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High-purity amorphous silica originated in rice husks via carboxylic acid leaching process

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Abstract The environmentally benign, harmless to human, and economically effective process to produce high-purity amorphous SiO_2 materials from rice husks has been established by using a carboxylic acid leaching, not the conventional strong acids. TG-DTA measurement and GCMS analysis indicated that the leaching was effective for the hydrolysis of celluloses and hemicelluloses contained in rice husks at 473–873 K, which produced the same results in using the conventional sulfuric acid. In particular, the formation of furfurals and levoglucosans occurred via the hydrolysis at 473 K and 673 K, respectively, when using rice husks leached by citric acid solutions. The metallic impurities could be also removed from the husks via a chelate reaction between carboxyl groups (–COOH) and the metal elements. 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 air supplement of 50 mL/min or more. High-purity amorphous silica materials with 99 wt% or more were prepared from rice husks by applying the citric acid leaching treatment and burning process at 1073 K in air.

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 useful raw materials for industrial uses. 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 [1, 6]. 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, the 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 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 supplement 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 to prepare amorphous structured silica. For the evaluation of the carboxyl group (–COOH) of organic acids to remove metallic impurities via a chelate reaction, the citric acid leaching treatment was applied to rice straws including a few cadmium (Cd) elements, and the reduction effect was discussed.

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Experimental procedure

The raw materials of rice husks harvested in Niigata, Japan, were employed, and subjected to the carboxylic acid leaching treatment by using citric acid ($C_6H_8O_7$) solution. Sulfuric acid solution was also used as the comparison in the leaching treatment. Both acid materials are made by Kishida Chemical Co., Ltd, and the purity of the carboxylic acid and sulfuric acid is 99.5% and 98% or more, respectively. The concentration of each acid solution was 5 wt%, and temperature was controlled at 323 K. About 20 g of husks were immersed in the acid solution of 500 mL for 900 s. The water rinsing treatment on acid-leached husks was carried out to remove the acid solution from rice husks. Water rinsing after the leaching was repeated three and eight times, respectively, by citric acid and sulfuric acid. The water-rinsed materials were dried at 373 K for 3.6 ks in the electric furnace. As mentioned above, the main content of rice husks was cellulose and hemicellulose. Therefore, the cellulose powders made by Merck KGaA INC., having a mean particle size of 58 μm and purity of 94.8 wt%, were prepared, and their thermal resolution temperature was measured by TG-DTA equipment (Shimadzu DTG-60) under air or argon gas supplement with a flowing rate of 150 mL/min. In the case of rice husks, the same analysis was applied to evaluate the thermal resolution behavior. In particular, from a viewpoint of the hydrolysis of some organics in husks, its reactivity could be discussed quantitatively by the comparison of the exothermic heat in the TG-DTA profile. This is indicated when the cellulose and hemicellulose atomic structure changed 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 TG-DTA profiles. The flowing rate in the air supplement was controlled from 0 to 150 mL/min, and argon (Ar) gas was used for the comparison in this analysis. It was measured from 293 K to 1273 K with heating ratio of 10 K/min. To investigate the atomic structure changes of cellulose and hemicellulose by the acid leaching, GCMS analysis (Agilent 5973 N) was applied to the specimens after heating at 473 K for 360 s, 673 K for 60 s, and 873 K for 6 s. The hydrolysis behavior of the organics contained in the acid-leached husks at each sampling temperature could also be discussed by the identification of the mass spectra and their intensities. The effect of the citric acid with carboxyl groups on the removal of metal impurities contained in rice husks and straws is investigated. Three kinds of rice straws, which include Cadmium (Cd) content of 0, 23, and 82 ppm, are prepared as raw materials. They are also subjected to the citric acid leaching treatment at 323 K for 900 s. The concentrations of the acid solution are 5 wt% and 20 wt%. Cd contents of acid-leached straws and used solutions are measured by ICP optical emission spectrometer (HORIBA, ULTIMA-2). The burning process of dried husks took place at 873–1423 K in air to remove the organics from rice husks. A 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.

Result and discussion

Hydrolysis of organics by citric acid leaching

Rice husks and straws comprise cellulose, hemicellulose, and lignin. The previous work indicates that hemicellulose and lignin are rapidly digested by a short time acid leaching treatment while cellulose is only partially digested [7]. It means a high degree of resistance of the residual cellulose in the husks toward 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 indicates TG-DTA profiles of the conventional cellulose powders under the air and Ar gas flow condition both with a flow ratio of 150 mL/min. As shown in Fig. 1a, the DTA curve under the air supplement indicates two exothermic heats with the maximum peak temperatures at 628 K and 778 K by the complete combustion, which corresponds well with the previous results [7]. At the same time, Fig. 1b shows the drastic weight loss due to their thermal degradation. In particular, the reduction of weight at the temperature range from 573 to 613 K is significantly large, and the following second weight loss until 813 K is small. The latter is caused by the second exothermic heat due to the thermal resolution of cellulose powders in burning shown in (a). On the other hand, when using Ar gas atmosphere, the DTA curve reveals an endothermic heat at the peak temperature of 618 K due to its carbonization without combustion. The TG profile shows a weight loss at the same temperature as the above endothermic. In comparison to that under the air supplement, it reveals no second weight loss from 613 to 813 K. In other words, these results suggest that the burning over 613 K with a suitable air supplement is important to completely combust celluloses contained in rice husks. 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 473–493 K, and lower than that of the cellulose (543 K) as shown in Fig. 1a. This may be attributed to the content of hemicellulose and lignin elements in rice husks that have

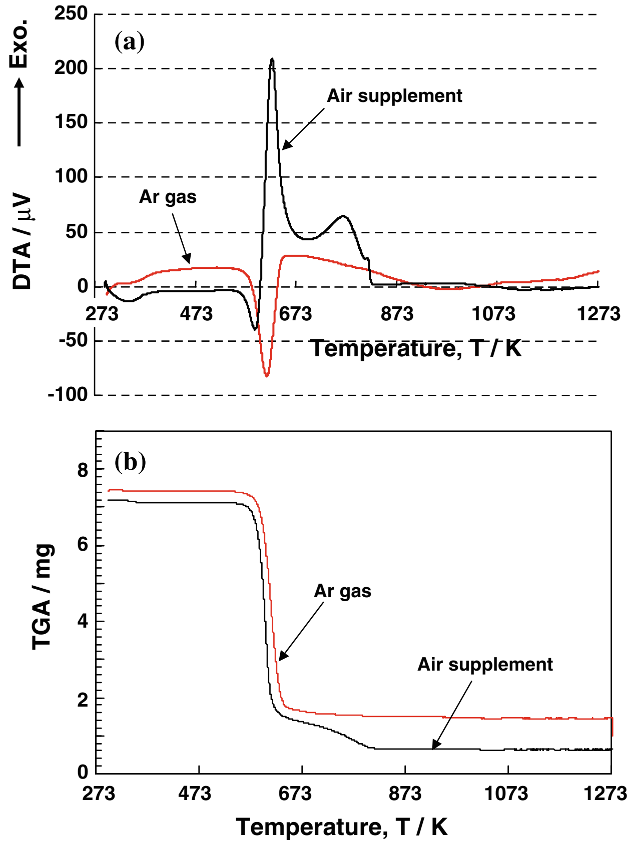

Fig. 1 TG-DTA profiles of cellulose measured in air and argon gas atmosphere

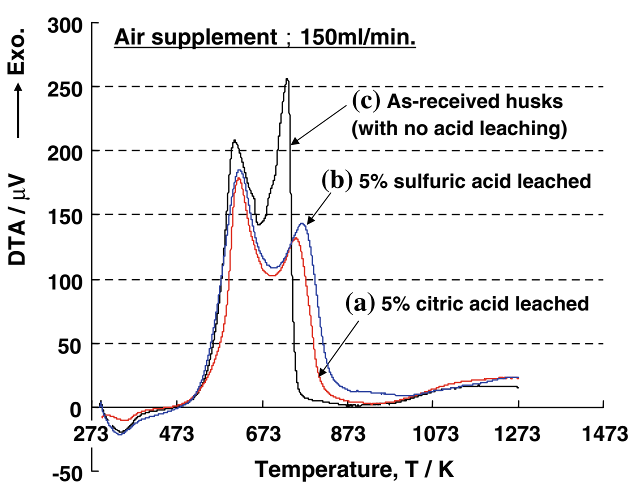

Fig. 2 DTA profile of rice husks with citric acid (a) and sulfuric acid leaching (b) compared to as-received raw materials (c)

significant influences on the initial temperature of the thermal degradation. They show two exothermic heat peaks, which have the same maximum points at 608–623 K and 723–743 K, respectively. While comparing their heat values, the difference between (a) and (b) is very little, but (c) has a significantly small heat compared to another. The

Table 1 Comparison of exothermic heat values of DTA profiles of each rice husks (kJ/g)

(kJ/g)	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

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 a possibility to accelerate the hydrolysis of organics contained in rice husks. For the investigation of this reaction behavior, GCMS analysis is carried out on each specimen. The heating conditions before the analysis are 473 K for 360 s, 673 K for 60 s, and 873 K for 6 s in air. Figure 3

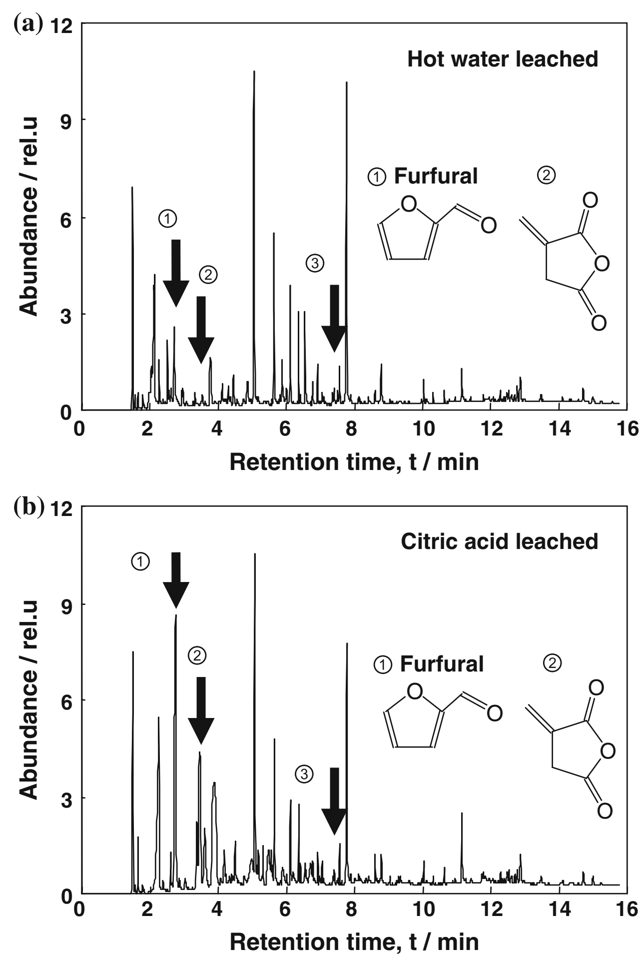

Fig. 3 GCMS results of rice husks via citric acid leaching and hot water rinsing (473 K for 360 s)

shows GCMS results of rice husks after hot water rinsing at 323 K (a), and citric acid solution (concentration; 5 wt%) leaching at 323 K (b). The heating condition in GCMS analysis of each sample was 473 K for 360 s. Spectra ①, ②, and ③ correspond to furfurals (C_4H_3O), and levoglucosans, respectively. In both specimens, the spectrum ③ of levoglucosans is very small compared to the furfural peaks. When applying the above heating condition to each sample, the furfurals were mainly formed, and a very little levoglucosans were also produced in each material with even acid leaching treatment.

Table 2 indicates the ion intensity of peaks ① and ② of each rice husk. The maximum intensity of both peaks in using the citric acid-leached materials is about 4–10 times as 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 is detected until 473 K. That means no effect of the heat treatment less than 473 K on the above hydrolysis of organics in rice husks. Accordingly, the citric acid leaching treatment of husks is effective to accelerate the atomic structure change of their hemicellulose to furfural via the hydrolysis and dehydration.

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

	Intensity of total ion	Max. intensity of peak ①	Max. intensity of peak ②
Hot water rinsed at 323 K			
$N = 1$	$1.35*10^9$	$2.35*10^6$	$3.82*10^5$
Citric acid leached at 323 K			
$N = 1$	$2.16*10^9$	$8.51*10^6$	$4.22*10^6$
$N = 2$	$2.15*10^9$	$8.22*10^6$	$4.06*10^6$

Figure 4 indicates GCMS results of hot water rinsed (a), and acid-leached materials (b) and (c) after heating 673 K for 60 s. In the all 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 673 K. With regard to the peak ③, the formation of levoglucosans shown in (a) indicates an extremely small peak intensity, and very few products of levoglucosans. On the other hand, the peak is clearly detected in the specimens (b) and (c). The ion intensity, however, is not so different between these two values. It means that the citric acid leaching is also effective for the hydrolysis of the cellulose contained in husks to produce levoglucosans, and its effect is almost same as that via the sulfuric acid leaching. Figure 5a shows DTA profiles of the citric acid-leached rice husks (acid concentration, 5 wt%) when changing the air supplement in the analysis. In the case of 50 mL/min or more, there is no change in the profile with the typical two exothermic heats

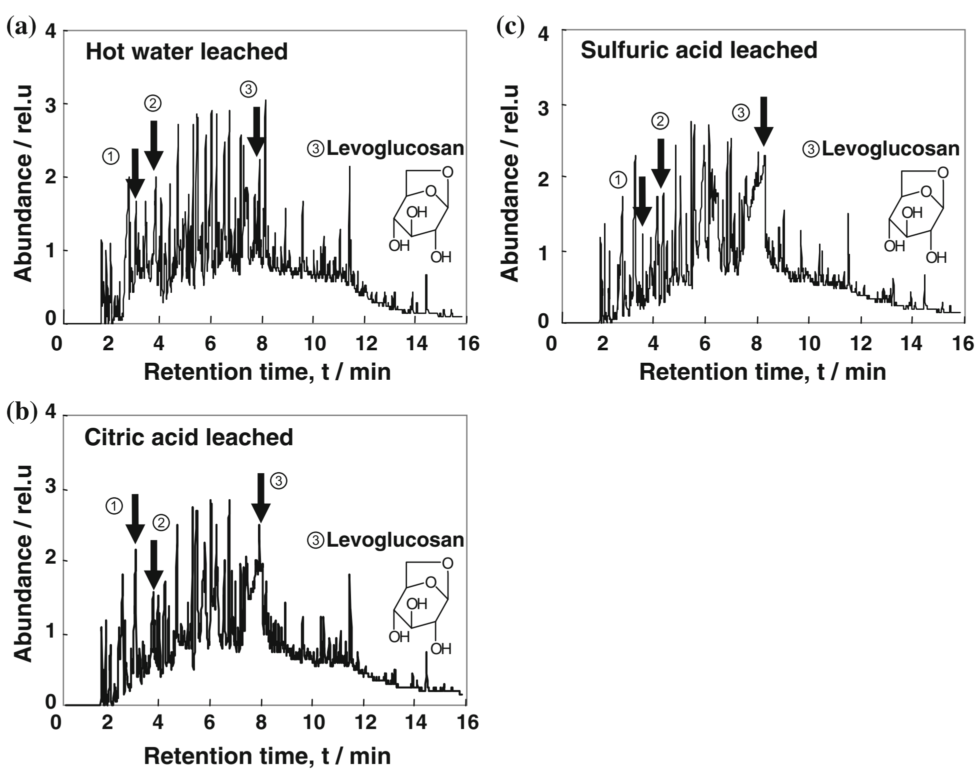

Fig. 4 GCMS results of rice husks via citric acid leaching and hot water rinsing (673 K for 60 s)

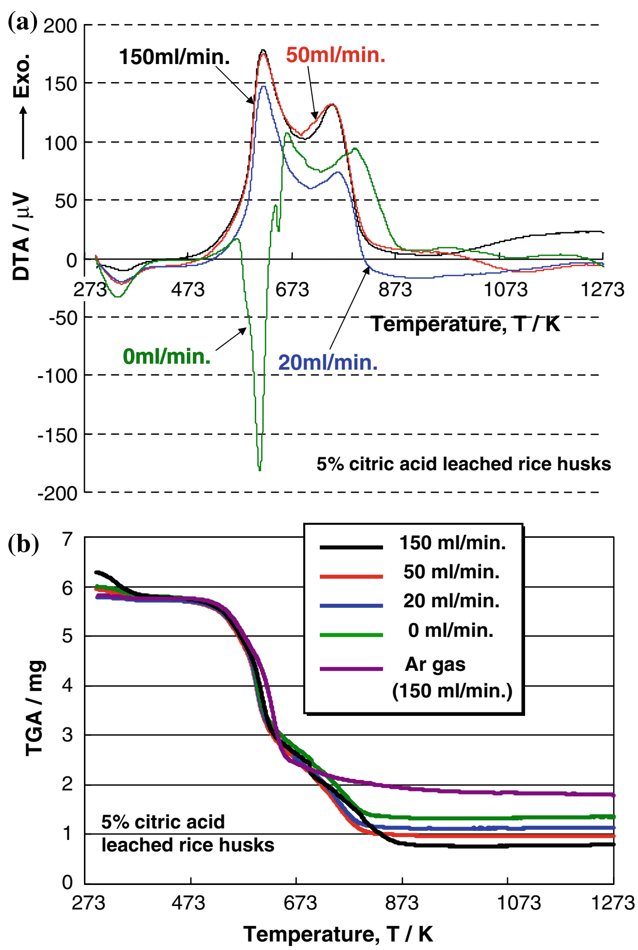

Fig. 5 TG-DTA profiles of citric acid-leached rice husks measured under various air supplement flowing rate

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 623 K with no air supplement in the analysis, and the color of the burned specimen remaining in the alumina cup is black. The others indicate 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 the insufficient air in burning causes the carbonization of organics at 573–673 K. In addition, the same result as no air supplement is obtained by using argon gas in TG-DTA analysis. With regard to the TG profiles shown in Fig. 5b, the total weight reduction after heating until 1,273 K gradually increases with increase in the air flow rate from 0 to 150 mL/min. Every curve except for Ar gas flow condition shows two-step reduction profile, which are same as that of cellulose powders under the air supplement shown in Fig. 1b. When using the Ar gas flow in TG-DTA analysis, the total weight reduction remarkably decreases, and the profile is similar to that of celluloses under Ar gas.

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 wt% such as potassium (kalium/K), calcium (Ca), sodium (natrium/Na), phosphorus (P), aluminum (Al), etc. According to the soil contents, some of hazardous metal elements such as cadmium (Cd) and lead (Pb) are included. It is reported that alkali metal impurities of K and Na cause the carbons to remain in ashes, which are originated in organics of husks. This is because the eutectic reaction between the alkali metals and SiO_2 element occurs during burning, and the carbon remains in the SiO_2 melt [8, 9]. Furthermore, "chemical activators" such as KOH, K_2CO_3, and Na_2CO_3 are easily produced by heating rice husks including the alkali metal impurities, and function as dehydrating agents and inhibit the formation of tar [10]. Then, K_2O may act as the "chemical activator" during the combustion, and unburned carbon remains in the ashes. It is well known the chelate reaction of carboxyl groups (–COOH) with metal elements easily occurs, and their metal complexes are formed [11]. The other previous studies show that citric acid and tartaric acid have a great potential to remove Cu^{2+} from aqueous solutions by using its carboxyl groups [12, 13]. Table 3 shows Cd contents of raw materials, used citric acid solutions, and rice straw ashes by ICP analysis. Material A containing no Cd is referred in this study. With increase in 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, Cd content of each straw is less than 0.001 ppm, which is the lowest limitation by ICP analysis when using 5 wt% and 20 wt% concentration. That is, the citric acid leaching is significantly effective to remove Cd elements via 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 citric acid solution with 5 wt% concentration is carried out at 323 K on rice husks. After water rinsing and drying in air, the acid-leached materials are burned in air at 1,073 K for

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

		Material A	Material B	Material C
Raw materials (ppm)		~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 1073 K via citric acid and sulfuric acid leaching, compared to no acid treatment (wt%)

(wt%)	SiO_2	Al_2O_3	MgO	Na_2O	P_2O_5	SO_2	K_2O	CaO	MnO	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	99.09	0.01	0.06	0.07	0.31	0.05	0.11	0.37	0.01	0.02	0.03	0.12

3.6 ks. The air supplement is 150 mL/min. As-received rice husks without any leaching treatment is 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 CaO, which cause the carbon to remain after burning as mentioned above, from rice husk ashes. As a result, SiO_2 content of ashes is 94.6 wt%, and their color is black and dark gray. On the other hand, a citric leaching treatment is significantly useful to remove these impurities and remained carbons less than about 0.1 wt%. K_2O content is about 1/30 of the ashes with no treatment, and the CaO content is 50% or less. The leaching effect by citric acid solution is almost same as that of the conventional sulfuric acid. As a result, the white ashes, having a high-purity of silica with 99 wt% or more, are obtained by burning the acid-leached rice husks under the suitable conditions.

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 [14], and belong to Group 1. The structure of rice husk ashes strongly depends on the burning temperature. Figure 6 shows XRD profiles of the ashes of citric acid-leached rice husks after burning at various temperatures in air. It indicates that the change from originally amorphous structures to crystal ones occurs by burning the husks at 1,323 K or more. The rice husk ashes include crystallized silica materials with tridymite and cristobalite structures [15]. In the case of the ashes of as-received rice husks, the cristobalite peaks are detected at 1,073 K, and their intensity gradually increases with increase in the combustion temperature. The transformation to tridymite starts at 1,273 K. These results correspond well with the previous study [16]. As mentioned above, the metallic contaminations of rice husks are effective for the eutectic reaction with SiO_2 during heating, and the crystallization occurs when the melted SiO_2 elements are slowly solidified.

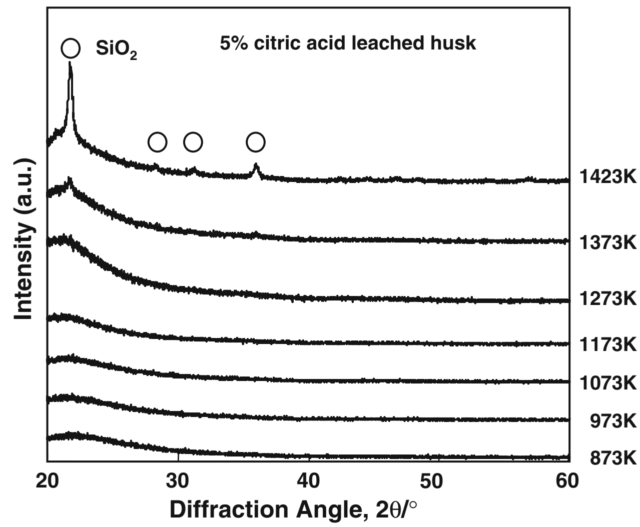

Fig. 6 XRD profiles of rice husk ashes of citric acid-leached rice husks after burning at various temperatures in air

Therefore, the rice husks with very few metallic impurities via acid leaching treatment shows a higher crystallization temperature of 1,323 K or more than untreated ones without any leaching.

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 air-combustion process. The acid leaching treatment is significantly effective to accelerate the hydrolysis of cellulose of rice husks and reduce metallic impurities by chelation of the carboxyl groups. A suitable air supplement from 473 to 873 K is important, and TG-DTA results indicate 50 mL/min or more is required to completely combust the organics of husks. The optimized burning temperature of acid-leached rice husks is less than 1,273 K to prepare amorphous silica materials with a purity of 99 wt% or more.

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References

1. Yelcin N, Sevinc V (2001) Ceram Int 27:219
2. Park BD, Wi SG, Lee KH, Singh AP, Yoon TH, Kim YS (2003) Biomass Bioenergy 25:319
3. Nehdi M, Quette JD, Damatty AE (2003) Cem Concr Res 33:1203
4. Krishnarao RV, Godkhindi MM (1992) Ceram Int 18:185
5. Naskar MK, Chatterjee M (2004) J Eur Ceram Soc 24:3499
6. Chakraverti A, Mishra P, Banergee HD (1988) J Mater Sci 23:21. doi:10.1007/BF01174029
7. Rahman IA, Ismail J, Osman H (1997) J Mater Chem 7:1505
8. Concha R, Maria DA, Jose MC (1996) J Am Ceram Soc 79:2012
9. Venezia AM, La Parola V (2001) J Solid State Chem 161:373
10. Naskar MK, Chatterjee M (2004) J Eur Ceram Soc 24:3499
11. Lenz GR, Martell AE (1964) Biochemistry 3:750
12. Zhu B, Fan T, Zhang D (2008) J Hazard Mater 153:300
13. Wong KK, Lee CK, Low KS, Haron MJ (2003) Chemosphere 50:23
14. IARC (1993) IARC monographs on the evaluation of carcinogenic risks to humans 58:41
15. Shinohara Y, Kohyama N (2004) Ind Health 42:277
16. Kapur PC (1935) Powder Technol 44:63