

Quality Determination of Nickel-Loaded Silica Prepared from Poaceous Biomass

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Klason lignin or preacid hydrolysate of a poaceous biomass such as rice husk, rice straw (*Oryza sativa*), and wheat straw (*Triticum aestivum*) became a good source of highly pure silica by simple calcinations in the testing process for application of high-boiling solvent (HBS) pulping of agricultural byproduct. Especially, Klason lignin or preacid hydrolysis residue of rice husks offered highly purified silica, which was converted to an excellent Ni/SiO₂ catalyst for methanation of carbon dioxide. The Ni/SiO₂ catalyst showed superior properties after the following sequential treatments; preacid hydrolysis of rice husks, HBS pulping of the resultant residue, cellulase hydrolysis of the HBS pulp, calcinations of the resultant powder, impregnation of the silica sample with an aqueous solution of nickel nitrate, and final calcinations.

KEYWORDS: Ni/SiO₂ catalyst; HBS pulping; cellulase; methanation

INTRODUCTION

In view of the global environment and decline of crude oil deposits, the development of a sustainable society becomes one of the most important issues. Total utilization of cellulose, lignin, hemicelluloses, extractives, and ash from woody and poaceous biomass would lead to the securement of regenerable post-oil resources. High-boiling solvent (HBS) pulping using an aqueous solvent such as 1,3-butanediol (bp 208 °C) or 1,4-butanediol (bp 232 °C) is an organosolv pulping method (1). It has the following characteristics: (1) HBS-pulp bears comparison with Kraft pulp, (2) HBS pulping can be used for both softwood and hardwood, (3) vapor pressure is relatively low compared to other organosolv pulping methods, (4) there is no need to add a catalytic substance, (5) HBS is recoverable, and (6) recovered HBS (RHBS) has a stimulating effect on delignification (2–5). A delignification mechanism during HBS pulping was proposed using ¹H–¹³C correlation 2D NMR spectroscopy (6).

In accord with the above observations, we undertook a verification test and application of this new type of organosolv pulping (7) including HBS pulping of softwood, hardwood, and agricultural byproducts such as husk and straw from rice plants and wheat straw, preparation of monosaccharide by diluted-acid hydrolysis, enzymatic saccharization of HBS pulp, quality determination of silica contained in such agricultural residues, preparation of fiberboard, and application of HBS lignin to the medical field such as inhibition of replication of human immunodeficiency virus (HIV) using the reporter assays with pLTR-(HIV)-luc and pNF-κB-luc (8).

The primary purpose of this investigation is to explore the possibility of total utilization of major ingredients from woody or

poaceous biomass. Lignin is one of the main cell wall components in woody plants. The HBS-lignin obtained is a mixture of relatively low molecular weight lignin compared to the Kraft lignin, and such small molecules might be important for biomedical studies. On the other hand, because HBS pulping of agricultural husks is also possible, utilization of cellulose, hemicelluloses, and silica from poaceous biomass would be worth pursuing. **Figure 1** represents a model biomass refinery process utilizing the HBS pulping system.

The demand for new materials and products from biomass is growing, and interest in naturally formed silica biomineralization is also increasing (9). Silica is important as a catalyst carrier as well as adsorbent material or column packing. For example, Ni/SiO₂ is an important industrial catalyst (10, 11), which is used for hydrogen refining, hydrogenation of olefin, and steam re-forming of hydrocarbon, etc. In this paper, we describe the physical and chemical properties of silica prepared from rice husks, rice straw, and wheat straw, its characteristics in Ni/SiO₂ prepared from the above silica, and its ability to catalyze the methanation reaction of CO₂ (CO₂ + 4H₂ → CH₄ + 2H₂O).

EXPERIMENTAL PROCEDURES

Materials. Agricultural byproducts used were rice husks, rice straw (*Oryza sativa*), and wheat straw (*Triticum aestivum*) provided from the Experiment Farm of Hokkaido University and HOKUREN Federation of Agricultural Cooperatives. All poaceous samples were air-dried; straws were cut into 3 cm lengths and stored.

HBS Cooking with Agricultural Byproducts. Cooking was conducted in 100 mL stainless steel pressure vessels using 70% HBS (1,4-butanediol) for agricultural byproducts. The vessels were immersed in a 4 L autoclave equipped with a hot oil bath as previously described (2). Analytical cookings were conducted in five 20-mL stainless steel pressure vessels. The time to maximum temperature (473 K) was 90 min, and each vessel was singly taken out from the hot oil bath at each 30, 60, 90, 120, and

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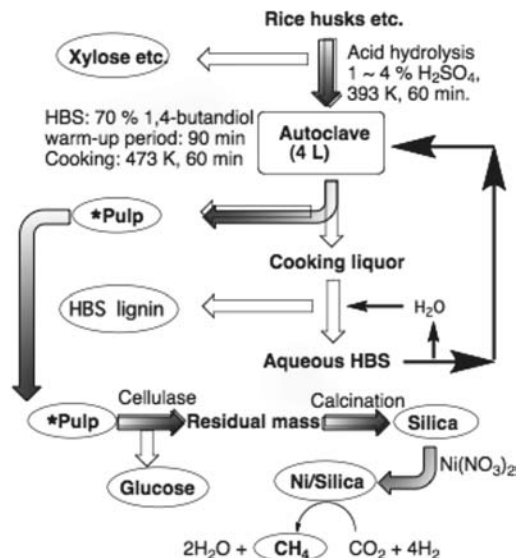


Figure 1. Schematic diagram of a model biomass refinery process utilizing the HBS pulping system: silica and Ni/silica preparations incorporated in the HBS pulping system are indicated by bold arrows with gradation; preparations of xylose, pulp, HBS lignin, and glucose are shown by white outline arrows; flow of recyclable HBS is shown by bold arrows.

180 min to determine the optimum delignification conditions. Yields of pulp, Klason lignin, and ash were determined according to a previously described method (2).

Preparation of Silica and Ni/SiO₂ Catalysts. In the first method (method A), the agricultural waste was incinerated in air at 873 K for 7 h after calcining over a gas burner. The acid treatment in the second method (method B) is essentially the same as the preparation of Klason lignin; the waste was immersed in 72 wt % sulfuric acid and kept at room temperature for 2 h under reduced pressure to allow the acid permeate into the sample. During this treatment, the mixture was stirred several times. Then, distilled water was added slowly to reduce the acid concentration to 4 wt %. The resulting mixture was autoclaved at 393 K for 1 h, filtered out, washed with distilled hot water, and dried. The resulting Klason lignin was incinerated under the same conditions as method A. In the third method (method C), the waste was autoclaved in 4 wt % sulfuric acid at 393 K for 1 h, filtered out, washed with distilled hot water, and dried. The prehydrolytic residue of the waste was incinerated under the same conditions as method A. Henceforth, the silica samples obtained are designated silica-1A, silica-2B, etc. The numbers 1, 2, and 3 denote the sources of silica are rice husk, rice straw, or wheat straw, respectively, and A, B, and C indicate the methods employed for the preparation of the samples. Silica-1CHC (silica-1C-HBS pulping-cellulase treatment) was prepared from the rice husks that were supplied to the sequential processing: 1% sulfuric acid treatment at 393 K for 1 h, HBS pulping of the resultant residue at 473 K for 1 h, cellulase treatment (conditions: pH 5.0, 323 K, 24 h, 2 mg of protein/mL, cellulase; 6200–7580 IU/g, *Tricoderma* cellulase (Genecor), a gift from Mitsui Engineering and Shipbuilding Co. Ltd.) of the resultant residue, and incineration of the resultant solid as in the case of method A. For comparison, a silica gel purchased from Aldrich (Davisil 646) was also employed. It was designated silica-D.

Supported nickel catalysts were prepared by impregnation of the silica samples with an aqueous solution of nickel nitrate. The catalysts were calcined in air at 773 K for 3 h and reduced with a pure H₂ stream at 873 K for 3 h. The nominal content of Ni was 5 wt % for all of the reduced catalysts.

Characterization. Chemical composition was determined by X-ray fluorescence (XRF) spectroscopy. X-ray powder diffraction (XRD) patterns were recorded on a diffractometer (JEOL JDX-8030) using nickel-filtered Cu K α radiation. BET surface area and pore size distribution were obtained from nitrogen adsorption–desorption measurements using an automatic physisorption instrument (Quantchrome NOVA 1200). The crystallite sizes of NiO of the calcined catalysts and those of Ni of the reduced catalysts were determined from the full width at half-maximum of NiO(012) and Ni(100) XRD peaks by the Scherrer equation, $d = 0.92L/(b \cos \theta)$.

Table 1. Yield of HBS Pulping of Agricultural Byproduct

| | HBS pulp (%) | KL ^a in pulp (%) | ash in pulp (%) | HBS lignin (%) |
|-------------|--------------|-----------------------------|-----------------|----------------|
| rice husks | 57.0 | 2.5 | 39.5 | 18.5 |
| rice straw | 41.2 | 0.7 | 37.6 | 23.8 |
| wheat straw | 32.5 | 2.0 | 24.1 | 28.9 |

^a Klason lignin corrected by amount of ash.

Temperature-Programmed Reduction (TPR). The reducibility of NiO species on the calcined catalysts was studied by a TPR method. The calcined catalyst (0.25 g) was packed in a fixed bed flow reactor and heated from room temperature to approximate 1000 K at a rate of 5 K/min in a stream of 4% H₂–N₂ mixture at a total flow rate of 50 cm³/min. The concentration of H₂ in the outflow from the reactor was determined by gas chromatography.

CO₂ Methanation. Methanation of CO₂ was carried out over the supported nickel catalysts at atmospheric pressure in a differential flow reactor. The calcined catalyst (0.5 g) was packed in the reactor and reduced with H₂ at 873 K for 3 h. After the reduction, the catalyst was subjected to a CO₂–H₂ mixture (CO₂/H₂ = 1:9) at a total flow rate of 100 cm³/min. Gases in the outflow were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Sugar Content in Hemicelluloses of Agricultural Byproducts.

Before the start of HBS pulping of agricultural byproducts, we confirmed that HBS pulping of softwood and hardwood proceeded in a reproducible fashion as described previously (1, 2). To utilize HBS pulp and HBS lignin of agricultural byproducts, we first analyzed components of rice husks, rice straw, and wheat straw, respectively, and then HBS pulping of these samples was executed. Among them, rice husks showed an ideal result in the yield of HBS pulp, Klason lignin of HBS pulp, ash, and HBS lignin (Table 1). Method B is associated with preparation of Klason lignin. Table 1 indicates that a major component of Klason lignin obtained from HBS pulp is silica, of which yields from Klason lignin are 94.0% from rice husks, 98.2% from rice straw, and 92.3% from wheat straw, respectively. Prehydrolysis of HBS pulping is needed to utilize hemicelluloses contained in the woody and poaceous biomass, and prehydrolysis using aqueous sulfuric acid is associated with method C and preparation of silica-1CHC. Rice husks are a good source of xylose, because only the supernatant fluid from acid-hydrolyzed rice husks was abundant in xylose (Xyl, 77.8%; Ara, 11.1%; Glc, 5.8%; Gal, 4.7%; and Man, 0.6%, in constituent sugar analysis for 1% H₂SO₄ hydrolytic solution of rice husks), whereas treatments of rice straw and wheat straw gave glucose and xylose as major components (Glc, 55.1%; Xyl, 30.6%; Ara, 6.5%; Man, 4.7%; and Gal, 3.1%, for 1% H₂SO₄ hydrolytic solution of rice straw; Glc, 38.3%; Xyl, 33.4%; Man, 17.0%; Ara, 8.2%; and Gal, 2.7%, for 1%-H₂SO₄ hydrolytic solution of wheat straw). These results suggest that rice husks contain arabinoxylan as a major hemicellulose, whereas straws contain glucose-rich polysaccharides such as xyloglucan and glucomannan, as well as arabinoxylan. The yield of HBS pulp and the ratio of ash in the pulp, prepared from rice husks, were highest among the agricultural waste. In addition, each amount of ash in the waste (21.8% ash in rice husks, 15.6% in rice straw, and 8.9% in wheat straw, which were determined by a composition analysis) was comparable to each total amount of ash deduced from the yield of HBS pulp (22.5% ash from rice husks, 15.4% from rice straw, and 7.8% from wheat straw). These data indicate that almost all silica is accumulated in HBS pulp that is involved in the preparation of silica-1CHC, and Klason lignin associated with method B retains silica, too, because these ashes are evaluated as silica in this study. Therefore, preparation of silica-1CHC could be carried out without loss of silica.

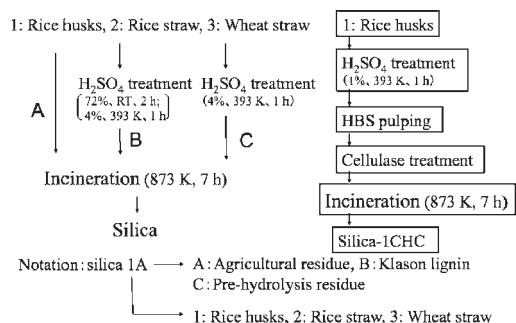


Figure 2. Preparation of silica. Poaceous biomass was treated by three methods: method A without acid treatment, methods B and C with acid treatment. Silica-1CHC was prepared via HBS pulping system from rice husks.

Table 2. Chemical Compositions of Silica Prepared from Poaceous Biomass

| silica | concentration (mol %) | | | | | | |
|--------|-----------------------|-----|-----|------|-----|-----|-----|
| | Si | Na | Mg | K | Ca | P | S |
| 1A | 83.7 | | | 11.1 | 2.1 | 2.0 | |
| 2A | 73.0 | | 2.1 | 11.8 | 4.8 | 3.8 | 1.0 |
| 3A | 52.0 | 3.3 | 2.4 | 24.6 | 6.0 | 7.5 | 3.4 |
| 1B | 99.3 | | | | | | 0.1 |
| 2B | 99.8 | | | | | | |
| 3B | 99.1 | | | | | | |
| 1C | 99.6 | | | | | | 0.1 |
| 2C | 99.8 | | | | | | 0.1 |
| 3C | 98.1 | | | 0.9 | | | 0.6 |
| 1CHC | 99.7 | | | | | | 0.3 |

Preparation of Silica from Agricultural Byproducts. Preparation of silica from rice husks, rice straw, and wheat straw was carried out as shown in **Figure 2**. Method A indicates incineration of agricultural residue without any acid treatment, whereas methods B and C indicate incineration of Klason lignin (treatment of agricultural residue with 72% H_2SO_4 at room temperature for 2 h followed by 4% H_2SO_4 treatment at 393 K for 1 h) and incineration of prehydrolysis residue (treatment of agricultural residue with 4% H_2SO_4 at 393 K for 1 h), respectively. Notation of silica shows that the number represents each agricultural residue and A, B, and C indicate incineration conditions mentioned under Experimental Procedures. For instance, silica-1A, silica-2B, and silica-3C mean silica prepared from rice husks by method A, silica prepared from rice straw by method B, and silica prepared from wheat straw by method C, respectively. Preacid hydrolysis with 1% H_2SO_4 , HBS pulping, and cellulase treatment are included in the preparation of silica-1CHC before incineration. Silica purchased from Aldrich (Davisil 646) was also employed for comparison. It was designated silica-D.

Quality Determination of Silica from Agricultural Byproducts. **Table 2** shows the chemical abundance of silica obtained from each agricultural byproduct. Silica-1A was prepared from rice husks composed of 83.7% silica and 11.1% potassium, whereas silica-2A and silica-3A were prepared from rice straw and wheat straw composed of 73.0 and 52.0% silica, respectively, including various other impurities such as potassium, calcium, phosphorus, sulfur, and magnesium. Especially, silica-3A showed a characteristic pattern in XRD analysis and a distinguishing configuration on the SEM image that might be formed as a consequence of sodium being one of the impurities (**Figures 3** and **4**). The sharp peaks observed in the XRD pattern of silica-3A could be assigned to cristobalite (crystallized silica) and potassium sulfate. The

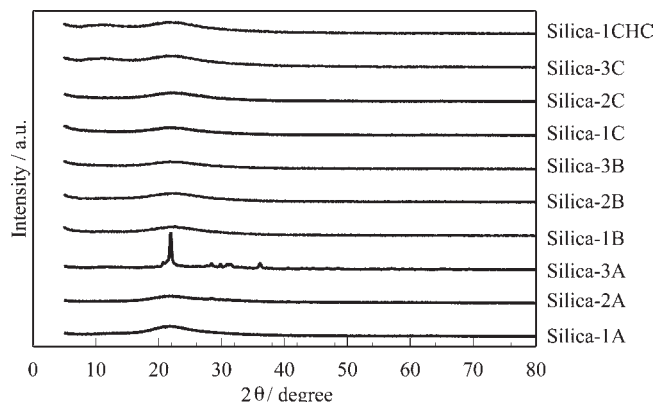
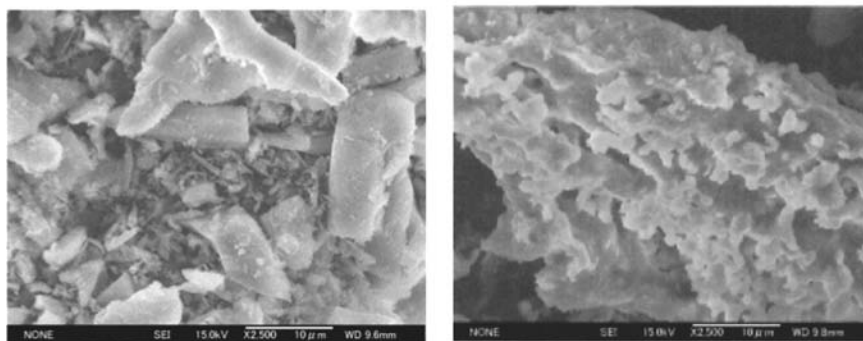


Figure 3. XRD pattern of silica prepared from poaceous biomass.

environment of silica in wheat straw is extremely different from those in rice straw and rice husks. The constituent ratio of ash is lowest among the poaceous biomass (ash: 8.9% in wheat straw, 15.6% in rice straw, 21.8% in rice husks), whereas those of extractives and unidentified components such as proteins except for Klason lignin and constituent sugar were highest. (Extractives: 11.1% in wheat straw, 2.4% in rice straw, 0.6% in rice husks. Unidentified components: 20.3% in wheat straw, 13.3% in rice straw, 7.1% in rice husks. Klason lignin: 9.5% in wheat straw, 3.5% in rice straw, 20.2% in rice husks. Constituent sugar: 50.3% in wheat straw, 65.2% in rice straw, 50.3% in rice husks). These data suggest that the environment abundant in extractives and unidentified components in wheat straw is better suited for crystallization of silica and/or other minerals. Venezia et al. reported that calcination at high temperature of amorphous silica, impregnated with alkali ion solutions, drives the transition to the different crystalline phases of silica. Among the considered ions, sodium acts as the greatest destabilizer of amorphous silica even when present in a small amount (12). As shown in **Table 2**, silica-3A contains 3.3% Na, which is not detected in the other silica samples. Thus, the sodium ions in wheat straw may be a cause of crystallization of silica-3A. B and C series silicas prepared from Klason lignin and preacid treatment of the agricultural residue were much purer silicas, >98.1%.

Quality Determination of NiO/SiO₂ Catalysts from Agricultural Byproducts. To complete high dispersion of reactants, a catalyst carrier requires a broad specific surface area (BET surface area) (13) and large pore volume. Its pore size is also important, because small pore size sometimes decreases the overall reaction rate by dispersion in the fine pores. Silica-B and silica-C prepared from Klason lignin and acid hydrolysis residue have adequate specific surface, pore volume, and pore size and are assumed to be useful as catalyst carriers as shown in **Table 3**. BET surfaces and pore volumes of silica-1A, silica-2A, and silica-3A are very low compared with those of silica-B and silica-C series. Although silica-A series have relatively large pore diameters, the pores are shallow as shown in **Figure 5**. The low surface area and the small pore volume of silica-3A would result from its high crystallinity as shown in **Figure 3**. On the other hand, impurities involved in silica-1A and silica-2A might block their pores, resulting in the inhibition of the formation of the broad specific surface area and large pore volume with depth observed in silica-B and silica-C series. NiO/SiO₂ catalysts were prepared by using silica-1A, silica-1B, and silica-1C from rice husks. XRD patterns of NiO/SiO₂ catalysts after calcinations of acid-treated samples (silica-C series) and Klason lignin samples (silica-B series) showed three significant peaks resulted from NiO, whereas those without any acid treatment showed deranged patterns (silica-2A and silica-3A) as

SEM Image (x 2500)



Silica 1A

Silica 3A

Figure 4. SEM images of silica-1A and silica-3A. Silica from wheat straw (silica-3A) shows characteristic structure on the surface caused by impurities.

Table 3. Textural Properties of Silica Prepared from Poaceous Biomass

| silica | BET surface area (m ² /g) | pore volume (cm ³ /g) | average pore diameter (nm) |
|--------|--------------------------------------|----------------------------------|----------------------------|
| 1A | 43 | 0.185 | 8.5 |
| 2A | 11 | 0.051 | 8.7 |
| 3A | 3 | 0.008 | 4.5 |
| 1B | 298 | 0.401 | 2.7 |
| 2B | 186 | 0.310 | 3.3 |
| 3B | 291 | 0.398 | 2.7 |
| 1C | 364 | 0.410 | 3.2 |
| 2C | 277 | 0.371 | 2.7 |
| 3C | 235 | 0.373 | 3.1 |
| 1CHC | 247 | 0.334 | 2.7 |
| D | 294 | 0.96 | 15 |

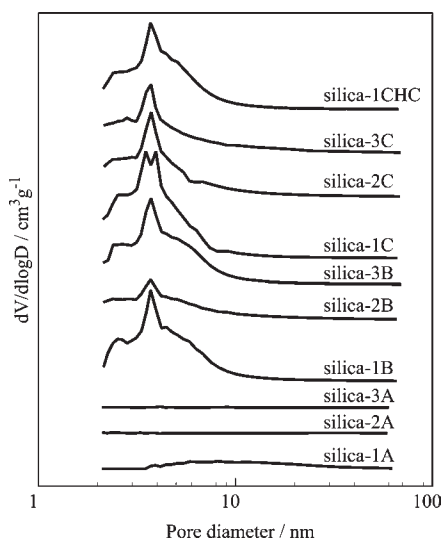


Figure 5. Pore size distribution curves of silica prepared from poaceous biomass.

shown in **Figure 6**. XRD patterns of Ni/SiO₂ catalysts after hydrogen reduction showed a similar tendency; those of silica-1A and silica-2A as well as the acid-treated series (silica-C series) and Klason lignin samples (silica-B series) showed three relatively clear peaks attributed to Ni, whereas that of silica-3A showed many sharp peaks originating from silica-3A along with those of Ni (data not shown). These data suggested that silica-B and -C series would have excellent catalytic activity for hydrogen

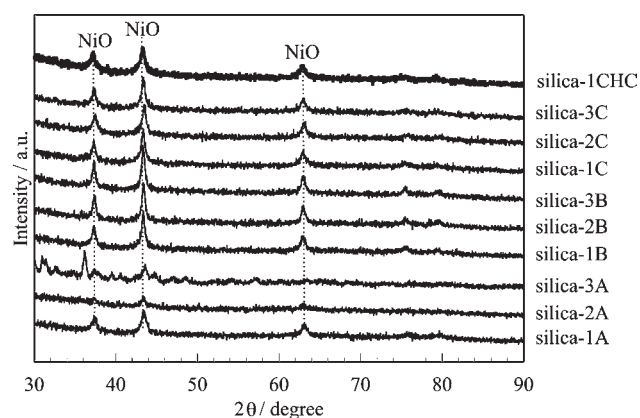


Figure 6. XRD pattern of NiO/silica catalyst prepared from poaceous biomass.

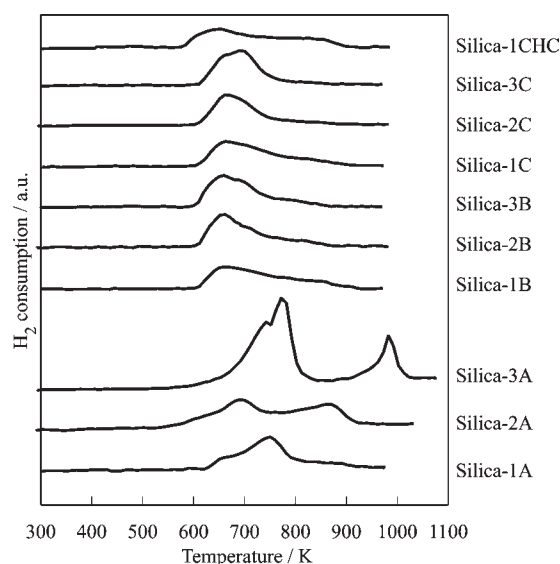


Figure 7. TPR profile of NiO/silica catalyst prepared from poaceous biomass.

reduction of CO₂, and silica-1A might have some catalytic activity, too. The reducibility of each NiO was examined by TPR. **Figure 7** represents the TPR profiles of the calcined catalysts, and all of the catalysts except Ni/silica-3C in the acid-treated B and C series revealed a highest TPR peak at 650 K,

Table 4. CO₂ Methanation over Silica-Supported Ni Catalyst Prepared from Poaceous Biomass^a

| catalyst | diameter ^b (nm) | formation rate ($\mu\text{mol min}^{-1} \text{g}^{-1}$) | | S_{CH_4} ^c (%) |
|----------------|----------------------------|---|------|------------------------------------|
| | | CH ₄ | CO | |
| Ni/silica-1A | 10 | 0.1 | 12.2 | 0.8 |
| Ni/silica-2A | 21 | 0.0 | 0.4 | 0.0 |
| Ni/silica-3A | 53 | 0.0 | 0.0 | |
| Ni/silica-1B | 20 | 18.9 | 2.1 | 90.0 |
| Ni/silica-2B | 22 | 11.9 | 2.5 | 82.6 |
| Ni/silica-3B | 27 | 11.2 | 3.6 | 75.7 |
| Ni/silica-1C | 21 | 19.5 | 3.4 | 85.5 |
| Ni/silica-2C | 21 | 12.3 | 4.3 | 74.1 |
| Ni/silica-3C | 20 | 2.1 | 12.3 | 14.5 |
| Ni/silica-1CHC | 30 | 28.0 | 3.5 | 88.9 |
| Ni/silica-D | 20 | 21.7 | 9.1 | 70.5 |

^a Reaction conditions: catalyst, 0.5 g; total flow rate, 100 cm³/min; CO₂, 0.1 atm; H₂, 0.9 atm; temperature, 523 K. ^b Diameter of Ni particles determined by XRD. ^c Selectivity to CH₄ (= CH₄/(CH₄ + CO)).

which was assigned to the reduction of NiO to Ni (14–16). TPR profiles of A-series silica without acid treatment are rather complex, and the TPR peaks at 780, 870, and 990 K could be assigned to the reduction of the carbon species remaining on the catalyst supports, because the total amounts of hydrogen consumed were more than twice as much as that of NiO over these catalysts.

The NiO/SiO₂ catalysts were reduced with H₂ and then used for CO₂ methanation experiments. The results of methanation reaction of CO₂ (CO₂ + 4H₂ → CH₄ + 2H₂O) with these catalysts are shown in **Table 4**. Silica-1A afforded CO and a small amount of CH₄, whereas silica-1B and silica-1C selectively generated CH₄. These results might be correlated to the fact that silica-1B and silica-1C are highly pure compared to silica-1A, which contains potassium, calcium, and sulfur. CO₂ methanation proceeds through the formation of CO, which dissociates to surface carbon species and oxygen species over the Ni surface and is further hydrogenated to CH₄ and H₂O (11, 17–19). The cause of CO formation by silica-1A may be due to impurities that disturb the second reaction step. It is highly suggested that the inorganic impurities of the support migrate to the surface of Ni particles and retard the reaction (19). The activities of Ni/silica-1B and -1C are comparable with that of the catalyst supported on the highly pure commercial silica (Ni/silica-D) and showed rather greater selectivity on methanation (CH₄/CH₄ + CO) than Ni/silica-D.

Effect of HBS Pulping and Cellulase Treatment on Preparation of Ni/SiO₂ Catalyst. To determine the effect of refinement of HBS lignin and glucose as well as xylose-rich monosaccharide on the preparation of the Ni/SiO₂ catalyst, we next carried out sequential batch processing: HBS pulping of rice husks treated with 1% H₂SO₄, cellulase treatment of the resultant HBS pulp, and incineration of the residual solid. The obtained silica (silica-1CHC, silica-1C-HBS pulping-cellulase treatment) showed textural properties and XRD pattern similar to those of silica-B and -C series (**Figure 3**). The pattern of pore size of silica-1CHC shows resemblance to that of silica-C series, too, as shown in **Figure 5**. The NiO/SiO₂ catalyst (Ni/silica-1CHC) was prepared from silica-1CHC, impregnated with an aqueous solution of nickel nitrate. The XRD pattern of Ni/silica-1CHC after hydrogen reduction was similar to that of Ni/silica-1C, whereas the diameter (30 nm) of the Ni particle of Ni/silica-1CHC determined by XRD was larger than those (each 20 nm) of Ni/silica-1C and Ni/silica-D as shown in **Table 4**. The formation rate of methane catalyzed by Ni/silica-1CHC was higher (28 $\mu\text{mol min}^{-1} \text{g}^{-1}$) than those of Ni/silica-1C (19.5 $\mu\text{mol min}^{-1} \text{g}^{-1}$) and Ni/silica-D (21.7 $\mu\text{mol min}^{-1} \text{g}^{-1}$), and the selectivity to methane with the

catalyst was excellent (CH₄/(CH₄ + CO) = 88.9%). The relationship between catalytic activities and silica prepared with different methods from various biomasses could be deduced from **Tables 2–4** and **Figures 5–7**. Catalytic activities of Ni/silica prepared from silica-A series are nothing or very poor, because of the presence of impurities, small BET surface area, and small pore volume. Catalytic activities of Ni/silica prepared from silica-B and -C series were high except for Ni/silica-3C, the support of which contains impurities such as potassium and sulfur. Alkaline metal impurities such as potassium and sodium cause the carbons to remain in ashes as reported previously (20). All active Ni/silica prepared with methods B and C showed a characteristic TPR peak at 650 K, whereas nonactive Ni/silica prepared with method A showed different TPR peaks at 700, 840, 780, 870, and 990 K as shown in **Figure 7**, and silica-A series did not show the characteristic pore size distribution pattern as indicated in **Figure 5**. Therefore, acid treatment is essential for the preparation of Ni/silica catalyst from agricultural biomass. The most active Ni/silica catalyst, Ni/silica-1CHC, has the diagnostic characters as the excellent catalyst. Although no essential difference among Ni/silica-1CHC, Ni/silica-1B, and Ni/silica-1C has been detected except for chemical composition and subtle differences among the profiles of TPR evaluation, the successive removals of hemicellulose, lignin, and cellulose might be useful for the elimination of undetected impurities, because the hierarchical microshell structure of rice husk makes it difficult to eliminate trace amounts of carbon and other impurities by methods B and C, and even the other leaching method (21).

The HBS pulping process was found to be an attractive method not only for the production of pulp (1–5) but also for the production of medicinal lead compounds such as anti-HIV drugs (8). In this study, we focused our attention on utilization of silica prepared from poaceous biomass related to the HBS pulping process. Especially, rice is a staple for a large part of the world's population, and rice husks are a major agricultural byproduct produced annually in various area such as the East, South and Southeast Asia (22). Rice husks used in this study were determined to contain 50.3% of constituent sugar, 21.8% of ash, 20.2% of Klason lignin, 0.6% of extractives, and 7.1% of other components. HBS pulping of rice husks produced HBS pulp containing 39.5% of silica in 57.0% yield, which means almost all silica contained in the agricultural byproduct remained in the HBS pulp. HBS pulping of rice husks gave HBS pulps maintaining their original shapes, which were held with cellulose and silica. Cellulase treatment of the HBS pulp gave glucose, and its yield was 27.4% at a maximum. Although some innovative method might be needed to improve the yield of glucose, rice husks could be good sources of xylose obtained by preacid hydrolysis, glucose obtained by cellulase treatment of HBS pulp, HBS lignin that could be used as medicinal substances (8), and highly pure silica, which would be used for various silica-supported metal catalysts including Ni/SiO₂, Cu/SiO₂, Al/SiO₂, and Fe/SiO₂ (23–31), from the viewpoint of biomass refinery process.

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