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Hydrolysis of Sugars Using Magnetic Silica Nanoparticles with Sulfonic Acid Groups

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$CoFe_2O_4$-embedded silica nanoparticles containing sulfonic acid groups were found to be highly active solid acid catalysts for hydrolysis of disaccharides (sucrose and cellobiose) and polysaccharides (starch and cellulose) with facile magnetic separation.

Biomass utilization has received much attention due to depletion of fossil fuels and global warming issues. Lignocellulosic biomass composed of cellulose, hemicellulose, and lignin is considered a desirable biomass resource. Cellulose decomposition is one of the most important biorefinery processes for the production of biofuels and bioplastics.[1–4] Recently, solid acid catalysts have been applied for the cellulose hydrolysis as a replacement of liquid sulfuric acid.[5–10] SO_3H-appended carbon materials including sulfonated activated carbon,[5] amorphous carbon,[6] mesoporous carbon,[7] and silica/carbon hybrids[8] are found to be active for the reaction. Although these sulfonated materials are potential candidates, further developments of solid acids are required because the hydrolysis is carried out at the interface between the solid surface and macromolecular cellulose, resulting in poor accessibility of the substrate with active sites.

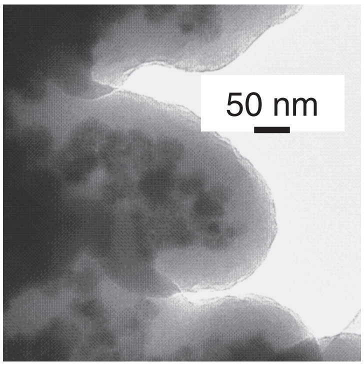
In this regard, we considered that the use of nanoparticles as a solid catalyst is a powerful approach to overcome the difficulty of the solid–solid reaction. The nanoparticle acid catalysts are expected to be dispersed in water solution, resulting in facile interaction with cellulose. However, the use of nanoparticle catalysts simultaneously suffers from the difficulty of catalyst recovery from the solution by sedimentation or filtration. In order to prevent this problem, we adopted magnetic separation by using magnetic nanoparticles. Recently, magnetic separation of catalyst has been widely investigated for several reactions including acid–base reactions[11–15] and redox reactions.[16,17] Magnetic solid acid catalysts have been applied to esterification,[11] deacetalization,[12] *N*-formylation,[13] and hydrolysis.[14] Herein, we prepared sulfonic acid-appended magnetic silica nanoparticles and applied them to hydrolysis of sugars including sucrose, cellobiose, starch, and cellulose.

The sulfonic acid bearing magnetic silica nanoparticles were prepared as follows (See Supporting Information).[12,18,19] First, magnetic $CoFe_2O_4$ nanoparticles (MNPs) were synthesized by using $CoCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, and sodium dodecyl sulfate in the presence of methylamine. After dispersion of MNPs in ethanol solution, a mixture of isopropanol and water was added to the solution with sonication. Second, 3-sulfanylpropyltrimethoxysilane (SPTMS) was added to the solution in the presence of aqueous NH_3 with sonication. After washing three times with water and drying in vacuo overnight, the silica-coated magnetic nanoparticles functionalized with thiol groups (MNPs@SiO_2–SH) were obtained. Third, silica-coated magnetic nanoparticles functionalized with sulfonic acid groups (MNPs@SiO_2–SO_3H) were prepared by oxidation of thiol groups by using 30% aqueous H_2O_2 solution. After washing with water and drying, MNPs@SiO_2–SO_3H catalyst was obtained.

X-ray diffraction (XRD) patterns revealed the formation of $CoFe_2O_4$ nanoparticles (See Supporting Information, Figure S1[19]). The spinel structure of $CoFe_2O_4$ was maintained after silica coating and successive thiol oxidation. Figure 1 shows transmission electron microscopy (TEM) images of MNPs@SiO_2–SH and MNPs@SiO_2–SO_3H samples. Aggregation of nanoparticles of ca. 20–50 nm in size were observed for $CoFe_2O_4$ MNPs (Figure S2[19]). These $CoFe_2O_4$ nanoparticles were successfully coated with silica formed by condensation of SPTMS. The silica layer thickness of MNPs@SiO_2–SH was ca. 50–60 nm. No change of morphology was observed before and after the thiol oxidation.

Hydrolysis of sucrose was first examined by using MNPs, MNPs@SiO_2–SH, and MNPs@SiO_2–SO_3H samples. Sucrose is a disaccharide derived from glucose and fructose which consists

(A) MNPs@SiO_2-SH



(B) MNPs@SiO_2-SO_3H

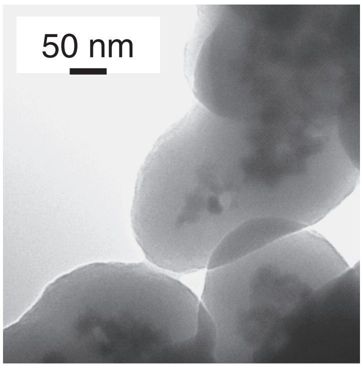
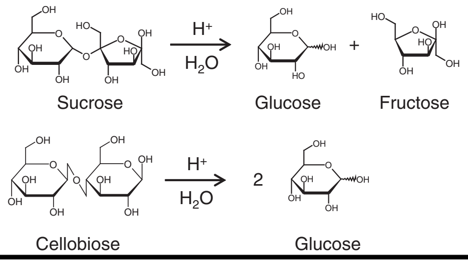


Figure 1. TEM images of (A) MNPs@SiO_2–SH and (B) MNPs@SiO_2–SO_3H.

Table 1. Hydrolysis of disaccharides using MNPs@SiO_2–SO_3H



Entry	Catalyst	Sucrose hydrolysis[a]	Cellobiose hydrolysis[b]
		Glucose yield/%	Glucose yield/%
1	MNPs[c]	0	0
2	MNPs@SiO_2–SH[c]	0	0
3	MNPs@SiO_2–SO_3H	93 (0.62[d])	88 (0.64[e])
4	Amberlyst-15	22 (0.16[d])	34 (0.21[e])

[a] *Reaction conditions*: Sucrose (0.3 g), catalyst (amount of SO_3H: 75 µmol), water (3.0 mL), 373 K, 20 min. [b] *Reaction conditions*: Cellobiose (0.3 g), catalyst (amount of SO_3H: 75 µmol), H_2O (3.0 mL), 393 K, 18 h. [c] 0.14 g was used. [d] Turnover frequency (min^{-1}). [e] Turnover frequency (h^{-1}).

of α-1,2-glycosidic bonds. Sucrose was not hydrolyzed in the presence of MNPs (Table 1, Entry 1) and MNPs@SiO_2–SH (Table 1, Entry 2) due to the absence of sulfonic acid groups. MNPs@SiO_2–SO_3H exhibited high catalytic performance for sucrose hydrolysis, resulting in 93% glucose yield for 20 min accompanied with equivalent fructose yield (Table 1, Entry 3). Acid–base titration by using NaOH indicated that MNPs@SiO_2–SO_3H have 0.5 mmol g^{-1} acid sites. Turnover frequency (TOF) of the catalyst was, therefore, estimated to be 0.62 min^{-1}. Under the same reaction conditions, a strongly acidic ion-exchange resin, Amberlyst-15 (sulfonated polystyrene-based cation-exchangeable resin) was used as a comparison. The resin also showed hydrolysis activity (Table 1, Entry 4). TOF for Amberlyst-15 was, however, much lower (0.16 min^{-1}) than that of MNPs@SiO_2–SO_3H. The MNPs@SiO_2–SO_3H catalyst also exhibited high performance for hydrolysis of cellobiose, a disaccharide derived from two glucose units which consists of β-1,4-glycosidic bonds.

Magnetic properties of MNPs@SiO_2–SO_3H were investigated by using a superconducting quantum interference device (SQUID) (Figure S3[19]). The saturation magnetization of the MNPs@SiO_2–SO_3H was 5.9 emu g^{-1} at 300 K, which is enough for magnetic separation. Actually, the MNPs@SiO_2–SO_3H could be easily recovered by Neodymium magnet after the reaction as shown in Figure 2 (see also Figure S4[19]). After the reaction, the catalyst was washed with water and dried in vacuo overnight. The catalyst could be recycled at least three times without significant loss of activity. For cellobiose hydrolysis {Reaction conditions: cellobiose (0.3 g), catalyst (amount of SO_3H: 75 µmol), H_2O (3.0 mL), 393 K, 9 h}, glucose yield was 59%, 50%, and 63% for fresh, 1st reuse, and 2nd reuse catalyst, respectively.

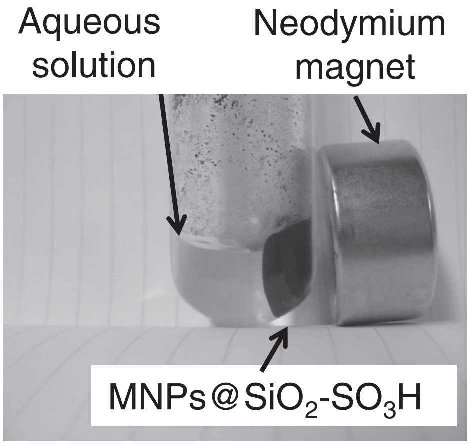


Figure 2. Magnetic separation of MNPs@SiO_2–SO_3H after sucrose hydrolysis.

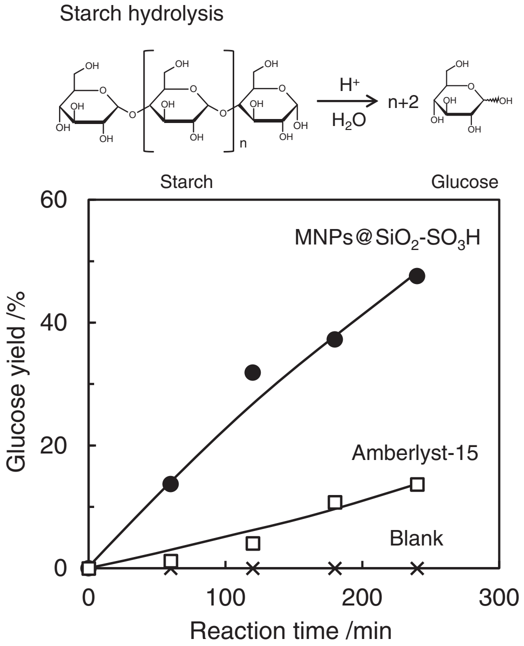
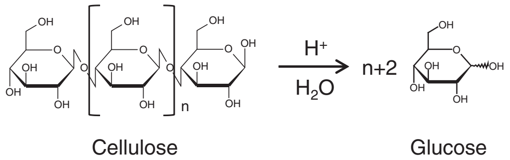


Figure 3. Starch hydrolysis over MNPs@SiO_2–SO_3H (Reaction conditions: starch (0.2 g), catalyst (amount of SO_3H: 0.48 mmol), H_2O (5 mL), 403 K).

Next, hydrolysis of starch, a polysaccharide derived from glucose with α-glycosidic bonds was examined. The results are shown in Figure 3. Again, MNPs@SiO_2–SO_3H showed much higher activity for the polysaccharide hydrolysis than Amberlyst-15. The catalyst afforded 48% glucose yield after 4 h whereas Amberlyst-15 provided 14% yield. TOFs of each catalysts were 0.33 and 0.08 h^{-1} for MNPs@SiO_2–SO_3H and Amberlyst-15, respectively. The MNPs@SiO_2–SO_3H catalyst could be recovered from the solution by magnet, and reused for further reactions (Figure S4[19]).

Hydrolysis of cellulose is one of the most important processes for the production of second generation biofuels from sustainable feedstocks rather than first generation biofuels from edible feedstocks. Due to the rigid structure composed of 1,4-β-glycosidic bond and additional intramolecular hydrogen bonds, the hydrolysis of cellulose is much more difficult than that of

Table 2. Cellulose hydrolysis using MNPs@SiO_2–SO_3H



Catalyst	Acid amount /mmol g^{-1}	TRS[b] /%	Glucose yield[c] /%	TON[d]
MNPs@SiO_2–SO_3H	0.5	30.2	7.0	3.8
Amberlyst-15	4.8	29.3	6.2	0.4

[a]*Reaction conditions*: Cellulose (0.15 g),[19] catalyst (0.15 g), water (1.5 mL), 423 K, 3 h. [b]Total reducing sugars determined by the DNS method. [c]Determined by HPLC. [d]Turnover number.

starch. We have examined hydrolysis of cellulose by using MNPs@SiO_2–SO_3H catalyst.[19] The solid acid catalyst was dispered in cellulose containing water, and heated at 423 K for 3 h. The results are shown in Table 2. The reaction conditions used were higher substrate concentration (10 wt %) and moderate catalyst/cellulose ratio (1 w/w) compared to previous studies.[5–10] Total reducing sugars (TRS) were determined by using 3,5-dinitrosalicylic acid (DNS). 30% yield of TRS with 7% yield of glucose were obtained by using MNPs@SiO_2–SO_3H catalyst. The use of the same weight of Amberlyst-15 afforded comparable results. It should be noted that turnover number of MNPs@SiO_2–SO_3H was 3.8, much higher than that of Amberlyst-15 (0.4). Again, the MNPs@SiO_2–SO_3H could be recovered from the solution by magnet.

In summary, $CoFe_2O_4$-embedded silica nanoparticles with sulfonic acid groups were fabricated and applied to hydrolysis of sugars including sucrose, cellobiose, starch, and cellulose. The catalyst could be easily recovered from the solution by magnet, and reused for further reactions. The magnetic solid acid catalyst exhibited much higher activity than strongly acidic ion-exchange resins.

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19 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.