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Polysaccharide Hydrolysis and Metallic Impurities Removal Behavior of Rice Husks in Citric Acid Leaching Treatment[†]

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Abstract

   Rice husk is one of the representative non-eatable biomasses, and contains 70~75 mass% organics such as cellulose and hemi-cellulose and 15~20 mass% silica (SiO_2) elements. From a viewpoint of the wide use of the biomass energy, its cost reduction is strongly required by selecting suitable raw materials as biomass fuels and optimizing the operating conditions. In the present study, rice husk was selected as input raw fuel materials because after extracting the above organics as the biomass energy from rice husks, their residues consisting of high-purity amorphous silica would be an industrial resource with added value, and resulted in the total cost reduction of the biomass energy. For high-purification of silica materials originating in rice husk residues, the citric acid leaching treatment and the following water rinsing process of rice husks were used to remove metallic impurities such as Na, K, Ca, Mg, Fe, Cu, etc. In this study, the optimization of the operating parameters such as the concentration and temperature of citric acid solution, the stirring time in the acid leaching and water rinsing treatment, and combustion temperature were examined out for the removal of metallic impurities and the hydrolysis reaction of the polysaccharides. XRF and ICP analysis were used to quantitatively evaluate the residual content of impurities and carbon elements. GC-MS and FT-IR analysis of rice husks after leaching were conducted to examine their hydrolysis behavior.

KEY WORDS: (rice husk) (silica) (hydrolysis) (polysaccharide) (monosaccharide) (metallic impurity)

1. Introduction

   Rice husks and straws are representative agricultural wastes, and have an annual yield of about 127 million tons in the world in 2008 [1]. At this moment, most of them are of no practical use, and cause environmental problems. For example, the combustion of 1 ton of rice husks in the field causes about 0.15 kg CO_2 gas emission. Furthermore, they release 0.09kg methane (CH_4) gas when left and decomposed on the ground [2]. From a viewpoint of the reuse of rice husks and straws as fuel resources, It is reported that they contain about 65~75 mass% polysaccharide organics such as cellulose and hemi-cellulose [3], which are suitable resources for energy generation [4, 5]. That is, rice husks and straws could be used as bio-mass materials. Furthermore, one of their features is a large content of amorphous silica (about 12~20 mass%) [3, 6], and suggests a possibility to reuse such silica originated in rice husks as raw materials, for example fertilizer, reinforcement of concretes, and ceramics materials [7~9]. Many previous studies have developed some processes to prepare silica materials by combusting rice husks [10~13]. From a purification of silica originated in rice husks, a strong acid solution washing process was used to remove the alkali metal impurities (Na and K) from the husks [14~16], because they have a eutectic reaction with SiO_2, causing a drastic decrease of its melting point from 1986K to 1062K [17, 18]. As a result, a large amount of carbon remained in the rice husk ashes, and the silica purity was 96~98% or less. The authors have also established an environmentally benign process to produce rice husk silica with completely amorphous structures and high-purity of 99% and over by using citric acid solution leaching treatment before combustion [19, 20]. In the present study, from a view point of high purification of amorphous silica, the optimization of the process parameters in the acid leaching treatment and combustion of rice husks was examined. In particular, the effect of the citric acid concentration on the hydrolysis behavior of organics was investigated by using GC-MS analysis, and the removal mechanism of metallic impurities was also discussed.

2. Experimental

   Input raw materials are rice husks harvested in Niigata to produce high-purity amorphous silica materials. The previous study clarifies that the citric acid solution leaching treatment and air combustion of rice husks are

useful for the removal of the metallic impurities, in particular alkali metal elements, contained in rice husks [19, 20]. 30g of rice husks were put into 500ml citric acid solution in a Griffin beaker. In the present study, the concentration and temperature of the citric acid solution, and stirring time in the solution were selected as the operating parameters. This is because the chelate reaction [21] between carboxyl groups (-COOH) and metallic impurities contained in husks strongly depends on the above parameters. The hydrolysis of polysaccharides such as cellulose and hemi-cellulose is also dependent on them. The concentration was controlled from 1% to 7% by changing the mixing ratio of citric acid powders (Kishida Chemical Co., purity; 99.5%) and distilled water. The beaker was placed on the stirrer (AS ONE, hot stirrer, HS-5BHSD), and the solution temperature was kept at 298K ~ 353K. The rotating speed of the magnetic stirrer bar in the solution was controlled at 960 rpm, and the stirring time was 900 s~7.2 ks. After the acid leaching process, the water rinsing treatment of the rice husks was carried out in distilled water at 293K for 900s to remove the citric acids from the husks. The stirrer was also used in the water rinsing, and the magnetic bar was rotated under 960 rpm speed. The materials were dried at 373K for 3.6 ks in the muffle furnace in air atmosphere, and then burned at 1073K for 1.8 ks in the same furnace, where the air flow rate was controlled at 0.42 ml/s by using a small air-compressor. The burning temperature of 1073K was applied in this study to prevent the crystallization of amorphous silica contained in the husks [16]. The content of each metallic oxide of rice husk ashes was measured by X-Ray Fluorescence Spectroscopy
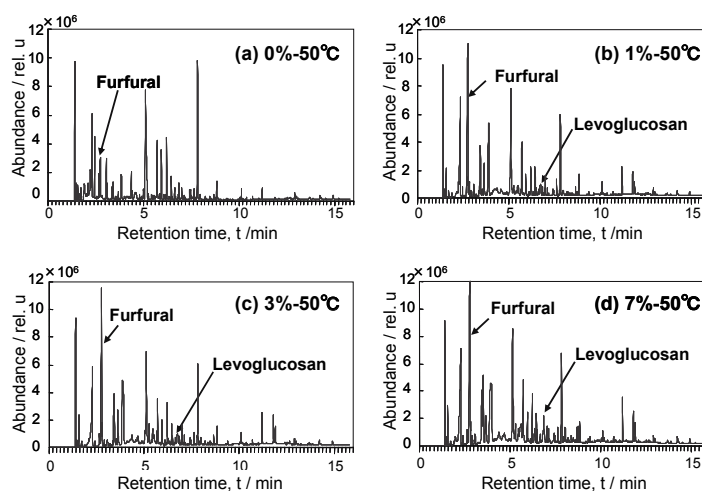
(XRF, PANalytical, X-ray spectrometer PW2400), and carbon analyzer (HORIBA, EMIA-902V) was employed to measure the carbon content of the ashes. Fourier Transform-Infrared Spectrometer (FT-IR, Nicolet, MagnaIR-560 with Dura-ATR, Sens-IR) analysis was applied to the ashes to investigate the structures remaining from the organic elements and silica materials. In order to quantitatively evaluate the hydrolysis behavior of the polysaccharides of rice husks by the citric acid leaching treatment, Gas Chromatograph Mass Spectrometer (GC-MS, Agilent Technologies, Agilent-5973N) was applied to the acid-leached specimens after air drying at 373K. The heat treatment was carried out at 473 K for 360 s before GC-MS analysis [20]. The hydrolysis behavior of the organics could be investigated by comparing the identification of the mass spectra and their intensities, and the effect of the citric acid concentration on the polysaccharide hydrolysis was discussed.

3. Results

Table 1 shows the chemical compositions of rice husk ashes via the citric acid solution leaching treatment with different concentrations. The solution temperature of 323K and stirring time of 3.6 ks were used in the above leaching process. 0% indicates the use of hot distilled water rinsing at 323K instead of the citric acid solution. As shown in Table 1, when employing the citric acid solution with a concentration of 1% and over, the silica (SiO_2) purity of each ash is approximately 99.5% or more. It means the purification of this silica material obviously progresses compared to that with a purity of 97.25% via the hot distilled water leached treatment. Concerning the content of alkali metal elements (Na and K) remained in the ashes, the use of the citric acid solution is remarkably effective to reduce them. In particular, Na_2O has been completely removed from the rice husks by using the

Table 1 Quantitative analysis of silica (SiO_2) and impurities contents included in rice husk ashes by employing citric acid leaching with various concentrations (leaching temperature; 323K, soaking time; 3.6ks, water rinsing time; 900s, air-burning conditions; 1073K×1.8ks).

(mass%)	Concentration of citric acid solution				
	0%	1%	3%	5%	7%
SiO_2	97.25	99.52	99.54	99.56	99.47
MgO	0.29	0.04	0.03	0.02	0.03
Na_2O	0.13	0.00	0.00	0.00	0.00
P_2O_5	0.09	0.11	0.12	0.13	0.13
S	0.03	0.02	0.02	0.02	0.01
K_2O	1.39	0.03	0.02	0.01	0.02
CaO	0.46	0.16	0.13	0.11	0.12
Cr_2O_3	0.00	0.00	0.01	0.00	0.04
MnO	0.13	0.02	0.02	0.01	0.02
Fe_2O_3	0.02	0.02	0.05	0.02	0.04
NiO	0.00	0.00	0.00	0.00	0.02
CuO	0.00	0.00	0.00	0.00	0.00
MoO_3	0.00	0.00	0.00	0.00	0.00
C	0.15	0.08	0.06	0.04	0.03

Fig. 1 GC-MS analysis results of rice husks via citric acid solution leaching treatment using various solution concentrations of 0% (a), 3% (b), 5% (c), and 7% (d) (solution temperature; 323K, pre-heating condition; 473K for 360s).
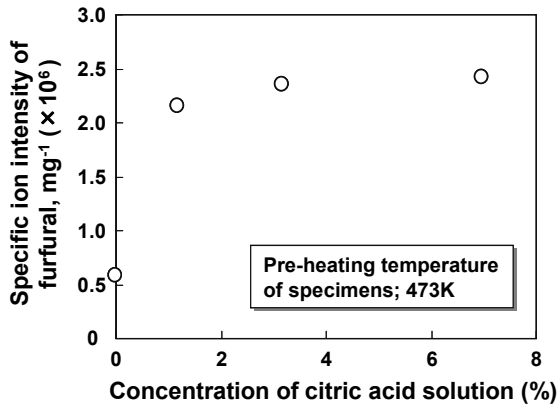
Fig. 2 Specific ion intensity of furfural spectrum in GC-MS results of rice husks via citric acid leaching treatment as a function of acid solution concentration.

Table 2 Quantitative analysis of silica (SiO_2) and impurities contents included in rice husk ashes by employing citric acid leaching with various temperatures (citric acid solution concentration; 5%, soaking time; 3.6ks, water rinsing time; 900s, air combustion conditions; 1073K $\times$ 1.8ks).

	Citric acid solution temperature				
(mass%)	298K	313K	323K	333K	353K
SiO_2	99.25	99.54	99.56	99.58	99.77
MgO	0.07	0.05	0.02	0.09	0.04
Na_2O	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.13	0.12	0.13	0.12	0.10
S	0.02	0.02	0.02	0.00	0.00
K_2O	0.08	0.02	0.01	0.02	0.00
CaO	0.27	0.14	0.11	0.08	0.03
Cr_2O_3	0.00	0.00	0.00	0.00	0.00
MnO	0.05	0.02	0.01	0.01	0.00
Fe_2O_3	0.03	0.02	0.02	0.02	0.02
NiO	0.00	0.00	0.00	0.00	0.00
CuO	0.02	0.00	0.00	0.00	0.00
MoO_3	0.00	0.04	0.00	0.00	0.00
C	0.05	0.06	0.04	0.02	0.03

citric acid solution leaching with 1% or more concentration. The content of MgO and MnO also is extremely reduced, and the reduction rate is 85~93% by comparing the remained content via citric acid solution and hot distilled water leaching treatment. It is also obvious that the citric acid solution leaching treatment is necessary for the removal of Ca elements from rice husks. However, its reduction rate of about 65~76% is smaller than those of MgO and MnO as mentioned above. **Figure 1** indicates GC-MS analysis results of air-dried rice husks via the citric acid leaching and the following water rinsing treatment. The concentration of the citric acid solution used in this analysis is 0% (a), 1% (b), 3% (c) and 7% (d). The spectrum corresponding to furfural, which is a monosaccharide formed from hemi-cellulose elements via the hydrolysis and dehydration reaction [22], is detected in the citric acid leached husks (b) ~ (d) except for the hot water leaching (a). It also reveals no obvious difference of the spectrum intensity between 1% and 7% concentration.

Figure 2 shows the dependence of the ion intensity of furfural spectrum on the concentration of the citric acid solution. When using 1% citric acid solution, the ion intensity is 2.21×10^6 (mg^{-1}), and about 4 times that in the use of the hot distilled water shown in **Fig.1 (a).** It slightly increases with increasing the concentration from 1% to 7%. These results suggest that the citric acid solution leaching treatment with 1% concentration is enough for hydrolysis of hemi-cellulose contained in rice husks to furfurals of monosaccharides. The previous study shows that the metallic impurities such as Na, K, Ca, Mg, Fe, Al and Mn are contained in the rice husk organics consisting of hemi-cellulose and cellulose [23]. When hydrolysis reaction of the polysaccharides progresses by the citric acid leaching treatment, the simple structures of monosaccharides (furfural and levoglucosan) are formed in the rice husks [22]. As a result, this reaction brings carboxyl groups into contact with the above impurities, and their metal complexes are synthesized and discharged into the solution. Therefore, as shown in Table 1, the content of each metallic

impurity oxide of the ashes are drastically reduced by the citric acid solution leaching treatment. In addition, it is obvious the reduction of alkali metals of Na and K is effective to decrease the carbon content of the ashes. This is because a decrease of their impurities prevents a eutectic reaction of SiO_2 accompanied by the drastic reduction of SiO_2 melting temperature from 1986K to 1062K, and no melting of silica of rice husks happens during combustion at 1073K. In consequence, the organics do not remain in the silica materials, and most of them are completely burned.

Table 2 shows the chemical compositions of rice husk ashes via the citric acid solution leaching treatment under different solution temperature. The solution concentration of 5% and stirring time of 3.6 ks were used. With increase in the temperature, most of the impurities are removed, and the purification of rice husk silica (SiO_2) with 99.77% takes place via the citric acid solution leaching at 353K. In the case of Na_2O, even the room temperature leaching treatment is enough to remove Na impurities from rice husks. On the other hand, CaO content of the ashes gradually decreases with increasing the solution temperature. **Figure 3 (a)** indicates the Ca content in the used citric acid solution after the leaching treatment as a function of the solution temperature. The CaO content of the ashes shown in **Fig.3 (b)** is originates from **Table 3**. The content of Ca elements discharged into the acid solution during acid leaching process gradually increases with increasing the temperature. By using these measurements, a discharged rate of Ca element from rice husks by the citric acid leaching is calculated. In this calculation, it is assumed that Ca is removed by only the acid leaching treatment, not the
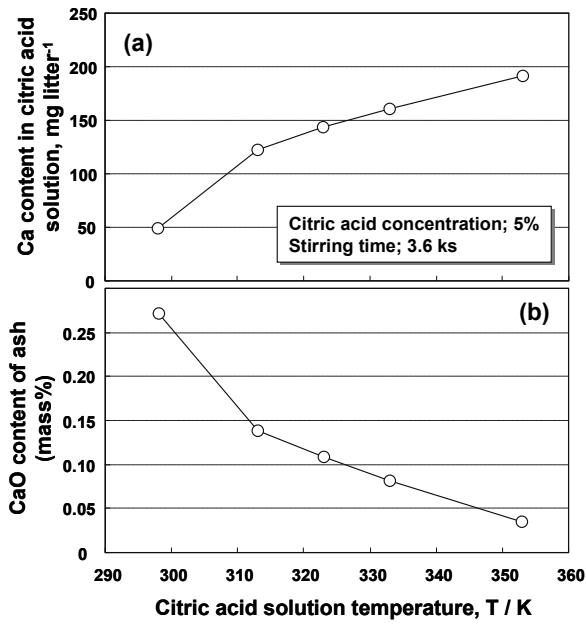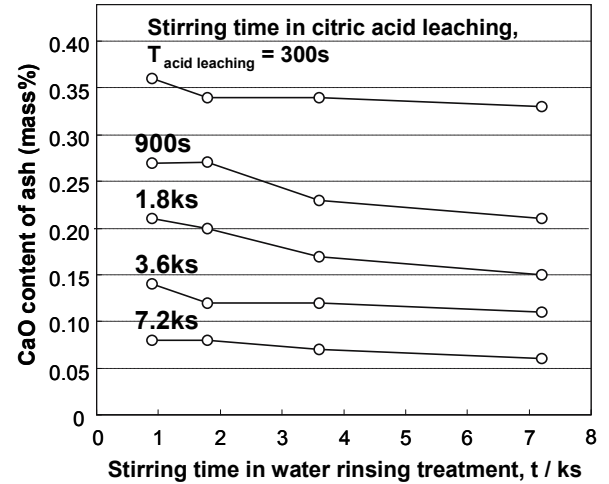
Fig. 3 Ca content in citric acid solution (a) and CaO content of ash (b) dependence on citric acid solution temperature (citric acid solution concentration; 5%, stirring time; 3.6 ks, air combustion temperature; 1073K).

Table 3 Dependence of discharged rate of Ca from rice husks into citric acid solution on solution temperature (concentration of citric acid solution; 5%, stirring time; 3.6 ks).

Temperature, T/ K	298	313	323	333	353
Discharged rate (%)	34.0	72.0	78.9	85.3	94.5

following water rinsing process. That is, the original Ca content of rice husks is the sum of the Ca content in the burned ashes and the citric acid solution. As shown in Table 3, the discharged rate of Ca element is 34% under the ambient temperature acid leaching treatment (298K). It suddenly increases to 72% when the hot acid solution of 313K is employed. Furthermore, an increase in the solution temperature remarkably increases the discharged rate of Ca elements. This means that both of the Ca complexes formated by the chelate and hydrolysis reaction of polysaccharides progress more effectively in the hot citric acid solution, and result in discharging the complexes from the monosaccharides. The effects of the stirring time during the citric acid leaching and the following water rinsing treatment on the CaO content of the rice husk ashes was evaluated. The 5% citric acid solution of 323K was used in the acid leaching process. As shown in **Fig.4**, both the above parameters are useful to reduce the CaO impurity content. In particular, the citric acid leaching time is much dominant on the reduction of Ca element. Accordingly, not only the chelate reaction between Ca elements and carboxyl groups, but also the polysaccharide hydrolysis during the acid leaching treatment dominate the purification of SiO_2 of the rice husk ashes.


Fig. 4 CaO content of rice husk ashes via citric acid leaching with various stirring time as a function of water rinsing time (citric acid solution; 5% and 323K, water rinsing at 298K, air combustion conditions; 1073K×1.8ks).
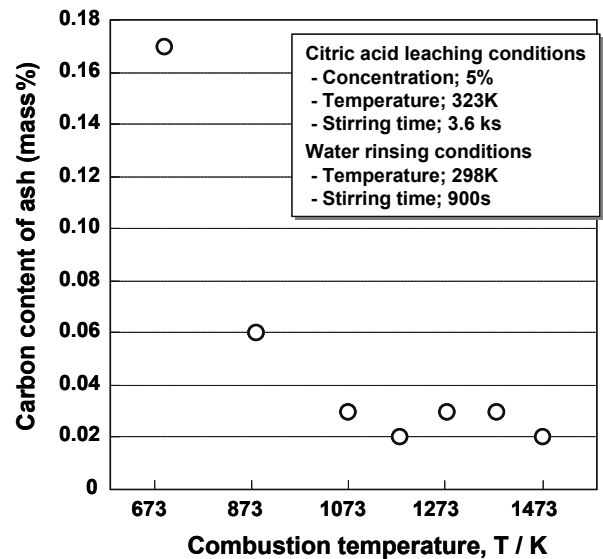
Fig. 5 Dependence of carbon content of rice husk ashes on combustion temperature (citric acid solution concentration; 5%, temperature; 323K and stirring time; 3.6 ks).

The previous studies have mentioned the effect of the combustion temperature on the crystal structure of the silica materials contained in rice husk ashes [24, 25]. In general, the temperature of 973K and over in burning rice husks causes the crystallization of SiO_2 in the ashes when raw rice husks without any leaching treatments are used as starting materials. However, in the use of those via the citric acid leaching treatment, SiO_2 crystallization temperature drastically increases from 973K to 1323K. This is because a eutectic phenomenon of SiO_2 is prevented by reducing alkali metal impurities of the starting materials as mentioned above. At the same time, the combustion temperature also affects the remaining
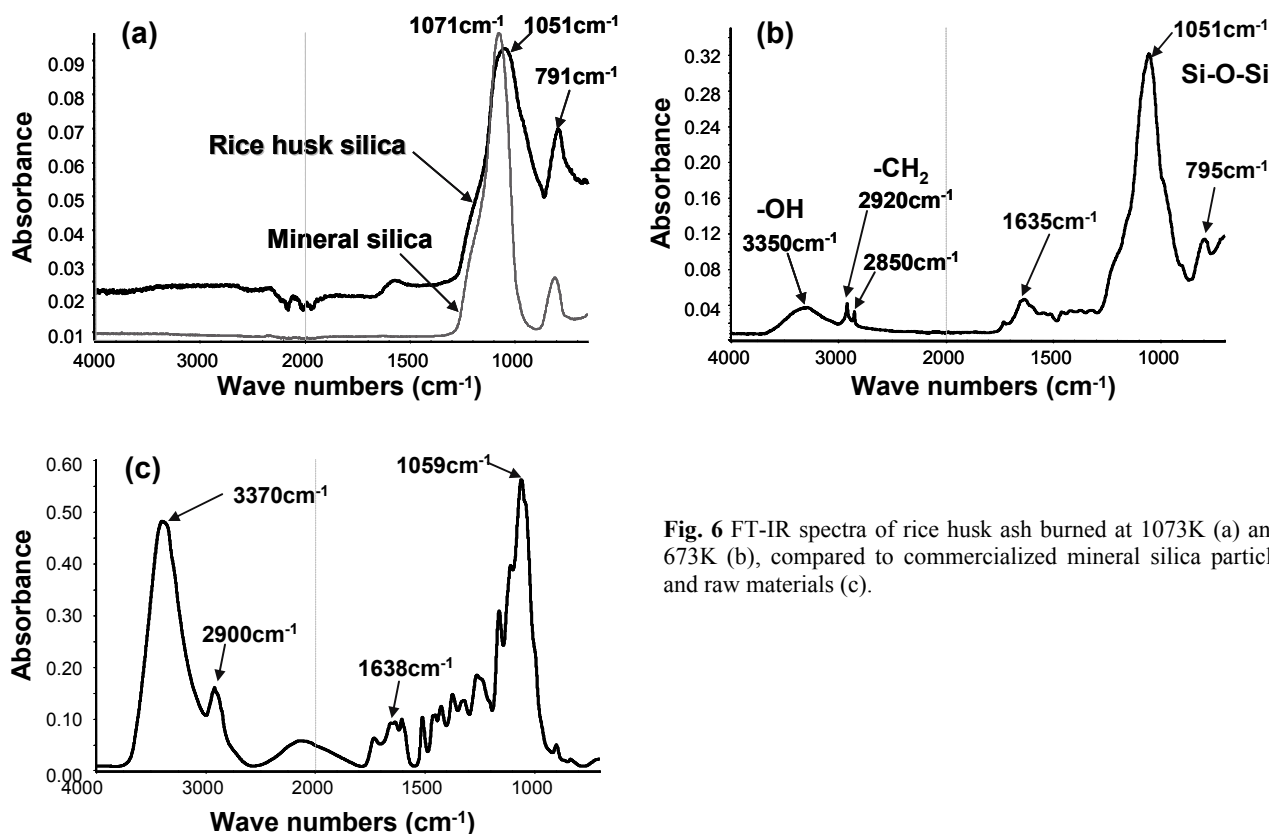
Fig. 6 FT-IR spectra of rice husk ash burned at 1073K (a) and 673K (b), compared to commercialized mineral silica particle and raw materials (c).

carbon content of the rice husk ashes. The dependence of the carbon content of the ashes on the combustion temperature is shown in **Fig.5**. The content was measured by ICP analysis. 5% citric acid solution was used, and the stirring temperature and time during the acid leaching treatment were 323K and 3.6 ks, respectively. It is obvious that the remaining carbon content remarkably decreases from 0.17 mass% to 0.02~0.03 mass% by changing the combustion temperature from 673K to 1073K and over. In additions, there is no significant difference of the carbon content by burning the husks over 1073K. The previous study indicates the exothermic heat of DTA profiles of rice husks due to the organics such as cellulose and hemi-cellulose is completely finished at 973K when the rice husks via the citric acid leaching treatment is used. That is, the thermal resolution of most of the organics progresses over 973K. **Figure 6** indicates the results of FT-IR analysis of rice husk ashes combusted at 1073K (a) and 673K (b). The infrared spectrum of the commercial mineral silica powders and raw rice husks is also shown in (a) and (c), respectively. The infrared spectra at 1051 cm^{-1} and 791 cm^{-1} due to Si-O-Si stretching modes [26] are detected in (a), and correspond to those of the conventional mineral silica materials. No spectrum of about 3370~2850 cm^{-1} due to the polysaccharides [26, 27] of raw rice husks is observed. This result means very little carbon originating from the cellulose and /or hemi-cellulose elements remains in the ashes after combustion at 1073K. This corresponds well to the carbon measurement by ICP analysis shown in **Fig.5**. On the other hand, the specimen burned at 673K

shown in (b) indicates not only 1051 and 791 cm^{-1} spectra (Si-O-Si bond) but also small spectra at 3350, 2920 and 2850 cm^{-1} corresponding to OH stretching mode and CH₂ stretch vibrations [27], which are also detected in the raw rice husks (c). This means a small amount of the original organics still remains in the ashes after combustion at 673K, and results in the increase of the carbon content at 673K as shown in **Fig.5**. Accordingly, the combustion temperature of 1073~1273K is suitable for the preparation of high-purity amorphous silica materials originated from rice husks via the citric acid leaching treatment.

4. Conclusion

For a high purification of amorphous silica originating in rice husks, optimization of the operating parameters in the citric acid leaching treatment and air combustion of rice husks was examined. When using the citric acid solution with a concentration of 1% or more, ICP analysis indicated that the alkali metal impurities could be remarkably reduced from rice husks by the acid leaching treatment. In particular, alkali metal elements of Na and K were completely removed. GC-MS analysis showed the progress of the hydrolysis reaction of their hemi-cellulose during the leaching process. As a result, the remaining carbon content in rice husk ashes was remarkably reduced to 0.02~0.04 mass% after combustion at 1073~1273K. The removal ability of Ca element of rice husks during the citric acid leaching treatment depended on not only the concentration but also the solution temperature and stirring time. This was

because the monosaccharide formation via hydrolysis of carbohydrates caused a reactivity of Ca elements with carboxyl groups to synthesize their metal complexes during the hot acid leaching treatment. The combustion temperature at 1073K or more was enough to thermally remove the original carbohydrates from rice husks, and resulted in a very small carbon content of 0.02~0.03 mass%. On the other hand, when the combustion temperature of 673K was employed, FT-IR analysis showed CH_2 and OH stretching modes with 3350~2850 cm^{-1} spectra originated in the carbohydrates of the rice husks, and their ashes with 0.17 mass% carbon were obtained. Under the suitable acid leaching and air combusting conditions, high-purity amorphous silica materials with 99.5~99.77 mass% were produced from rice husks.

Acknowledgements

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