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講演概要

「籾殻再資源化によるバイオマス由来のエネルギーと資源の抽出」

農業廃棄物の一つである籾殻の成分の約 70%がセルロース、ヘミセルロース、リグニン等の炭水化物、約 15~20%がシリカである。また、世界各地で発生している年間の総生産量が、約 8,000 万トンに達する豊富なバイオマス原料である。本講演では、シリカ中の炭水化物から熱エネルギーを抽出した後に発生する残渣を用いた高純度アモルファスシリカの生成プロセスなかでも、高純度化に向けた酸洗浄処理技術と、そのシリカの利用について紹介する。

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著書・解説・他

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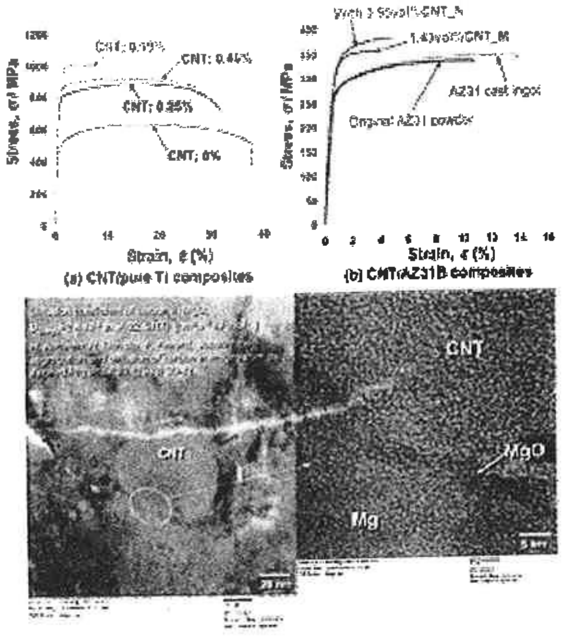
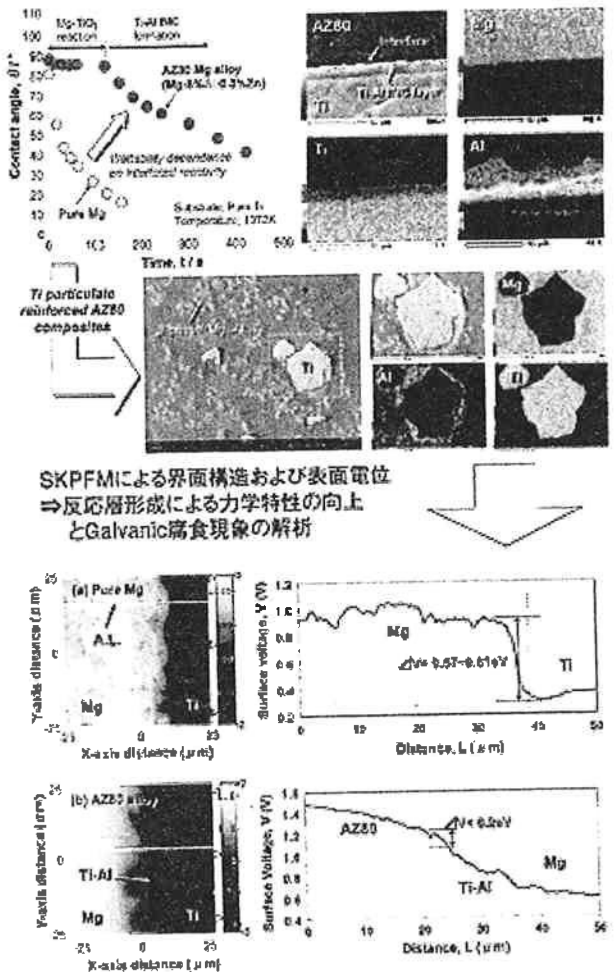
研究テーマ

1. 単分散カーボンナノチューブの真の機能発現に向けた複合化材料設計
2. 急冷凝固プロセスによる高強靭性・高エネルギー吸収性マグネシウム合金
3. バイオマスの高度再資源化：籾殻由来多孔質アモルファス・シリカの生成
4. 完全鉛フリー・高強度快削性黄銅合金の創製
5. 高温濡れ現象解析による新たな複合材料設計
6. 走査型原子間力顕微鏡 SKPFM による界面構造解析
7. その場合成による TiO2 ナノ粒子分散チタン粉末合金の高品質化プロセス



カーボンナノチューブの単分散化湿式プロセスを用いた CNT 被覆金属基複合粉末と複合材料の強化機構（MWCNT／pure Ti powder composites (a) and MWCNT/AZ31B powder composites (b) および CNT-Mg 界面における表面酸化膜の HR-TEM 観察結果）



マグネシウム（Mg）とチタン（Ti）の高温濡れ性に及ぼす Mg 合金中のアルミニウム（Al）による Ti-Al 化合物層の影響およびチタン粒子分散 Mg-Al 合金の組織構造―走査型ケルビンプローブ顕微鏡による Mg-Ti 界面での表面電位に及ぼす Ti-Al 化合物反応層の影響

籾殻の完全再資源化によるバイオマス由来のエネルギーと資源の抽出

21 世紀に入り，地球温暖化による環境負荷・自然災害への危機感の高まりに加え，原油価格の高騰・変動による国民生活への実質的な影響が現れることでバイオマスエネルギーというキーワードは，世界中に急速に認知された．そこでは，カーボン・ニュートラルな環境軽負荷型新エネルギーとしてバイオマスエネルギーを位置づけ，低炭素社会の形成への寄与が期待されている．その一つであるバイオエタノールの世界の生産量推移において，2007 年の生産量は 2001 年の約2倍となり，その 74%を米国とブラジルの2国で占めている．両国は，世界の穀物生産量において高いシェアを有するが，特に，ブラジルでは，政府のエネルギー政策によりガソリンに比べてエタノールの価格が安く，税制優遇措置もあるため，ガソリン，エタノールのいずれでも走行できるフレキシブル・フューエル・ビークル（Flexible Fuel Vehicle, FFV）の比率が増大していることも大きな要因である．しかしながら，トウモロコシや小麦といった穀物をバイオマス燃料として急速に転換利用したため，食品素材としてのこれら穀物の需給バランスが崩れ，品薄・品切れや急激な価格上昇などによる食生活への影響が生じた．勿論，これら穀物に対する投機的な活動も価格高騰の要因の一つになっている．そこで，エネルギー資源として大量処理する際のバイオマスとして，食料資源として利用されない有機物であり，食品素材およびその加工製品の循環経路に直接関与しない「非食部バイオマス」が着目された．有力な候補として，例えば，稲藁，麦藁，籾殻，林地残材（間伐材・被害木）などが現在，取り上げられている．

もみ殻由来のエネルギー

バイオマスとして利用する素材は，安定供給されることが前提であるが，併せてその集荷と搬送といったロジスティックを考慮したプロセス設計を行う必要がある．例えば，奥地で採取された間伐材はその搬送に多額の費用を要する場合，集荷域でのエネルギー生成と利用といったオンサイトでの実用化を考える必要がある．もみ殻や稲わらのように 0.1～0.2g/cm^3 といった低比重の素材は，搬送費が他のバイオマスに比べて著しく高くなることを考えると，例えば，それらの集荷場であるカントリーエレベータの周辺でのエネルギー生成・回収が求められる．そこで，本稿では，もみ殻を対象としたエネルギー回収の現状を紹介した上で，それに関連する我々の調査・研究成果について触れたいと思う．

米は，日本を含めて世界中で年間生産量が安定しており，そこから発生するもみ殻には，重量基準で約 70～75%の有機物（セルロース・ヘミセルロースなど）が含まれており，有力なバイオマスである．国際連合食糧農業機関（Food and Agriculture Organization of the United Nations, FAO）の統計によれば，2006 年の世界のもみ殻発生量は約 127 百万トンと報告されている．しかも，カントリーエレベータやそれに類似した玄米の集荷場が各地域に存在するシステムは世界共通であり，日本国内であっても年間を通じて安定的にもみ殻を排出することが可能である．ゆえに，これらに隣接してバイオマスエネルギーの生成工場を設置することは，バイオマスの集荷・搬送費に関わるコストを大幅に削減できる有効な方策の一つである．もみ殻の利用方法として，主に家畜用敷き材や飼料への添加などが行われているが，全発生量に対して僅かな比率に過ぎない．大部分は，放置や野焼き処分など有効利用されていないのが現状である．野焼きの場合には，もみ殻1トンから約 0.15kg の CO_2ガスが発生し，また，同量のもみ殻を放置すると，腐敗によって約 0.09kg のメタンガス（温暖化係数は CO_2 ガス対比で約 21）が発生する．日本国内においても，年間平均で約 3 百万トンという単位で発生するもみ殻に対して，野焼きや投棄といった行為を続ければ，近い将来，地球規模での環境破壊を誘発する可能性は否めない．よって，農業廃棄物であるもみ殻をバイオマスとして利用することは，前記の環境負荷の低減にも直接的に寄与すると考えられる．

次に，もみ殻の具体的な利用方法について紹介する．世界の米どころである東南アジア諸国では，既にもみ殻を投入燃料としたバイオマスエネルギー事業を実施しており，なかでも，年間約 63 百万トンのもみ殻が発生するタイ王国では，日系企業の支援により複数のもみ殻発電所が稼動している．一例として，同国コンケーン県ロイエットにて Roi-et Green Co.,Ltd. が保有する 10MW 級発電所で使用するもみ殻の屋外ストックと操業時の燃焼状況を写真1に示す．本発電所は 2003 年より稼動しており，1 日あたり約 300 トンの籾殻を 1000 度で燃焼し，その発熱量を利用して発電・送電している．その際，石炭火力発電と同様，もみ殻の燃焼後には写真2に示すような焼成灰（Ash）を排出する．その成分は，重量比率でシリカ（SiO_2）が約 84～88%と最も多く，他には有機成分由来の残留炭素（C）や，K, Ca, Na, P, Al, Fe など土壌由来の金属元素が不純物レベルとして含まれる．なお，焼成灰が黒色を呈しているのは，その炭素が2~3%程度，灰の内部に残留するためである．シリカが残渣の主成分であることから土壌に戻すための農業用途の他，コンクリート用混和材といった安価な低級素原料としての利用に限定される．そのため，経済性バランスを考えて，再利用できない余剰のもみ殻焼成灰は，河川投棄や有償廃棄処分されている．

他方，発酵プロセスを利用したもみ殻や稲わらからのエタノールの精製に関する研究が国内外で進められている．現状では，ラボレベルでの検証段階であるが，利用可能な品質のエタノールの精製に成功している．しかしながら，この場合も実用化を想定した工程内残渣の有効利用が課題である．ここで排出される残渣には，シリカの他にリグニンが含まれることから，製造工程内での燃焼用原料としての再利用が考えられるが，最終的には，この場合もシリカを主成分とした焼成灰の取り扱いが問題となる．

バイオマスのマテリアルフローと再資源化

先に紹介したもみ殻の直接燃焼による熱・電気エネルギーの回収や，加水分解・発酵法によるエタノール精製のいずれにおいても，シリカを主成分としたもみ殻残渣が発生する．もみ殻のバイオマス利用に関する研究ならびに実用化は進められているものの，同時に排出される残渣の適切な処理・処分，あるいは有価物資源としての再利用に関する検討は十分ではない．言い換えると，もみ殻を余すことなく，エネルギーや資源として利活用できるプロセス技術の構築は，もみ殻由来バイオマスエネルギーの広範囲における持続的な利用に際して，経済性の観点のみならず，地球環境への負荷軽減の点からも重要な課題といえる．そこで，工程内での排出残渣の再資源化を含めたバイオマスエネルギー生成におけるマテリアルフローを図1に示す．前述の通り，残渣の主成分であるシリカは，工業・農業用資源の他，食品や菓子，医薬品用添加素材など，広範囲で使用されている．用途にもよるが，シリカ純度が99%を超える品質を安定的に確保できれば，有効な素材・資源となり得る．また，従来の鉱物系シリカとは異なる特徴として，反応活性な非晶質（アモルファス）であることと，多孔質構造を有するといった点が挙げられる．これらの特徴を活かした高付加価値資源への適用が大いに期待できる．技術の詳細[1]は講演で説明するため，本紙面では割愛するが，焼成灰中の残留炭素がシリカの純度を低下させる主要因であり，これを誘発する現象が，もみ殻に微量に含まれる Na と K といったアルカリ金属とシリカとの共晶反応による低温溶融である．しかも，もみ殻の燃焼時にシリカの溶融が生じた場合，その凝固過程で結晶構造へと変化することで特徴を損なう．そこで，環境・人体への負荷が小さく，かつ優れた経済性のもとで，もみ殻に含まれる微量なアルカリ金属元素をはじめとする不純物を除去する方法として，希薄なクエン酸水溶液による洗浄処理プロセスを確立した．その結果，酸洗浄処理もみ殻を大気燃焼すると，表1に示すようにシリカ成分は99%を超える高純度化を達成し，不純物含有量も従来の燃焼灰に比べて著しく低減することに成功した[2]．

このように化石燃料の代替としてバイオマスを有効活用し，地球環境に配慮した低炭素社会を構築する一つの方策として，非食部バイオマスであるもみ殻を出発原料とし，エネルギーと残渣資源（高純度シリカ）を経済性よく併産できるラボ技術を構築できたと考える．しかし，ここからが本当の技術開発である．スケールアップ技術の確立やクエン酸洗浄液の再利用と廃棄処理，それに基づくシリカ純度の安定性の評価など様々な課題がある．なかでも，もみ殻由来の高純度シリカを如何にして高付加価値資源・素材として利活用するかを民間企業の知恵を借りて解決しなければいけない．ゴールはまだまだ先である．

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写真2 もみ殻発電所から排出された焼成灰の外観

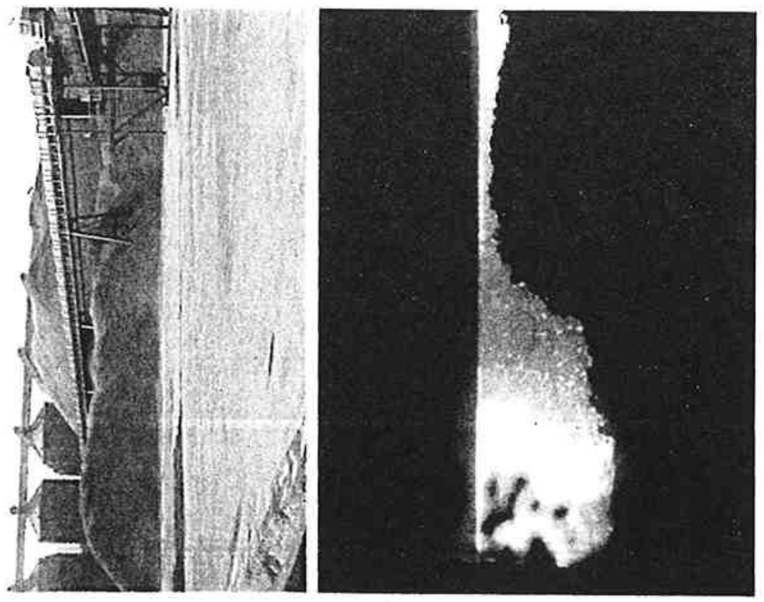

写真1 タイで操業するもみ殻発電所
（上）もみ殻の屋外ストック，（下）もみ殻の燃焼状況

表1　クエン酸洗浄処理を施したもみ殻と原料もみ殻を用いた燃焼灰の成分分析結果

(mass%)	SiO_2	MgO	Na_2O	P_2O_5	K_2O	CaO	MnO	Al_2O_3	Fe_2O_3	CuO	MoO_3	C
開発製法	99.25	0.07	0	0.11	0.06	0.14	0.02	0.01	0.02	0	0.01	0.03
原料もみ殻	91.72	0.48	0.11	0.49	3.76	0.72	0.31	0.07	0.18	0.08	0.01	2.07

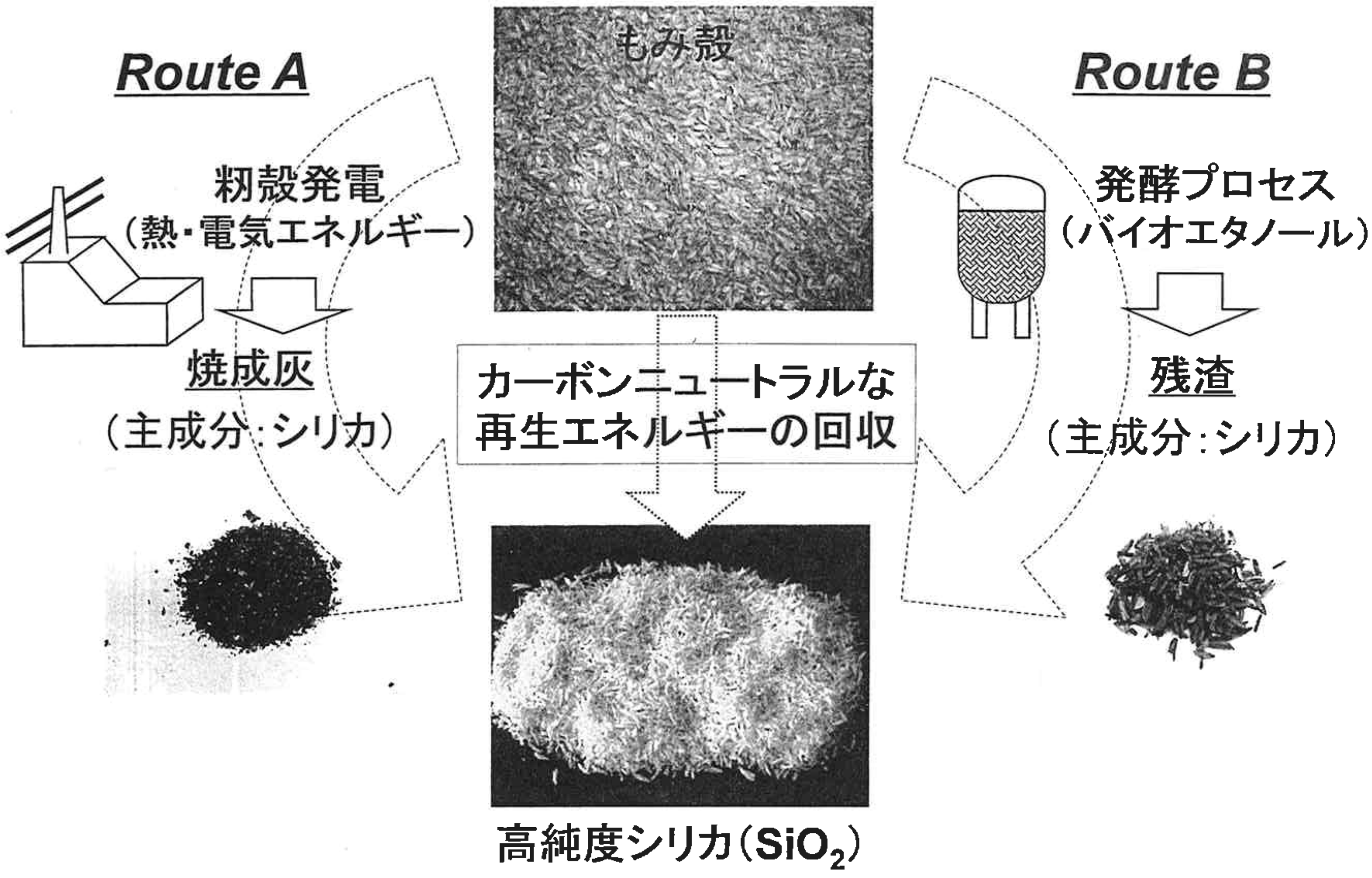

図1　もみ殻の再資源化におけるマテリアル・フロー：バイオマスエネルギーと高付加価値素材（高純度シリカ）の生成

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High-purification of amorphous silica originated from rice husks by combination of polysaccharide hydrolysis and metallic impurities removal

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ABSTRACT

Rice husks and straw, containing 70–75 mass% organics and 15–20 mass% amorphous silica (SiO_2), are representative non-eatable biomasses. After the use of the organic elements as fuels, the leavings including large amounts of silica can be used as industrial materials when their purity is 99 mass% or more. Hence, the reuse of high-purity silica will be significantly effective in reducing the total cost of biomass energy in using rice husks and straws. To attain high-purity silica from the remains of the rice husks after air combustion, the optimization of the process conditions of the citric acid leaching treatment and water rinsing process of rice husks were conducted to remove the metallic impurities such as Na, K, Ca, Mg, Fe, Cu, etc. from husks and promote the hydrolysis reaction of polysaccharides. When the citric acid solution with a concentration of 1 mass% or more was used, alkali metal oxides of Na_2O and K_2O were completely removed. GC–MS analysis showed the progress of the hydrolysis reaction of their hemi-cellulose of rice husks during the leaching process. Carbon content of ashes was drastically reduced to 0.02–0.04 mass% after combustion at 1073–1273 K, and high-purity amorphous silica with 99.5–99.77 mass% were produced from rice husks.

1. Introduction

Rice husks and straws are representative agricultural wastes in the world. The annual yield of rice husks was about 127 million tons in 2008 (FAO, 2008). At this moment, most of them are not practically reused, and cause the environmental problems. For example, the combustion of 1 ton rice husks in the field causes about 0.15 kg CO_2 gas emission. Approximate 0.09 kg methane (CH_4) gas is produced when 1 ton rice husks are left on the ground and naturally decomposed (Klass, 1998). From a viewpoint of the reuse of rice husks and straws as fuel resources, they are useful biomass materials. This is because they contain about 65–75 mass% polysaccharide organics such as cellulose and hemi-cellulose (Aristidou and Penttilä, 2000) and become suitable fuel resources for energy generation (Jain et al., 1994; Fang et al., 2004). On the other hand, amorphous silica materials of about 12–20 mass% are contained in rice husks and straws (Aristidou and Penttilä, 2000; Yalçin and Sevinç, 2001), and certainly remain in their leavings after using the organic elements as fuels. In general, silica is useful industrial materials such as fertilizer, reinforcement of concretes, and ceramics materials (Della et al., 2002; Sensale, 2006; Krishnarao and Godkhindi, 1992). A lot of previous studies have suggested some processes to produce silica materials by combusting rice husks (Chakraverti et al., 1988; Kalapathy et al., 2000; Patel et al., 1987; Rozainee et al., 2008). From a high-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 (Liou and Wu, 2009; Chakraverti et al., 1988; Rhaman et al., 1997). This is because metal impurities of Na and K elements have a eutectic reaction with SiO_2 during combustion of rice husks (Allendorf and Spear, 2001; Besmann and Spear, 2002). For example, when Na_2O and SiO_2 coexists in rice husks, the ternary oxides, $Na_6Si_8O_{19}$ and $Na_2Si_2O_5$ with a eutectic melting point of 1062 K (Morey et al., 1930; Richet et al., 2006) are formed during combustion in air, and results in a drastic decrease of the melting point of SiO_2 from 1986 to 1062 K occurs (Yazhenskikh et al., 2006; Haltera and Mysen, 2004). Therefore, the carbon elements originated from organics of rice husks easily dissolve and remain in such ternary Si–Na–O and Si–K–O oxides in liquid phase during combustion at 1073–1273 K. As a result, the purity of silica materials contained in the rice husk leavings was 96–98 mass% or less. Furthermore, a large part of amorphous silica changes to crystalline structures after solidification of the above ternary oxides. The authors have established an environmentally benign process to produce rice husk silica with a high-purity of 99 mass% and over by using the citric acid solution leaching treatment before combustion (Umeda et al., 2007; Umeda and Kondoh, 2008). Such silica materials also showed completely amorphous structures even after combustion at 1273 K in

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air because the metal impurities were removed from husks during the above acid leaching treatment. The use of the citric acid solution is effective for the chelate reaction (Norman and Earnshaw, 1997) between carboxyl groups (–COOH) and metallic impurities contained in husks, and results in the removal of such impurities as metal complexes from rice husks during the leaching treatment. In the present study, from a view point of a higher purification of amorphous silica, the optimization of the process parameters in the acid leaching treatment and combustion of rice husks was discussed. In particular, the effect of the citric acid concentration on the polysaccharide hydrolysis behavior of organics was investigated by using GC–MS analysis, and the removal mechanism of metallic impurities was also discussed.

2. Experimental

Rice husks harvested in Niigata were used as input raw materials to produce high-purity amorphous silica materials. As mentioned above, 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 (Umeda et al., 2007; Umeda and Kondoh, 2008). Citric acid powders, having a mean particle size of 1.22 mm, were dissolved in the distilled water at the ambient temperature to prepare citric acid solutions. 30 g rice husks were put into 500 ml citric acid solution in 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 between –COOH groups and metallic impurities strongly depends on the above parameters and the hydrolysis of polysaccharides of cellulose and hemi-cellulose is also dependent on them. The concentration was controlled from 1 to 7 mass% by changing the mixing ratio of citric acid powders (Kishida Chemical Co., purity: 99.5 mass%) and distilled water. The beaker was placed on the stirrer (AS ONE, hot stirrer, HS-5BHSD), and the solution temperature was changed from 298 to 353 K. The rotating speed of the magnetic stirrer bar in the solution was controlled at 960 rpm, and the stirring time was 15–120 min. After the acid leaching process, the water rinsing treatment of the rice husks was carried out in the distilled water at 293 K for 900 s to remove the citric acid content from the husks. The stirrer was also used in the water rinsing process, and the magnetic bar was rotated under 960 rpm speed. The materials were dried at 373 K for 60 min in the muffle furnace in atmosphere, and then combusted at 1073 K for 30 min in the same furnace. The combustion temperature of 1073 K was used in this study to prevent the crystallization of amorphous silica contained in the husks (Rhaman et al., 1997). The airflow rate in the combustion was 0.42 ml/s by using a small air-compressor. The content of each metallic oxide impurity of the ashes was measured by X-ray fluorescence spectroscopy (XRF, PANalytical, X-ray spectrometer PW2400). 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 also carried out to investigate structures of the remained carbides originated from the organic elements and silica materials. In order to quantitatively evaluate the hydrolysis behavior of the polysaccharides of rice husks by using the citric acid leaching treatment, gas chromatograph–mass spectrometer (GC–MS, Agilent Technologies, Agilent-5973N) was applied to the acid-leached specimens after air dry at 373 K. As mentioned in the previous report (Umeda and Kondoh, 2008), the same heat treatment of them was conducted at 473 K for 360 s before GC–MS analysis. The hydrolysis behavior of the organics was 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.

Table 1
Quantitative analysis of silica (SiO_2) and impurities contents of rice husk ashes by using citric acid leaching treatment with various concentrations (leaching temperature; 323 K, soaking time; 60 min, water rinsing time; 15 min, air-burning conditions; 1073 K × 30 min).

	Concentration of citric acid solution (wt.%)				
Mass%	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

3. Results and discussion

3.1. *Effect of citric acid solution leaching and water rinsing conditions on removal of metallic impurities*

Table 1 shows chemical compositions of the rice husk ashes via the citric acid solution leaching treatment with different concentration. The solution temperature was 323 K and the stirring time of 60 min was used in the leaching process. The concentration of 0 mass% means the use of the warm distilled water rinsing treatment at 323 K instead of the citric acid solution. As shown in Table 1, when the concentration of the citric acid solution is over 1 mass%, the silica (SiO_2) purity of each ash is approximately 99.5 mass% or more. On the other hand, a silica purity of 97.25 mass% was obtained by using the warm distilled water leached treatment (0 mass%). It means the use of the citric acid leaching treatment obviously caused the remarkable reduction of the total content of metal oxide impurities, and resulted in a high-purification of silica materials contained in the rice husk ashes. Concerning the content of alkali metal oxides (Na_2O and K_2O) remained in the ashes, the application of the citric acid solution is remarkably effective in reducing them. In particular, Na_2O has been completely removed from the rice husks by using the citric acid solution of 1 mass% or more concentration. When the warm distilled water (0 mass%) was employed, the content of K_2O and carbon remained in the ashes was 1.39 and 0.15 mass%, respectively. The previous result indicates that K_2O and carbon content of rice husk ashes was 3.69 and 0.61 mass%, respectively when raw rice husks with no leaching treatment were used (Umeda and Kondoh, 2008). This means that even the warm distilled water leaching treatment is effective for the removal or reduction of K impurities from rice husks. This is because the hydrolysis reaction of polysaccharides such as cellulose and hemi-cellulose occurred during leaching treatment by using warm distilled water at 323 K for 60 min, and the chelate between K impurities and –COOH groups easily took place. The reason for the reduction of carbon content is due to the removal of K_2O impurities, causing a eutectic reaction of SiO_2 elements at lower temperature and their liquid phase. The content of MgO and MnO impurities remained in the ashes is also extremely reduced by using the citric acid solution, and their reduction ratio is 85–93% when comparing to the oxide impurities of the ashes via the warm distilled water leaching treatment (0 mass%). Furthermore, it is obvious that the citric acid solution leaching treatment is also effective in removing Ca elements from rice husks. However, its reduction ratio of about 65–76% is smaller than those of MgO and MnO as men-

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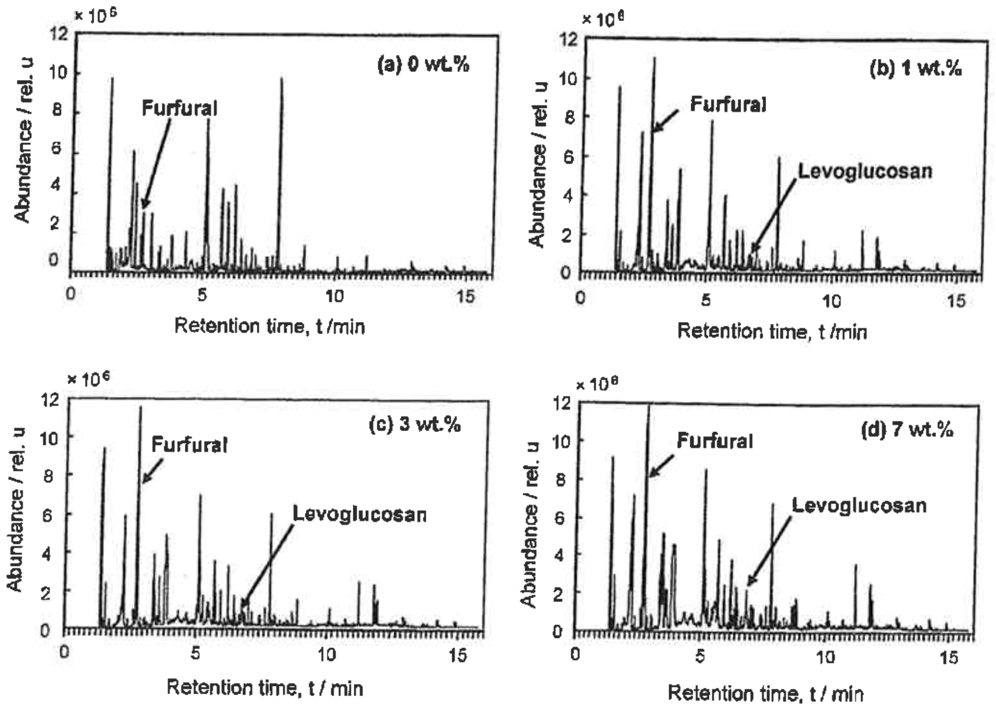

Fig. 1. GC–MS analysis results of rice husks via citric acid solution leaching treatment using various solution concentrations of 0 mass% (a), 3 mass% (b), 5 mass% (c), and 7 mass% (d) (solution temperature; 323 K, pre-heating condition; 473 K for 6 min).

tioned above. Fig. 1 indicates GC–MS analysis results of air-dried rice husks via the citric acid leaching and the next water rinsing treatment. The concentration of the citric acid solution used in this analysis is 0 mass% (a), 1 mass% (b), 3 mass% (c) and 7 mass% (d). The spectrum corresponding to furfural, which is a monosaccharide formed from hemi-cellulose via hydrolysis and dehydration reaction (Saha, 2003), is clearly detected in specimens of the citric acid-leached husks (b)–(d). As shown in (a), a small peak of furfural is also detected. It means the warm water leaching treatment at 323 K is also slightly effective in the hydrolysis and dehydration reaction of hemi-cellulose. It also reveals no obvious difference of the spectrum intensity between 1 and 7 mass% concentration. A very small spectrum of levoglucosan is detected in all materials shown in Fig. 1. Fig. 2 shows a dependence of the ion intensity of the furfural spectrum on the concentration of the citric acid solution. When 1 mass% citric acid solution is used, the ion intensity is 2.21×10^6 (mg^{-1}) and about four times as that in the use of the warm distilled water shown in Fig. 1(a). It slightly increases with increasing concentration from 1 to 7 mass%. These results suggest that the citric acid solution of 1 mass% concentration is enough for the progress of hydrolysis reaction of hemi-cellulose (polysaccharide) to furfural (monosaccharide) contained in rice husks. 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 (Horng, 2004). When the hydrolysis reaction of the polysaccharides progresses by the citric acid leaching treatment, the simple structures of monosaccharides such as furfural and levoglucosan are formed in the rice husks (Saha, 2003). As a result of this reaction, carboxyl groups easily pass through the monosaccharides and contact the above metallic impurities contained in rice husks. Their chelate complexes are formed and discharged from the husks into the acid 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, Table 1 obviously indicates that the reduction of alkali metal oxides of Na_2O and K_2O is effective to decrease the remained carbon content of the ashes. This is because a remarkable decrease of these oxide impurities, causing a liquid phase of SiO_2 by the eutectic reaction at 1062 K as mentioned above, prevents the dissolution of carbon elements in the melt SiO_2 during combustion at 1073 K. Hence, a very few organics remain in the ashes, and result in a high-purification of silica materials.

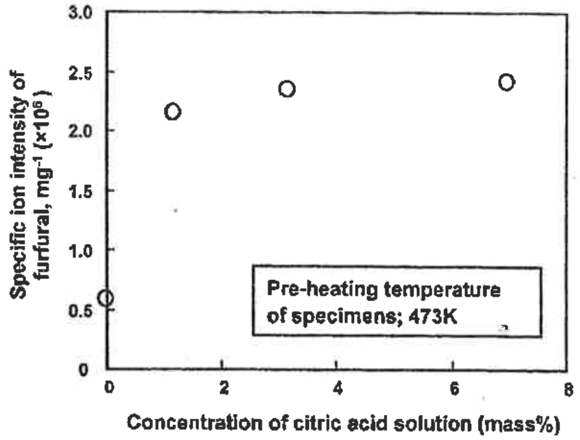

Fig. 2. Specific ion intensity of furfural spectrum in GC–MS results of rice husks via citric acid leaching treatment as a function of acid solution concentration.

Table 2 shows chemical compositions of the rice husk ashes when the citric acid solution with different temperature was used in the leaching treatment. The solution concentration and stirring time were 5 mass% and 60 min, respectively. The result in Table 1 indicates that the concentration of 1 mass% is enough for the removal of metallic impurities from the rice husks when the citric acid solution leaching is applied. However, Fig. 2 also suggests that a slight increase of the furfural spectrum intensity with increase in the solution concentration. Accordingly, 5 mass% concentration of the citric acid solution is applied to evaluate the effect of the solution temperature on the removal of metallic impurities. With increase in the temperature, most of the impurities are removed, and a purity of the silica is gradually improved. In particular, it reaches 99.77 mass% by using the citric acid solution of 353 K. In the case of Na_2O, even the acid leaching treatment at 298 K 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. It means that higher temperature of the acid solution is more effective in removing Ca impurity from the rice husks. Fig. 3(a) indicates the Ca content of 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 originated from Table 2. Ca elements are discharged into the acid solution during acid leaching process, and their content of the solution gradually increases with increasing the temperature. By using these measurements, a ratio of the content of Ca impurities discharged from rice husks to the original Ca content is estimated. In this calculation, it is assumed that Ca is removed by only the acid leaching treatment, not the next water rinsing process. Hence, the original Ca content of rice husks is the sum of that of the ashes and the used citric acid solution. As shown in Table 3, the ratio of Ca impurities discharged into the acid solution is 34% by using the ambient temperature acid leaching treatment (298 K). However, it suddenly increases to 72% when the warm acid solution of 313 K is employed. With increase in the solution temperature, the ratio gradually increases, and reaches 94.5% at 353 K. From a viewpoint of a chemical reaction, a higher temperature of the citric acid solution is effective for both formation of Ca complexes by the chelate and hydrolysis reaction from polysaccharides to monosaccharides, and results in the progress of a discharge of the complexes from rice husks.

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Table 2
Quantitative analysis of silica (SiO_2) and impurities contents of rice husk ashes by using citric acid leaching treatment at various temperatures (citric acid solution concentration; 5 mass%, soaking time; 60 min, water rinsing time; 15 min, air combustion conditions; 1073 K × 30 min).

	Citric acid solution temperature				
Mass%	298 K	313 K	323 K	333 K	353 K
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
MoOg	0.00	0.04	0.00	0.00	0.00
C	0.05	0.06	0.04	0.02	0.03

Table 3
Dependence of discharged rate of Ca from rice husks into citric acid solution on solution temperature (concentration of citric acid solution; 5 mass%, stirring time; 60 min).

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

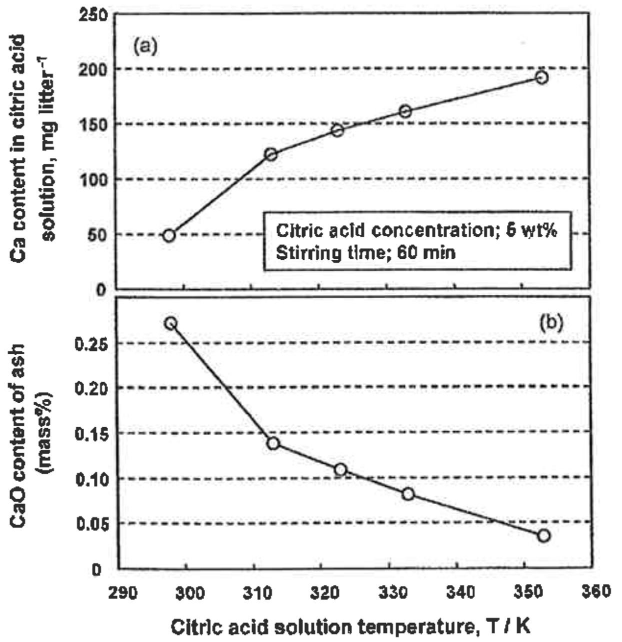

Fig. 3. Ca content in citric acid solution (a) and CaO content of ash (b) dependence on citric acid solution temperature (citric acid solution concentration; 5 mass%, stirring time; 60 min, air combustion temperature; 1073 K).

Fig. 4 indicates the effects of the stirring time during the citric acid leaching and the next water rinsing treatment on the CaO content of the rice husk ashes. The concentration and temperature of the citric acid solution were 5 mass% and 323 K, respectively. The stirring time in the acid leaching and water rinsing treatment are obviously useful to reduce the CaO impurity content. In particular, the citric acid leaching time is much dominant on the reduction of CaO elements. According to the above results shown in Tables 1, 2 and Fig. 1, it is concluded that not only the removal of metal impurities by the chelate reaction, but also the hydrolysis reaction of polysaccharides by the acid leaching treatment dominate largely a purification of SiO_2 elements of the rice husk ashes.

3.2. *Effect of combustion temperature on silica crystal structure and carbon content*

The previous studies have mentioned the effect of the combustion temperature on the crystallization behavior of silica materials contained in rice husk ashes (Ibrahim and Helmy, 1981; Shinohara and Kohyama, 2004). In general, the combustion temperature of rice husks at 973 K or more causes the crystallization of amorphous SiO_2 of the ashes when raw rice husks with no acid leaching treatment are used as starting materials. However, as shown in

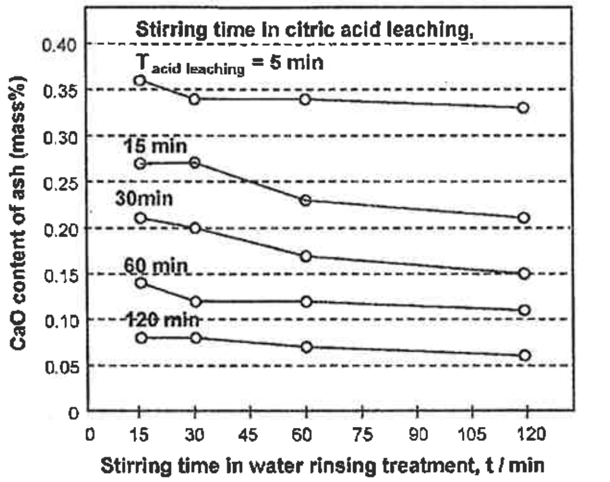

Fig. 4. CaO content of rice husk ashes via citric acid leaching with various stirring time as a function of water rinsing time (citric acid solution; 5 mass% and 323 K, water rinsing at 298 K, air combustion conditions; 1073 K × 30 min).

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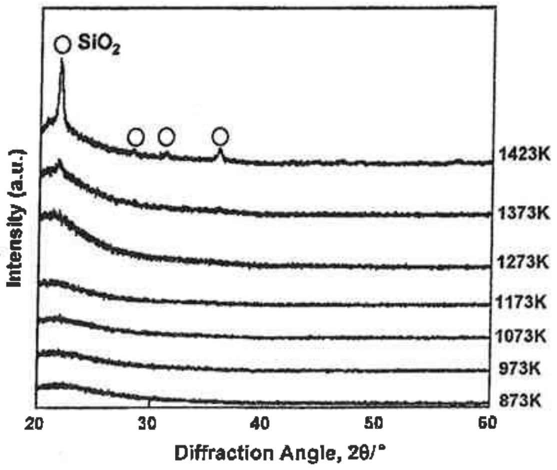

Fig. 5. XRD profiles of rice husk ashes after air combustion at various temperatures (concentration and temperature of citric acid solution leaching treatment are 5 mass% and 323 K, respectively).

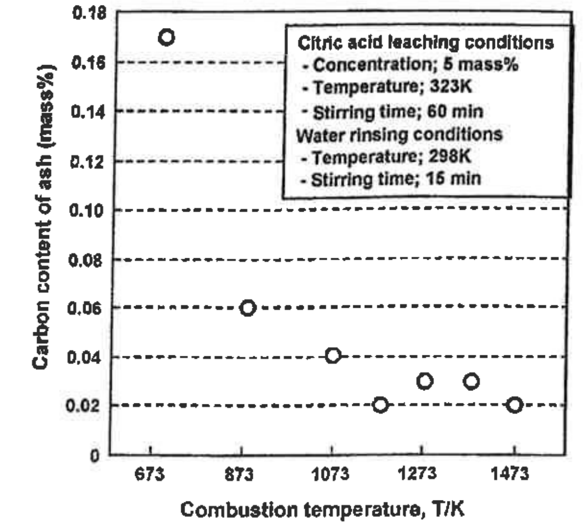

Fig. 6. Dependence of carbon content of rice husk ashes on combustion temperature (citric acid solution concentration; 5 mass%, temperature; 323 K and stirring time; 60 min).

Fig. 5, the crystallization temperature of amorphous silica drastically increases from 973 to 1323 K when the citric acid leaching process is applied to rice husks before combustion. This is because a eutectic phenomenon of SiO_2 via reaction with Na_2O or K_2O impurities is prevented by reducing the content of these alkali metal impurities from the rice husks as mentioned above. However, the heating time in the combustion is not significantly effective on the crystallization of amorphous silica originated in rice husks. This is because the crystallization phenomenon drastically occurs when the materials temperature reaches the critical level in combustion (Shinohara and Kohyama, 2004). Therefore, the heating time of 1.8 ks used in this study is enough to obtain the stable state of silica materials after combustion in air.

At the same time, the combustion temperature also affects the remained carbon content of their ashes. Fig. 6 shows a dependence of the carbon content of the ashes on the combustion temperature. The content was measured by ICP analysis. 5 mass% citric acid solution was used, and the stirring temperature and time during the acid leaching treatment were 323 K and 60 min, respectively. It is obvious that the remained carbon content remarkably decreases from 0.17 mass% to 0.02–0.03 mass% by changing the combustion temperature from 673 to 1073 K. In addition, there is no significant difference of the carbon content by burning the husks over 1073 K. DTA profiles of rice husks in the previous study indicate the exothermic heat due to a combustion of the organics was completely finished at 973 K when the husks via the citric acid leaching treatment was used (Umeda and Kondoh, 2008). It means that pyrolysis of the organics contained in rice husks progresses completely by combustion in air over 973 K. Fig. 7 shows the results of FT-IR analysis of rice husk ashes combusted at 1073 K (a) and 673 K (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 and 791 cm^{-1} due to Si–O–Si stretching modes (Ayres et al., 2007) are detected in (a), and correspond to those of the conventional mineral silica used as reference materials. No spectrum of about 3370–2850 cm^{-1} of the polysaccharides (Ayres et al., 2007; Wang and Sung, 2002) of raw rice husks is obviously observed. It means that a very few carbons originated from the cellulose and hemi-cellulose exist in the ashes after combustion at 1073 K. This result corresponds well to the carbon measurement by ICP analysis shown in Fig. 6. On the other hand, the specimen burned at 673 K shown in Fig. 7(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 CH_2 stretch vibrations (Wang and Sung, 2002), which are also detected in the raw rice husks (c). This means that some of original organics still exist in the ashes after combustion at 673 K, and result in the remarkably large content of the remained carbon elements of ashes burned at 673 K as shown in Fig. 6. Therefore, the combustion temperature of 1073–1273 K is suitable for the preparation of high-purity amorphous silica materials originated from rice husks via the citric acid leaching treatment.

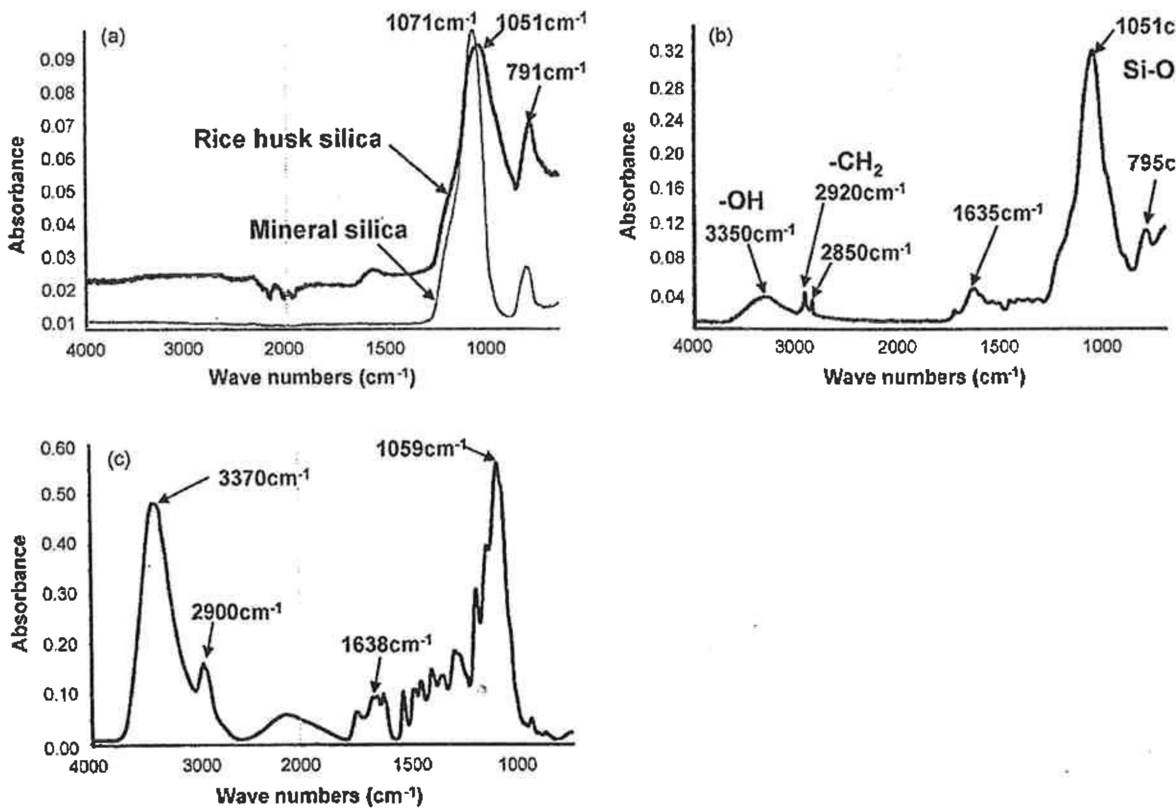

Fig. 7. FT-IR spectra of rice husk ash burned at 1073 K (a) and 673 K (b), compared to commercialized mineral silica particle and raw materials (c).

4. Conclusion

For a high-purification of amorphous silica originated in rice husks, the optimization of the operating parameters in the citric acid leaching treatment and air combustion of rice husks was discussed. When the citric acid solution with a concentration of 1 mass% or more was used, XRF analysis indicated that the metal oxide impurities could be obviously reduced from rice husks during the acid leaching treatment. In particular, the alkali metal oxides of Na_2O and K_2O were completely removed. GC–MS analysis showed the progress of the hydrolysis reaction of their hemi-cellulose of rice husks during the leaching process. As a result, the carbon content of the ashes was drastically reduced to 0.02–0.04 mass% after combustion at 1073–1273 K. The capability to remove Ca impurities from rice husks by the citric acid leaching treatment was dependent on not only the concentration of the acid solution but also the solution temperature and stirring time. The combustion temperature at 1073 K or more was enough to thermally resolve the original carbohydrates of rice husks, and resulted in a very few carbon contents of 0.02–0.03 mass%. On the other hand, when the combustion temperature of 673 K 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. Their ashes including 0.17 mass% carbons were obtained. In the use of the suitable conditions of the acid leaching and air combusting processes, high-purity amorphous silica materials with 99.5–99.77 mass% were produced from rice husks.

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