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Process Optimization to Prepare High-purity Amorphous Silica from Rice Husks via Citric Acid Leaching Treatment†

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Abstract

Rice husks or straws, one of the main agricultural wastes in South-east Asia, have a large possibility to be employed as usefully renewable resources to produce energy and high-purity silica (SiO_2), because they consist of about 70% organics such as cellulose or hemi-cellulose, and 20% amorphous SiO_2. The former is utilized as bio-mass energy; for example, thermal or electric energy, and bio-mass ethanol. High-purity silica can be used as raw materials in industrial application. It would be possible to extract silica elements from rice husks and straws by burning them in air because their main contents are organics. In the previous studies, a strong acid leaching treatment on rice husks before burning was carried out by using H_2SO_4, HCl and HNO_3 to prepare high-purity silica materials. This was available to accelerate the hydrolysis of celluloses and hemicelluloses contained in rice husks, and remove the above metallic impurities. A strong acid leaching treatment, however, is significantly hazardous to environment and human life, and causes an increase of the process cost. In this study, an environmentally benign, harmless to human and economically effective process to produce high-purity amorphous SiO_2 materials from rice husks has been established without using strong acids. From a viewpoint of being a harmless influence on the human body, carboxylic acids were used in the leaching treatment on rice husks. TG-DTA measurement and GCMS analysis indicated that the leaching was effective for the hydrolysis of celluloses and hemicelluloses contained in rice husks at 473K~873K, and produced the same results as using the conventional sulfuric acid. The metallic impurities could be also removed from the husks via a chelate reaction between carboxyl groups (-COOH) and the metal elements. In particular, it was clarified that cadmium (Cd) as completely removed from rice straws by this reaction. Concerning the burning conditions of rice husks after the acid leaching, it was necessary to supply a suitable amount of air to completely combust organics; for example it required an air supplement of 50 ml/min. or more. The burning temperature should be less than 1273K to obtain amorphous structured silica. High-purity amorphous silica materials with 99% or more purity were prepared from rice husks by applying the citric acid leaching treatment and burning process at 1073K in air.

KEY WORDS: (High-Purity Silica) (Amorphous) (Rice Husks) (Citric Acid Leaching) (Chelate) (DTA) (GCMS)

1. Introduction

Rice husks and straws are agricultural wastes produced in a large amount, and their annual world production amounts to about 80 million tons [1]. The major constituents of rice husks are ashes and organics such as cellulose, hemi-cellulose and lignin. The former mainly consists of silica and some metal impurities. The silicon (Si) atoms exist in the protuberances and hairs on the outer and inner epidermis of the rice husks [2]. Extensive researches have been carried out to extract SiO_2 elements from rice husks [3-5], because high-purity silica is a useful raw material for industrial application. In the previous studies, the strong acid leaching treatment was carried out on rice husks to remove metallic impurities and organics contained in them. Sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) solutions are conventionally used in leaching [6,7]. They are, however, significantly hazardous to the environment and humans. The strong acid leaching treatment also has an economical problem due to a necessary use of expensive materials with corrosion resistance to strong acids, water rinsing of husks, and a special disposal treatment of used strong acids. In this study, an environmentally benign, harmless to humans and economical process to produce high-purity amorphous SiO_2 from rice husks has been established by using the carboxylic acid leaching treatment. TG-DTA (Thermogravimetry-Differential

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Thermal Analysis) measurement and GCMS (Gas Chromatograph Mass Spectrometer) analysis were used to clarify the effect of the hydrolysis of the organic contents and its mechanism. The effect of air supplements in burning acid-leached husks was investigated to purify the silica element of ashes. XRD analysis was carried out on rice husk ashes to optimize the burning temperature and prepare amorphous structured silica. For the evaluation of the carboxyl group (-COOH) of organic acids in removing metallic impurities via a chelate reaction, the citric acid leaching treatment was applied to rice straws containing cadmium (Cd), and the reduction effect was discussed.

2. Experimental Procedure

The raw materials of rice husks harvested in Niigata, Japan are employed, and submitted to the carboxylic acid leaching treatment using citric acid ($C_6H_8O_7$). Sulfuric acid solution is also used as the comparison in the leaching treatment. 20g husks are sunk in the acid solution of 500ml for 15min. Each concentration is 5%, and temperature is controlled at 50 C. The waster rinsing treatment on acid-leached husks was carried out to remove the acid solution from rice husks. The repetition number of the water rinsing after the leaching by citric acid and sulfuric acid is three time and eight times, respectively. The water-rinsed materials are dried at 100 C for 3.6s in the electric furnace. As mentioned above, the main content of rice husks is cellulose and hemicellulose. First of all, the thermal resolution temperature of the cellulose powder, having a mean particle size of 58μm, was measured by TG-DTA equipment (Shimadzu DTG-60). In the case of rice husks, the same analysis was applied to evaluate the thermal resolution behavior. In particular, from the viewpoint of the hydrolysis of some organics in husks, its reactivity can be discussed quantitatively by the comparison of the exothermic heat in the TG-DTA profile. This indicates that when the cellulose and hemicellulose have atomic structure changes from the polysaccharide to monosaccharide via a hydrolysis, the exothermic heat was reduced. The optimization of the air supplement in the burning process of rice husks was also evaluated by the exothermic heat of the TG-DTA profiles. It was controlled from 0 to 150 ml/min., and argon (Ar) gas is used as the comparison in this analysis. It was measured from 20C to 1000C with heating ratio of 10C/min. To investigate the atomic structure changes of cellulose and hemicellulose by the acid leaching, GCMS analysis (Agilent 5973N) was applied to the specimens after heating at 200C for 360s, 400C for 60s and 600C for 6s. The hydrolysis behavior of the organics contained in the acid-leached husks at each sampling temperature can be also examined by the identification of the mass spectra and their intensities. The burning process of dried husks was conducted at 600~1150C in air to remove the organics from rice husks. The dependence of the crystallization of the silica elements on the burning temperature was examined by X-ray Diffraction (XRD) analysis (Shimadzu XRD-6100). The content of SiO_2, carbon and other metal impurities included in the rice husk ashes were investigated by XRF (X-ray fluorescence) and ICP (Inductively Coupled Plasma) analysis.

3. Results and Discussion

3.1 Hydrolysis of organics by citric acid leaching

Rice husks and straws are comprised of cellulose, hemicellulose and lignin. The previous work indicated that hemicellulose and lignin are rapidly digested by a short time acid leaching treatment while cellulose is only partially digested [8]. This means a high degree of resistance of the residual cellulose in the husks towards the acid digestion. Therefore, in this study, the hydrolysis of cellulose of rice husks by citric acid leaching treatment is discussed in detail. **Figure 1** shows two DTA profiles of the conventional cellulose powders under the air and Ar gas flow condition with a flow ratio of both is 150 ml/min. In the air supplement, the profile indicates two exothermic heats with the maximum peak temperature at 355C and 505C by the complete combustion, which corresponds well to the previous results [8]. At the same time, the drastic weight loss occurs due to their thermal degradation. On the other hand, when using Ar gas atmosphere, it reveals an endothermic heat at the peak temperature of 345C due to its carbonization without combustion. **Figure 2** reveals DTA profiles of rice husks with the citric acid (a), sulfuric acid (b) leaching, and no treatment (c). The initial temperature of the first exothermic heat due to the thermal degradation of organics in all materials is about 200~220C, and lower than that of the cellulose (270C) shown in Fig.1 (a). This may be attributed to the content of hemicellulose and lignin elements in rice husks, that have significant influences on the initial temperature of the thermal degradation. They show two exothermic heat peaks, which have the same maximum points at 335~350C and 450~470C, respectively. In comparing the heat values, the difference between (a) and (b) is very little, but (c) has a significantly small heat compared to another.

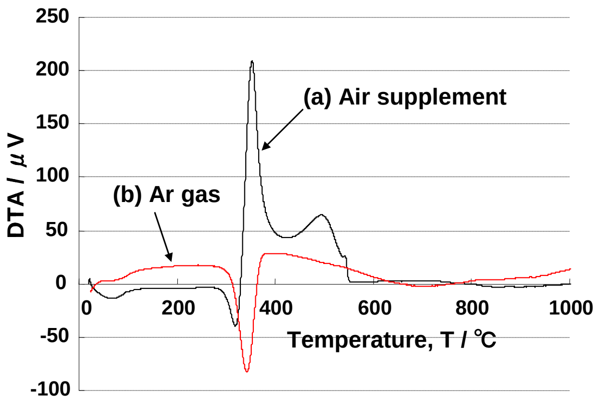

Fig.1 DTA profiles of cellulose measured in air (a) and argon gas atmosphere (b).

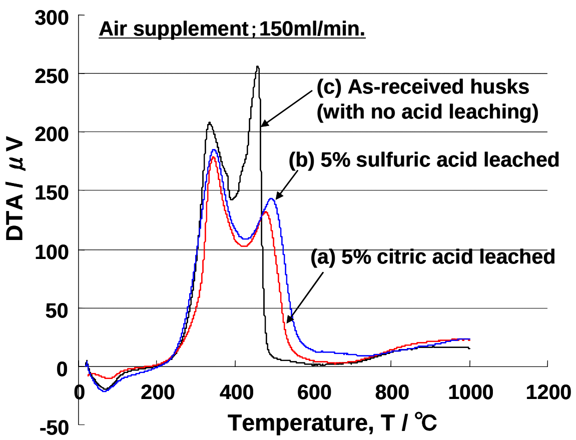

Fig.2 DTA profile of rice husks with citric acid (a) and sulfuric acid leaching (b) compared to as-received raw materials (c).

The measurement of the total exothermic heat of each specimen is shown in **Table 1**. The reduction of the exothermic heat in using acid-leached rice husks is about 17~28% against that of raw materials without any leaching treatment. The color of every specimen after TG-DTA analysis is completely white, that is, the ashes are high-purity silica materials. These results mean that the acid leaching treatment has the possibility of accelerating the hydrolysis of organics contained in rice husks. For the investigation of this reaction behavior, GCMS analysis was carried out on each specimen. The heating conditions before the analysis were 200C for 360s, 400C for 60s and 600C for 6s in air. **Figure 3** shows GCMS results of rice husks after hot water rinsing at 50C (a), and 5% citric acid leaching at 50C (b) when using a heating condition of 200C for 360s. Spectra ①, ② and ③ correspond to furfurals (C_4H_3O), and levoglucosan, respectively. In both specimens, the spectrum ③ is very small, and no formation of levoglucosan is detected by heating each material at 200C for 360s. **Table 2** indicates the ion intensity of peak ① and ② of each rice husks. The maximum intensity of both peaks in using the citric acid leached materials is about 4~10 times those of hot water rinsed specimens. In general, hemicelluloses, composing the cell wall, change to D-xylose ($C_5H_{10}O_5$) via a hydrolysis, and it forms furfurals by a dehydration reaction. In the TG-DTA profile of as-received raw rice husks, no weight reduction and no heat was detected until 200C.

Table 1 Comparison of exothermic heat values of DTA profiles of each rice husks.

	Citric acid leached	Sulfuric acid leached	As-received (raw material)
Ave.	**28.1**	**32.4**	**38.8**
N=1	**27.3**	**31.4**	**39.5**
N=2	**28.9**	**33.3**	**38.0**

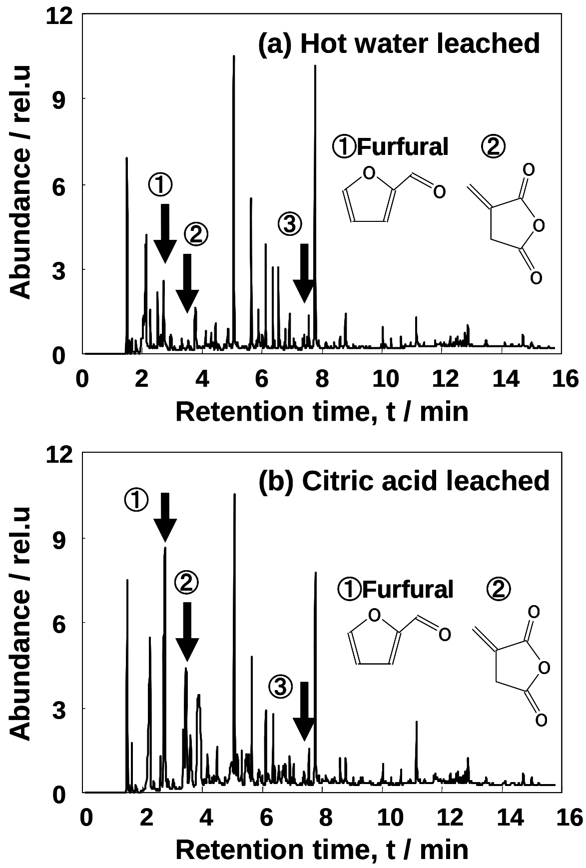

Fig.3 GCMS results of rice husks via citric acid leaching and hot water rinsing (200C for 360s).

Table 2 Ion intensity of GCMS analysis on rice husks via citric acid and hot water leaching.

	Intensity of total ion	Max. intensity of peak①	Max. intensity of peak②
Hot water	**1.35*10⁹**	**2.35*10⁶**	**3.82*10⁵**
Citric acid N=1	**2.16*10⁹**	**8.51*10⁶**	**4.22*10⁶**
N=2	**2.15*10⁹**	**8.22*10⁶**	**4.06*10⁶**

This means no effect of the heat treatment less than 200C on the above hydrolysis of organics in rice husks. Accordingly, the citric acid leaching treatment of husks is effective in accelerating the atomic structure change of their hemicellulose to furfural via the hydrolysis and dehydration. **Figure 4** indicates GCMS results of hot water rinsed (a), and acid-leached materials (b) and (c) after heating 400C for 60s. In all the specimens, the peaks ① and ② are detected, and the difference of their ion intensities is very small. That is, the above hydrolysis to produce furfurals is carried out when heating rice husks at 400C. Concerning the peak ③, corresponding to the formation of levoglucosan, (a) shows an extremely small peak intensity, and very few products of levoglucosan. On the other hand, the peak is clearly detected in the specimen (b) and (c). The ion intensity, however, is not so different between these two values. This means that the citric acid leaching is also effective for the hydrolysis of the cellulose contained in husks to produce levoglucosan, and its effect is almost same as that via the sulfuric acid leaching. **Figure 5** shows DTA profiles of 5% citric acid-leached rice husks when changing the air supplement in the analysis. In the case of 50 ml/min. or more, there is no change of the profile with the typical two exothermic heats as mentioned above. When reducing the air supplement to 20 ml/min., the exothermic heat value is reduced. Finally, the profile reveals the endothermic heat at 350C with no air supplement in the analysis, and the color of the burned specimen remaining in the alumina cup is black. The others indicated pure white ashes. This result suggests that a suitable air supplement with 50 ml/min. or more is necessary to completely combust the organics of rice husks, and insufficient air in burning causes the carbonization of organics at 300~400C.

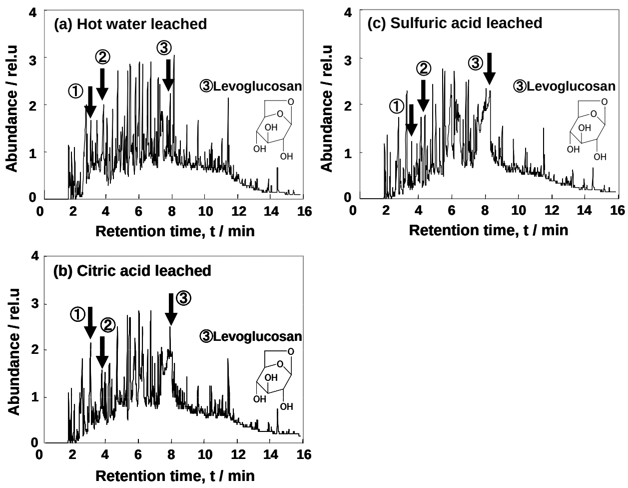

Fig.4 GCMS results of rice husks via citric acid leaching and hot water rinsing (400C for 60s).

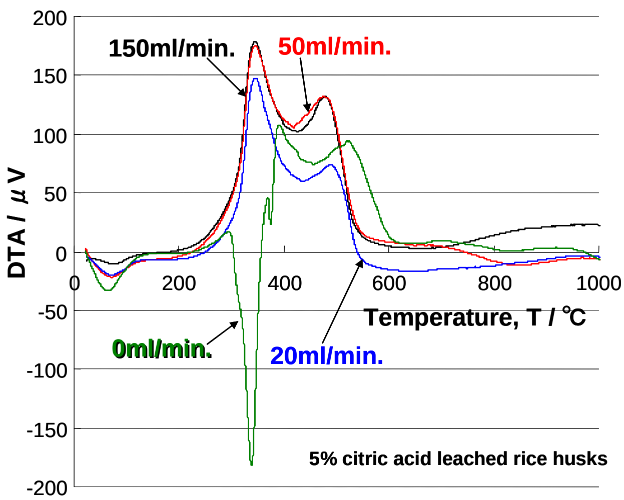

Fig.5 DTA profiles of citric acid leached rice husks measured under various air supplement flow rate.

3.2 Reduction of metallic impurities by chelate reaction of carboxyl groups

In general, rice husks and straws contain the metallic impurities of about 0.8~1% such as Potassium (K), Calcium (Ca), Sodium (Na), Phosphorus (P), Aluminum (Al), etc. According to the soil contents, some hazardous metal elements may be included in them. It is reported that alkali metal impurities of K and Na cause the remained carbons in ashes, which are originated in organics of husks. This is because the eutectic reaction between the alkali metals and SiO_2 element occurs in burning, and the carbon remains in the melt SiO_2 [9, 10]. It is well known the chelate reaction of carboxyl groups (-COOH) with metal elements easily occurs, and their metal complexes are formed [11]. In this study, the effect of the citric acid with carboxyl groups on the removal of metal impurities contained in rice husks and straws was investigated. Three kinds of rice straws, which included Cadmium (Cd) contents of 0, 23ppm and 82ppm, were prepared as raw materials. They were also submitted to the citric acid leaching treatment at 50C for 900s. The concentration of the acid solution was 5% and 20%. Cd contents of acid leached straws and used solutions measured by ICP optical emission spectrometer (HORIBA, ULTIMA-2) are shown in **Table 3**. With increasing the Cd content of raw straws that of used citric acid solution after leaching gradually increases. The color of the solutions changes to dark orange due to the eluted Cd complexes. After the leaching treatment, the Cd content of each straw is less than 0.001ppm, which is the lowest limitation by ICP analysis when using 5% and 20% concentration. That is, the citric acid leaching is significantly effective in removing Cd elements via a chelate reaction from rice straws. By using the chelate of carboxyl groups of organic acids, the metallic impurities of rice husks are reduced. For example, the leaching treatment by 5% citric acid and 5% oxalic acid solutions is carried out at 50C on rice husks. After water rinsing and drying in air, the acid leached materials are burned in air at 800C for 3.6 ks. The air supplement is 150 ml/min. Raw rice husks without any leaching treatment were also used to prepare their ashes as a comparison. **Table 4** indicates chemical compositions of rice husk ashes via each leaching process. When using no acid leaching treatment, a lot of metallic oxides remain in the ashes as impurities. In particular, it is difficult to reduce K_2O and

Table 3 Cd contents of raw materials, used citric acid solutions and rice straw ashes by ICP analysis.

		Material A	Material B	Material C
Raw materials		~0	23	82
Used citric acid solution	5%	~0	0.085	0.383
	20%	~0	0.087	0.411
Rice straw ashes	5%	~0	~0	~0
	20%	~0	~0	~0

Table 4 Chemical compositions of rice husk ashes burned at 800C via carboxylic acid leaching and without any treatment.

	SiO_2	Al_2O_3	MgO	Na_2O	P_2O_5	S	K_2O	CaO	Mn	Fe_2O_3	BaO	Carbon
Without leaching	94.58	0.02	0.31	0.11	0.41	0.11	3.69	0.56	0.08	0.04	0.04	0.61
Citric acid leaching	99.14	0.03	0.08	0.06	0.29	0.03	0.12	0.16	0.01	0.03	0.03	0.09
Sulfuric acid leaching	90.99	0.01	0.06	0.07	0.31	0.05	0.11	0.37	0.01	0.02	0.03	0.12

CaO, which cause the remaining carbon after burning as mentioned above, from rice husk ashes. As a result, the SiO_2 content of ashes is 94.6%, and their color is black and dark gray. On the other hand, both citric and oxalic acid leaching treatments are significantly better at removing these impurities and remaining carbon. The white ashes have a high-purity of silica with 99% or more.

3.3 Combustion temperature of rice husks

It is important to prepare high-purity SiO_2 ashes with amorphous structures from rice husks, because IARC (International Agency for Research on Cancer), one part of WHO (World Health Organization), strongly points that the crystal SiO_2 particles have carcinogenic risks to humans [12], and belong to Group 1. The structure of rice husk ash strongly depends on the burning temperature. **Figure 6** shows XRD profiles of the ashes of citric acid leached rice husks after burned at various temperatures in air. It indicates that the changes from originally amorphous structures to crystal ones occur by burning the husks at 1323K or more. The rice husk ashes include crystallized silica materials with trydymite and cristobalite structures [13].

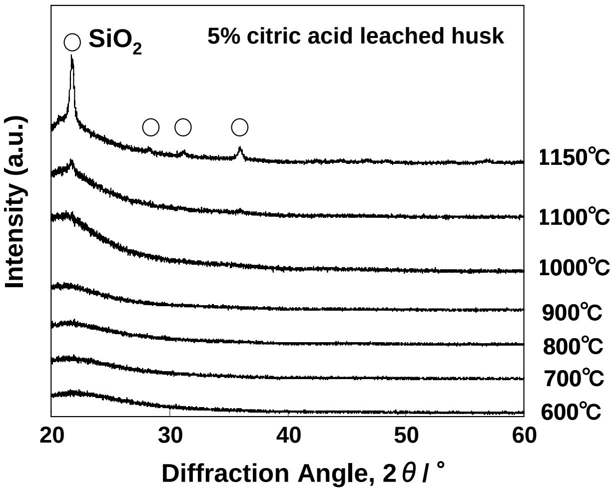

Fig.6 XRD profiles of rice husk ashes of citric acid leached rice husks after burned at various temperatures in air.

4. Conclusion

The recycling process of rice husks with a high safety and economical benefits was developed to produce high purity amorphous silica materials. It consists of a citric acid leaching and an air-combustion process. The acid leaching treatment is effective in accelerating the hydrolysis of cellulose of rice husks and reducing metallic impurities by the chelate action of the carboxyl groups. A suitable air supplement from 200 to 600C is important to completely combust the organics of husks. The optimized burning temperature of acid leached rice husks is less than 1073K to prepare amorphous silica materials.

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