations are attributed to the internal tetrahedron vibrations of zeolites. Peak B, observed at ~800-700 cm^{-1}, is the stretch assigned to the tetrahedral atoms, which are sensitive to Si-Al composition of the network. This stretch shifts to lower frequencies as the number of tetrahedral Al atoms increases. Peak C, observed at ~680-550 cm^{-1}, is due to the presence of double rings in the framework structures. This peak is observed for all zeolites having the same structure. Peak D, observed at ~500-400 cm^{-1}, is also a characteristic vibration of the internal tetrahedrons of zeolite structures (de Araujo *et al.*, 1999; Flanigen *et al.*, 1971).

The appearance of the same peaks for all samples suggest that the framework of the samples are similar to those of previously studied zeolites. In order to further confirm this assumption, the samples were subjected to XRD analysis.

X-ray Diffractometry (XRD). The structural framework of the zeolite samples were further studied using XRD. The obtained XRD pattern for the commercially available and synthesized zeolite y samples are shown in Figure 5. The presence of sharp peaks indicate that the samples analyzed exhibit crystallinity. The crystalline structure observed from the XRD patterns of the samples are comparable to the standard XRD pattern of faujasite – type cubic zeolite Y from the "Collection of Simulated XRD Powder Patterns for Zeolites" (Treacy and Higgins, 2007). Previous studies done by Wittayakun *et al.* (2014), Paragas *et al.* (2014), and Rosman *et al.* (2014) also exhibit the same XRD pattern. Thus, it can be concluded that the synthetic zeolites are indeed zeolite Y's of faujasite – type cubic lattice. Furthermore, the narrow width of the peaks reveal that the zeolite Y's have a small crystallite size (Flanigen EM *et al.*, 1971).

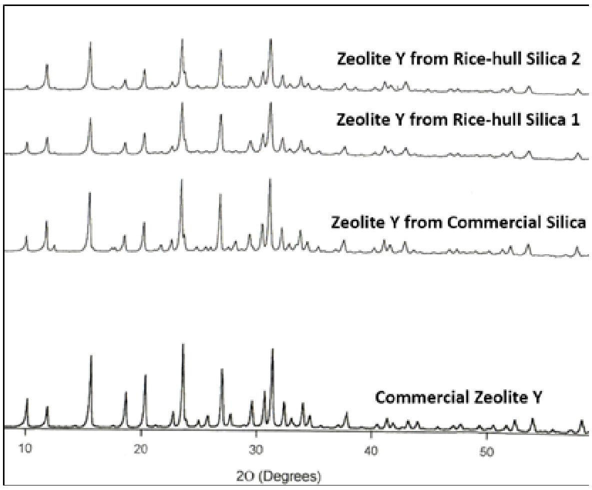

Figure 5. X-Ray Diffractogram for All Samples.

CONCLUSION

Dissolution of rice hulls in alkaline media yielded silica that was used in the hydrothermal synthesis of zeolite Y. FT-IR and XRD analyses confirmed that the structural framework of the synthetic zeolite Y's are the same in previously studied zeolite Y's. XRD also confirmed that the synthetic products are of the faujasite-type cubic zeolite Y's. The simple extraction method performed in the study reveal that rice hulls can be fully utilized as silica sources. This result not only lessens environmental concerns about rice hulls, it also increases the availability of an important raw material. Therefore, rice hull can be a viable source of silica. Furthermore, this study reveals an alternative and cheaper method for the synthesis of zeolites that can be used for a wide variety of applications.

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