FABRICATION OF HIGH PURITY SILICA FROM RICE HUSK AND ITS CONVERSION INTO ZSM-5

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ABSTRACT

A white rice husk ash with a silica content of more than 99% was produced from a rice husk by a citric acid treatment before heating the rice husk at 700 ºC to 1000 ºC. The white ash mostly consisted of an amorphous phase, and cristobalite usually found after heating rice husk was not detected. The amorphous phase was still formed although the rice husk was burned at 1000 ºC. These indicated that the citric acid dissolved part of the carbon compounds in the rice husk, followed by releasing of potassium and other alkali cations, and as a result, an amorphous high silica ash was formed without incorporation of crystal phases such as cristobalite. The white rice husk ash was successfully converted into ZSM-5, a zeolite widely used as a catalyst in the petroleum industries.

Keywords: amorphous silica, rice husk, rice husk ash, zeolite, zsm-5.

INTRODUCTION

Rice is the main food of many people around the world. The production of rice in the world was 480 million tons in 2013 [1]. During the rice milling process, rice husk is abundantly generated as a by-product. Most of the rice husk is commonly used as animal feed, compost, gardening, etc. [2]. However, the current demands for these utilities are decreasing. In Japan, about 2 million tons of rice husk is generated every year and about 60% of it is disposed as an industrial waste. Previously, Japanese farmers used to burn the rice husk in their fields, but recently private burning of rice husk is prohibited by Japanese regulations. Rice husk has to be combusted at high temperature or buried as industrial waste, which highly cost for the farmers.

The rice husk is a potential material as an alternative energy, for example, for power generation [3, 4]. A rice milling company in Thailand utilizes rice husk for electric power generation. On the other hand, a dry milk company in India has been using rice husk as fuels for boilers that produce steam. Some studies have developed the production of silicon and silicon carbide [5], and active carbon [6] using rice husk as a raw material. In our previous study, we succeeded in developing a smokeless boiler using rice husk as a fuel [7].

Combustion of the rice husk generally produces a rice husk ash (RHA), which contains high SiO2 (silica) and few alkali cations. The combustion temperature affects the silica content and the phase of the husk, which is amorphous or crystalline [8]. The high silica content of the rice husk ash suggests the possibility of it being converted into valuable materials, such as zeolites. Zeolite is an aluminosilicate having three-dimensional networks, and has unique properties due to the presence of channels or cavities with a certain size in its structure [9]. Zeolites have been widely applied in industry as a catalyst or for molecular separation.

ZSM-5 [H0.32(Si95.68Al0.32O192)], one of the zeolite species, is widely used in industry as a catalyst in oil refinement. ZSM-5 was also used as a catalyst in hydrocarbon cracking [10] and NOX removal [11]. This zeolite contains very few aluminium as compared to silicon. Because rice husk ash contains silica with high content, it is suitable for the synthesis of the ZSM-5, as indicated by previous studies [12, 13]. However, the rice husk ash is usually grayish in color due to remaining carbon materials, and most of the silica is the crystalline cristobalite. The grayish color of the RHA is not favorable as an industrial raw material, and crystalline cristobalite is difficult to be dissolved during the conversion process to silicate materials.

This study developed a process to produce white color silica from rice husk using a citric acid treatment before burning of the rice husk. The obtained white silica was then converted into ZSM-5. The objective of the study was to develop a method to obtain high purity silica and to convert it into an inexpensive but valuable material, ZSM-5.

METHODOLOGY

Fabrication of high purity silica

The rice husk was collected from rice harvesting in the autumn of 2010 from north east Matsuyama city, Ehime Prefecture, Japan. Into a series of 5.0 g of the rice husk was added 150 mL of a 4.0% citric acid aqueous solution, then the mixture was placed on a hot plate stirrer, and stirred at 50 ºC for 3 h. Thereafter, the husk was washed by de-ionized water then dried at 40 ºC. The TG-DTA (Thermo Gravimetry-Differential Thermal Analysis) measurement was done using the dried rice husk and the original rice husk (RIGAKU Thermo plus TG 8200). The dried husk was then heated at various temperatures, ranging from 700 ºC to 1000 ºC, in ambient air in a muffle furnace (Yamato FM 37). As a comparison, the untreated rice husk was combusted at the same temperatures.

The combustion products were rice husk ash, hereafter denoted as RHA for the untreated ash and CA-

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RHA for the acid-treated ash. X-ray diffraction (XRD) patterns of the RHA and CA-RHA were recorded using a Rigaku ULTIMA IV X-ray diffractometer with a Cu-K-alpha radiation (scanning rate = 2 o/min at 40 kV and 20 mA). The chemical composition was analyzed by X-ray fluorescence (XRF, Model RIX 2100, Rigaku Co.).

Conversion of ZSM-5 from rice husk ash

The RHA and CA-RHA (700 °C combusted products) were used for the ZSM-5 synthesis. The ratio of the starting material for the synthesis of ZSM-5 was SiO_2: 0.14NaOH: 0.12TPABr: 52.12H2O. The RHA and CA-RHA were utilized as the SiO2 (silica) source. Five grams of each ash was mixed with 2.66 g of tetra propyl ammonium bromide (TPABr) and 75 mL of a 0.15 M NaOH solution. The TPABr and NaOH reagents were purchased from Nacalay Tesque, Japan. The mixtures were stirred with a magnetic stirrer for 30 minutes. The mixtures were then transferred to a stainless steel autoclave, and heated at 180 °C for 14 h. A similar experiment involving the synthesis of ZSM-5 was also carried out at various temperatures and times. In this study, only one procedure was reported as a representative example. The heated products were washed several times with de-ionized water, then dried at 40 °C for 24 h. Some products were calcined at 500 ^{0}C for 2 h to remove the template (TPABr). The products were then characterized by XRD and SEM using an electron microscopy (HITACHI High Technology S-800).

RESULTS AND DISCUSSION

Fabrication of high purity silica

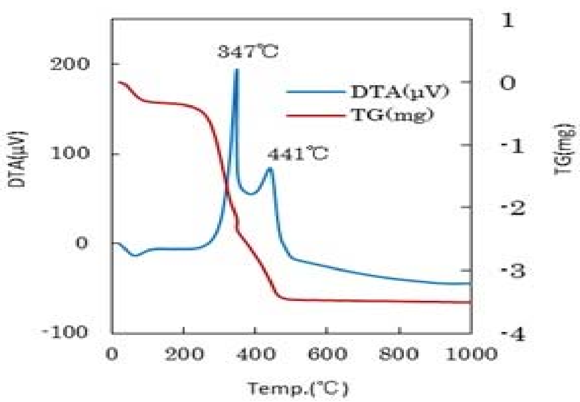

Figure-1. TG-DTA curve of the original rice husk.

Figure-1 and Figure-2 show the TG-DTA curves of the rice husk and the acid treated rice husk. Small endothermic peaks appeared at 70 °C due to water adsorbed on rice husks. Two sharp exothermic peaks appeared at 347 °C and 441 °C for the original rice husk. These peaks were ascribed to the combustion of carbon compounds. The difference in the exothermic temperature indicates the presence of carbon compounds with different combustion temperatures. For the acid treated rice husk, a strong exothermic peak appeared at 374 °C and a flat peak at around 478 °C. The flat peak indicates fewer carbon compounds as compared to that of the original rice husk.

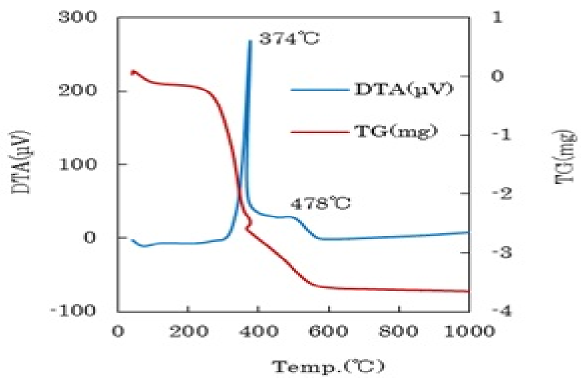

Figure-2. TG-DTA curve of the citric acid treated rice husk.

Figure-3. The photographs of CA-RHA (left) and RHA (right).

Figure-3 shows a photograph of the RHA and CA-RHA. It is clear that the CA-RHA is white, and the RHA is grey. The grey color is caused by unburned carbon compounds, ascribed to the exothermic peak at higher temperature. As shown in Figure-1, that peak (441 ^{0}C) for the rice husk is strong than that for the acid treated rice husk.

Table-1. Chemical composition of the RHA and the CA-RHA obtained at 700 oC.

% (weight)	SiO_2	K_2O	Al_2O_3	CaO	P_2O_5	Fe_2O_3
RHA	90.6	4.64	0.27	1.16	0.08	0.61
CA-RHA	99.4	0.09	UD*	0.25	0.23	0.07

UD* : undetectable

Table-1 shows the chemical compositions of RHA and CA-RHAs from the 700 °C combustion product. It is noted that CA-RHA has higher silica and lower potassium and calcium contents than those of the CA-RHA. This indicates that the citric acid treatment dissolved potassium and calcium from the rice husk.

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Figure-4 and Figure-5 show the XRD patterns of RHAs and the CA-RHAs. After heating at 700 °C, the both RHA and CA-RHA are amorphous. However at 800 °C or higher, the crystalline phase, cristobalite (SiO_2) and tridymite (SiO_2) were formed. However, for CA-RHAs, the XRD patterns exhibited an amorphous phase, even for a high combustion temperature (1000 °C). The formation of the cristobalite and trymidite is due to the presence of potassium and other alkali cations as reported by a previous study [14]. It seemed that the acid treatment dissolved some of the carbon compounds, then released potassium and other alkali cations from the rice husk, and as a result, the silica content increased (Table-1), and the amorphous white ash was obtained without incorporation of the crystalline phases, cristobalite and tridymite. As already mentioned, in the TG-DTA curve (Figure-2) the flat shape of the exothermic peak at 470 °C signified the decreased content of carbon compound due to the acid treatment.

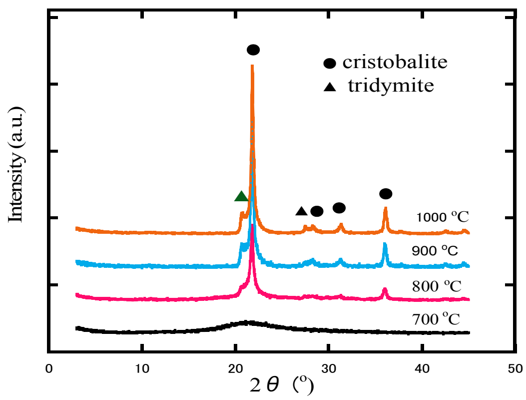

Figure-4. XRD patterns of the RHAs, the product of rice husk combustion at various temperatures.

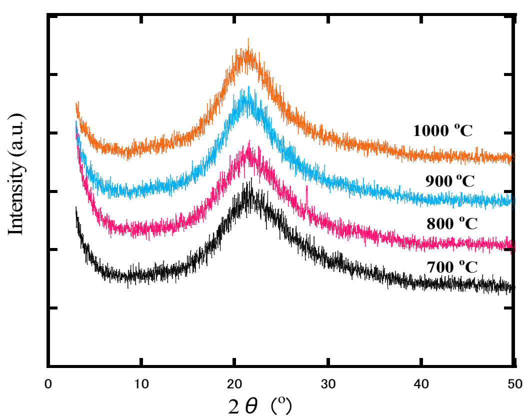

Figure-5. XRD patterns of CA-RHAs, the product of the acid treated rice husk combustion at various temperatures

The white amorphous high silica materials obtained in this study are favorable in industry, because the white color indicates a high purity, these materials are easy to be converted into other materials such as zeolites.

Conversion of ZSM-5 from rice husk ash

Figure-6 shows XRD patterns of the synthesized products from the RHA and the CA-RHA obtained by heating at 700 °C. According to the Zeolite Database [15] the diffraction peaks are those of ZSM-5, indicating that the ZSM-5 was successfully synthesized from the CA-RHA and the RHA. The ZSM-5 synthesized from the CA-RHA exhibited higher peak intensities, suggesting the high crystallization.

Figure-7 shows XRD patterns of the synthesized ZSM-5 after calcination. The intensities of the diffraction peaks at 2θ of 7.68° and 7.94° significantly increased as compared to the un-calcined sample due to the removal of the organic template (TPABr).

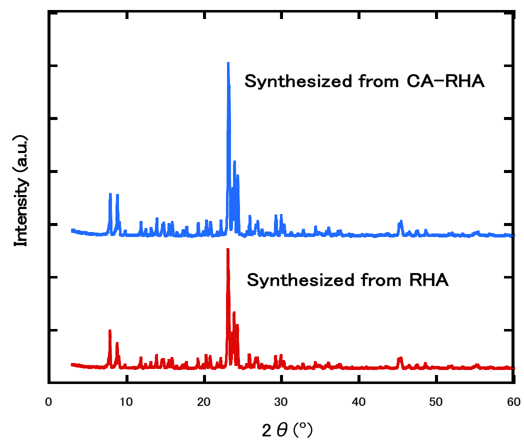

Figure-6. XRD patterns of the synthesized products from RHA (upper) and CA-RHA (bottom) (700 °C).

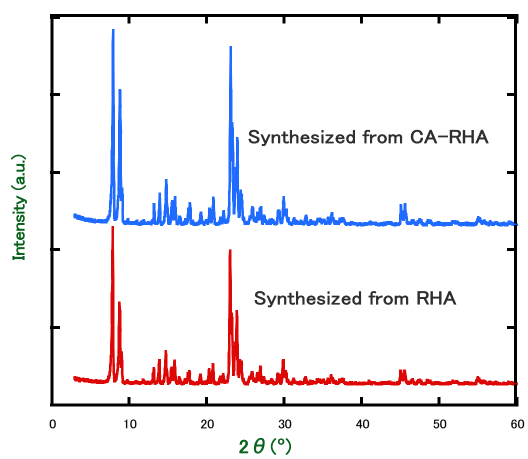

Figure-7. XRD patterns of calcined ZSM-5; synthesized from RHA (upper), and from CA-RHA (bottom) (700 °C).

Figure-8 shows SEM images of the ZSM-5 samples. Figures-8a and 8b are the SEM image of the

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ZSM-5 synthesized from the RHA, and Figures 8c and 8d are that synthesized from the CA-RHA. Generally, cubic crystals are noted in all cases, but impure material appeared in the figures-8a and 8b. Figure-8c image shows a uniform morphology without impurities, indicating that the sample is well crystalized, as supported by the XRD data (Figure-6 and Figure-7).

Furthermore, the morphology of both samples was slightly different from each other. The ZSM-5 synthesized from the RHA shows a cubic form, about 12 μm in size, while that synthesized from the CA-RHA has a rectangular form with the smaller size of 5.71 μm x 3.42 μm. These differences are ascribed to the presence or absence of aluminum (Table-1). A similar trend also occurred in case of synthesis of ZSM-11, in which the morphology of ZSM-11 turned from a long ellipse to a spherical [16].

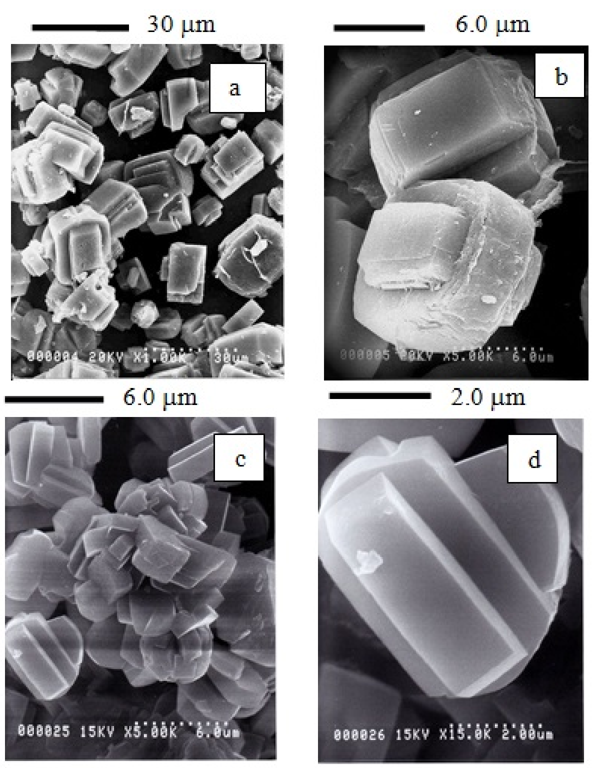

Figure-8. SEM images of the ZSM-5 samples; a and b are the ZSM-5 synthesized from RHA; c and d are that of synthesized from the CA-RHA (700 ^{o}C).

CONCLUSIONS

A White-colored rice husk ash with a silica content of more than 99% was successfully produced from a rice husk by a citric acid treatment before combustion of the rice husk. The obtained RHA was amorphous even when heated at 1000 ºC. The RHA was successfully converted into a valuable material, ZSM-5, with high crystallinity. Finally we concluded that a rice husk, known as waste, is a potential resource for the synthesis of valuable silicon materials for use in industry.

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