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Effects of Brønsted and Lewis acidities on activity and selectivity of heteropolyacid-based catalysts for hydrolysis of cellobiose and cellulose

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Heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$) and salts of metal cations (M^{n+}) and $PW_{12}O_{40}^{3-}$ ($M_{3/n}PW_{12}O_{40}$) act as effective homogeneous catalysts for selective hydrolysis of cellobiose and cellulose to glucose and total reducing sugars (TRS), respectively, in an aqueous phase. For Brønsted acid catalysts, including mineral acid and heteropolyacids, the activity for both reactions increases with a decrease in the deprotonation enthalpies (DPE), indicating that stronger Brønsted acidity is more favorable. For $M_{3/n}PW_{12}O_{40}$ of 11 kinds of metal ions (Ag^+, Ca^{2+}, Co^{2+}, Y^{3+}, Sn^{4+}, Sc^{3+}, Ru^{3+}, Fe^{3+}, Hf^{4+}, Ga^{3+} and Al^{3+}), the rate of cellulose hydrolysis increases with Lewis acidity of the cation, while the TRS selectivity was highest for cations with moderate Lewis acidity, such as Sn^{4+} and Ru^{3+}. For the hydrolysis of cellobiose, cellulose and lignocellulose, $H_3PW_{12}O_{40}$ and $Sn_{0.75}PW_{12}O_{40}$ showed higher TRS yield than H_2SO_4.

Introduction

Heteropoly acids and related polyoxometalates are known to act as efficient acid catalysts for various organic reactions.[1–4] Among them, a Keggin type of heteropolyacid $H_3PW_{12}O_{40}$ as Brønsted acid has the highest acid strength and has higher acidity than H_2SO_4. Salts of metal cation (M^{n+}) and $PW_{12}O_{40}^{3-}$ ($M_{3/n}PW_{12}O_{40}$) potentially show Lewis acidity[3,4] originating from the metal cation as electron pair accepters as well as Brønsted acidity generated from dissociation of coordinated water under the polarizing effect of the cation. Analogously to metal triflates, such as $Sc(CF_3SO_3)_3$,[5] $M_{3/n}PW_{12}O_{40}$ will act as a water tolerant acid catalyst with Lewis and Brønsted acidities. Recently, we have reported that polyvalent metal salts of dodecatungstophosphate ($M_{3/n}PW_{12}O_{40}$) act as effective heterogeneous Lewis acid catalysts for several acid-catalyzed reactions.[4]

Cellulose is the most abundant source of biomass, and holds impressive potential as an alternative to fossil fuels for sustainable production of fuels and chemicals.[6] Because of the protection of the β-1,4-glycosidic bonds by the tight packing of cellulose chains in microfibrils,[7] hydrolysis of cellulose requires severe conditions (at elevated temperature under high pressure) using mineral acids,[8] a Lewis acid[9] or sub- and super-critical water.[10] These severe conditions lead to degradation of sugars, which significantly lowers glucose selectivity and interferes with downstream applications. Hydrolysis with concentrated sulfuric acid (H_2SO_4) can be operated under less harsh conditions, but requires expensive corrosion-resistant reactors and has waste disposal problems. Recently, new homogeneous and heterogeneous systems such as mineral acids[11] or a Lewis acid[12] in an ionic liquid, SO_3H-immobilized solids,[13] and supported metal catalysts[14] have been developed that facilitate the hydrolysis of cellulose with moderate to good glucose yield. However, very few studies have focused on the effects of Brønsted and Lewis acidities on the catalytic activity and selectivity for this reaction. The concepts of catalyst design for cellulose hydrolysis are essential in order to develop a new biomass conversion system.

Here we report that heteropolyacids ($H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) and salts of metal cation (M^{n+}) and $PW_{12}O_{40}^{3-}$ ($M_{3/n}PW_{12}O_{40}$) catalyze hydrolysis of cellulose and lignocellulose with high selectivity to glucose or sugars. Cellobiose is a glucose dimer connected by a glycosidic bond and represents the simplest model molecule for cellulose. Thus, the hydrolysis of cellobiose, which has been examined as a model reaction for hydrolysis of a glycosidic bond,[13b,15,16] is also examined. Relationships between the Brønsted and Lewis acidities and catalytic efficiency (activity and selectivity) are discussed to obtain a catalyst design concept for the title reactions.

Experimental

Hydrates of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were purchased from Nippon Inorganic Color and Chemicals Co. $M_{3/n}PW_{12}O_{40}$ were prepared by stirring an aqueous solution containing $H_3PW_{12}O_{40}$ and the metal salts (chlorides for Sc, Ru, Sn, Hf and Al; nitrates for Ag, Ca, Co, Y, Fe, Ga, and Ag), followed by evaporation to dryness according to the literature method.[4] This preparation method assures the composition of the metal (M^{n+}) salts of $PW_{12}O_{40}^{3-}$ as $M_{3/n}PW_{12}O_{40}$. A sulfonic resin (Amberlyst-15, ion exchange capacity: 4.7 mmol g^{-1}) was purchased from Aldrich. As received Amberlyst-15 beads were crushed and sieved with a stainless mesh (100–282 mesh) to obtain Amberlyst-15 powder with a diameter in the range of 0.15–0.053 mm. H-BEA zeolite (JRC-Z-HB25, $SiO_2/Al_2O_3 = 25 \pm 5$) was supplied from the Catalysis Society of Japan. WO_3/ZrO_2 was prepared by impregnation of the hydrated zirconia with an aqueous solution of ammonium paratungstate at pH 10 with an aqueous NH_4OH solution, followed by drying at 100 °C and by calcining at

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600 °C. Sulfated ZrO_2 (denoted as SO_4^{2-}/ZrO_2) was prepared by mounting H_2SO_4 on the hydrated zirconia, followed by calcination at 600 °C.

$HClO_4$ (60 wt%), H_2SO_4 (98 wt%), H_3PO_4 (85 wt%), $Sc(CF_3SO_3)_3$, $LaCl_3$ and other chemicals were all commercially supplied. The cellulose powder (435236–250G) was purchased from Sigma-Aldrich. For ball-milling experiments, ZrO_2 balls (1 kg of 1 cm diameter balls) and 20 g of cellulose powder were loaded into a bottle, and the spinning speed was set at 250 rpm.

For hydrolysis of cellobiose, a mixture of a cellobiose (0.58 mmol) and catalyst in water (12 mL) was heated at 393 K in a pressure tube (50 cm^3) under nitrogen. The reaction samples were taken out periodically, and the products were analyzed by high-performance liquid chromatography (HPLC with RI detector, JASCO PU-2089, CO-2065, RI-2031) using Shim-pack SPR-Ca column (250 G 7.8 mm) and water as the mobile phase. In the case of solid acid catalysts, the reaction mixture was centrifuged and the filtered solution was used for the analyses. The estimated experimental error in cellobiose and glucose concentrations is *ca* 2%.

For hydrolysis of cellulose, cellulose powder (1.16 mmol of glucose unit) treated by the ball-milling for 48 h and catalyst were added in water (6 mL) and was heated at 423 K in a pressure tube (50 cm^3) under nitrogen. After 24 h, the reaction mixture was quenched with cold water, neutralized with 0.5 mol/L NaOH, and filtered. The aqueous solution was collected and subjected to total reducing sugars (TRS) analysis using a established method with 3,5-dinitrosalicylic acid (DNS method).[11,17] DNS regent (0.5 mL)[17] and 0.05 mL of reaction sample was heated for 5 min at 373 K, then cooled to room temperature, and mixed with 15 mL of deionized water. Using the absorbance at 500 nm measured with a JASCO V-750 spectrophotometer, the concentration of TRS was calculated based on a standard curve obtained with glucose. The estimated experimental error in TRS concentrations is *ca* 5%. For a selected run (with $H_3PW_{12}O_{40}$ catalyst), the glucose yield was also analyzed by the HPLC experiment mentioned above. Although selectivities for most of the catalytic results in Tables 1–3 were below 100%, we could not identify by-products by the HPLC analysis.

For the reaction of the lignocellulosic material, Japanese cedar wood powder (0.1–0.3 mm) was used. Analytical values of cellulose, hemicellulose, lignin, and water in untreated cedar powder are 52%, 24%, 10%, 14%, respectively.[18] The yield of TRS was calculated based on the weight percentage of the polysaccharides (76%) contained in the cedar.

Table 1 Hydrolysis of cellobiose with various acid catalysts[a]

Catalyst	H^+ (mol%)	Y_{Gl}/%	Conv./%	Sel./%
$H_3PW_{12}O_{40}$	36	51	53	96
$H_4SiW_{12}O_{40}$	48	53	61	86
$H_3PMo_{12}O_{40}$[b]	57	48	83	57
$H_4SiMo_{12}O_{40}$[b]	75	42	75	56
$HClO_4$	36	42	44	95
H_2SO_4	36	29	34	85
H_3PO_4	36	12	13	96
H-BEA zeolite	—	0.8	1.6	50

[a] Reaction conditions: cellobiose (0.2 g, 0.58 mmol), H_2O (12 mL), catalyst (0.2 g), 393 K, 24 h. [b] t = 48 h.

Table 2 Hydrolysis of cellulose with various acid catalysts[a]

Catalyst	Y_{TRS}/%	Conv./%	Sel.$_{TRS}$/%
$Sn_{0.75}PW_{12}O_{40}$	23	23	100
$H_3PW_{12}O_{40}$	18	18	100
$H_4SiW_{12}O_{40}$	17	17	99
$HClO_4$	12	14	87
H_2SO_4	10	14	72
H_3PO_4	4.6	7.6	61
$Sc(CF_3SO_3)_3$[b]	4.9	11	45
$LaCl_3$[b]	4.0	7.4	53
Amberlyst-15[c]	4.7	20	24
25 wt% WO_3/ZrO_2[c]	3.3	11	30
20 wt% SO_4^{2-}/ZrO_2[c]	4.4	17	26
H-BEA[c]	3.1	16	19

[a] Reaction conditions: cellulose (1.16 mmol of glucose unit), H_2O (6 mL), catalyst (H^+ = 18 mol%, $PW_{12}O_{40}^{3-}$ = 6 mol%), 423 K, 2 h. [b] Sc or La = 18 mol%. [c] Catalyst = 0.1 g.

Table 3 Hydrolysis of lignocellulose[a]

Catalyst	Y_{TRS}/%	Conv./%	Sel.$_{TRS}$/%
H_2SO_4	24	28	85
$H_3PW_{12}O_{40}$	32	39	82
$Sn_{0.75}PW_{12}O_{40}$	27	44	63

[a] Reaction conditions: cellulose (1.16 mmol of glucose unit), H_2O (6 mL), catalyst (H^+ = 18 mol%, $PW_{12}O_{40}^{3-}$ = 6 mol%), 423 K, 24 h.

Results and discussion

Hydrolysis of cellobiose

Initially, hydrolysis of cellobiose was tested by using 9 kinds of Brønsted acid including heteropolyacids and mineral acids (Table 1). A typical time course of the reaction is shown in Fig. 1. These acids selectively promoted the hydrolysis of cellobiose to glucose with selectivity above 85%, except for $H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$. The glucose yields for these catalysts were higher

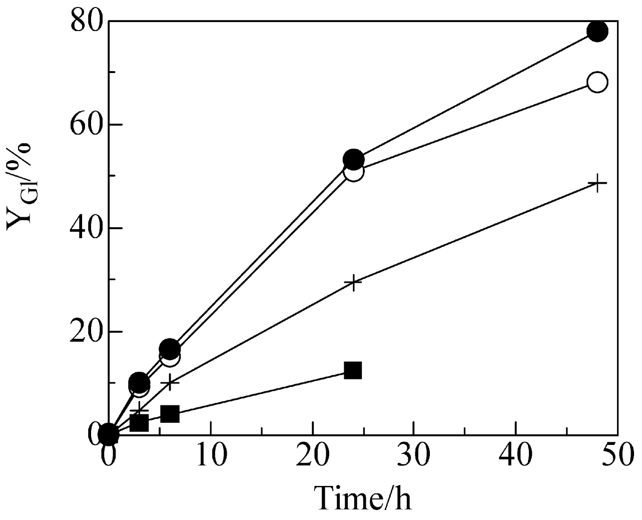

Fig. 1 Time course of cellobiose hydrolysis by (○) $H_3PW_{12}O_{40}$, (●) $H_4SiW_{12}O_{40}$, (+) H_2SO_4, (■) H_3PO_4. Conditions are shown in Table 1.

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than that of heterogeneous Brønsted acidic catalyst, H-BEA zeolite. The glucose yield after 24 h changed in the following order: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > HClO_4 > H_2SO_4 > H_3PO_4$. The acid strength of these compounds rigorously reflects the energy required to remove a proton from a Brønsted acid; this deprotonation energy (DPE) is a probe-independent intrinsic property of an acid.[2,19] Recently, Macht *et al.* showed that DPE available from DFT calculations can be a rigorous descriptor of acid strength of heteropolyacids.[2] To discuss the effect of Brønsted acidity on the activity and selectivity for this reaction, glucose yield, conversion and glucose selectivity are plotted in Fig. 2 as a function of DPE.[2,19] There are general tendencies that the glucose yield and conversion decrease with increase in DPE, while the selectivity does not depend on DPE. Also, there are general tendencies that the initial rate (after 3 h) for glucose formation and cellobiose consumption decrease with increase in DPE. These indicate that a stronger Brønsted acid is more favorable for the hydrolysis of a glycosidic bond.

Next, salts of $PW_{12}O_{40}^{3-}$ ($M_{3/n}PW_{12}O_{40}$) with 11 kinds of metal ions (Ag^+, Ca^{2+}, Co^{2+}, Y^{3+}, Sn^{4+}, Sc^{3+}, Ru^{3+}, Fe^{3+}, Hf^{4+}, Ga^{3+} and Al^{3+}) were tested for hydrolysis of cellobiose. In the initial period of the reaction ($t = 6$ h), initial rates for glucose formation and cellulose consumption were estimated, and the turnover frequency (TOF) per mole of $M_{3/n}PW_{12}O_{40}$ was estimated. TOFs for glucose formation and cellulose consumption and the glucose selectivity are plotted in Fig. 3 as a function of the ratio of charge and ionic radius, e/r. The e/r has been used as an approximate measure for the electron-withdrawing ability, or in other word, Lewis acidity of metal cations.[20] There are volcano type dependencies for TOFs for glucose formation and cellulose consumption, and the highest rates are observed for the catalyst with moderate Lewis acidity (e/r value), such as Sn^{4+}, Sc^{3+}, Ru^{3+}, Fe^{3+} and Ga^{3+}. The TRS selectivity is above 94%, except for $AgPW_{12}O_{40}$ (50% selectivity). It should be noted that the catalysts with moderate Lewis acidity show higher TOFs for glucose formation than $H_3PW_{12}O_{40}$.

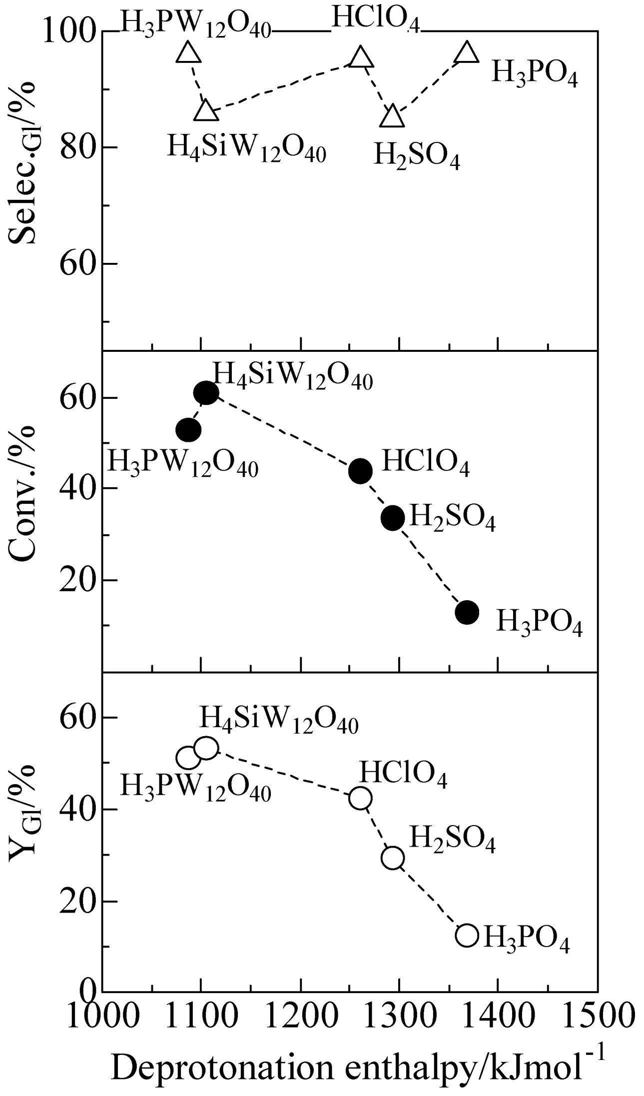

Fig. 2 Effect of deprotonation enthalpy (DPE)[4,10] of acid catalysts on (○) glucose yield, (●) cellobiose conversion, and (△) glucose selectivity for cellobiose hydrolysis (from Table 1).

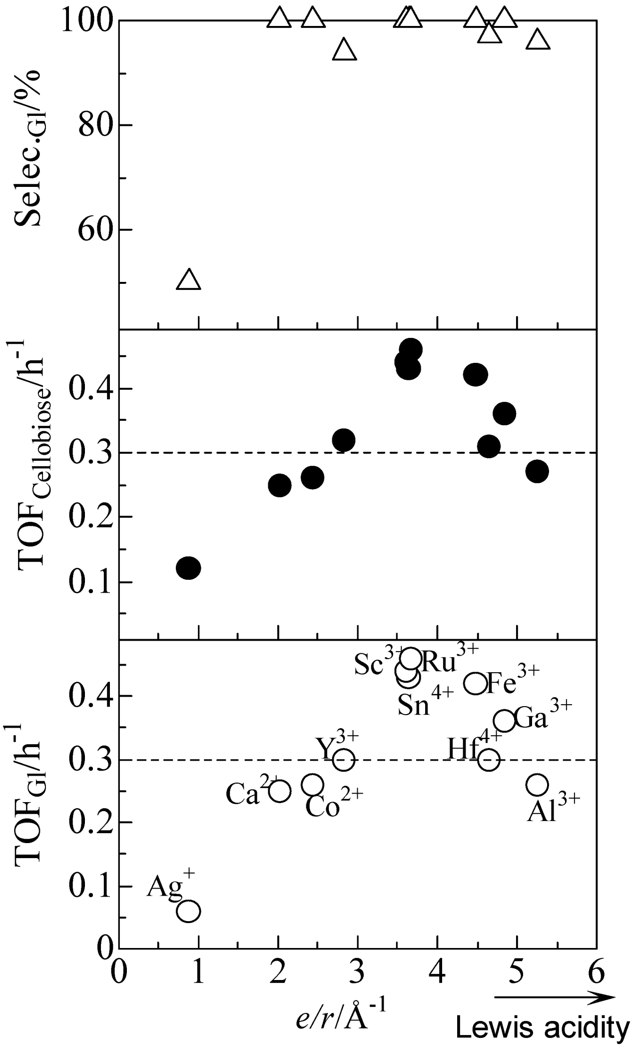

Fig. 3 Effect of the ratio of charge and ionic radius of the cation (M^{n+}) in $M_{n/3}PW_{12}O_{40}$ catalysts on (○) TOF for glucose formation, (●) TOF for cellobiose conversion, and (△) glucose selectivity for cellobiose hydrolysis at 393 K for 6 h. Conditions: cellobiose (0.2 g, 0.58 mmol), H_2O (12 mL), catalyst ($M_{n/3}PW_{12}O_{40}$ = 12 mol%). Dashed lines denotes TOFs for $H_3PW_{12}O_{40}$.

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Hydrolysis of cellulose and lignocellulose

First, we studied the effect of cellulose crystallinity on the catalytic activity of $H_3PW_{12}O_{40}$ as a representative catalyst. The XRD patterns of cellulose before and after the ball-milling are shown in Fig. 4. The XRD pattern before the treatment showed diffraction peaks of cellulose crystalline around 16°, 22°, and 34°. The crystalline peaks disappeared, and the amorphous halo peak appeared around 20° in the XRD pattern of the cellulose milled for 2 days, which indicated that the crystallinity of cellulose was markedly decreased by the ball-milling treatment of 2 days. To study the effect of crystallinity of cellulose on its reactivity, the hydrolysis of the cellulose before and after the ball-milling was tested using $H_3PW_{12}O_{40}$ catalyst. As shown in Fig. 5, TRS yield, cellulose conversion, and TRS selectivity increased with the ball-milling time up to 2 days. Further increase in the ball-milling time (4 days) did not increase the TRS yield (not shown). These result are consistent with the previous report by Zhao *et al.* on the effect of the ball-milling on the dilute H_2SO_4 catalyzed cellulose hydrolysis.[8c] Based on XRD and CP/MAS NMR results, they proposed that mechanical disruption of crystallinity by breaking hydrogen bonds in α-cellulose opens up the structure and makes more β-1,4 glycosidic bonds readily accessible to the acid. The XRD pattern of a lignocellulose, Japanese cedar wood powder, has a weak and broad crystalline peak at 22° together with an amorphous halo peak around 20°, indicating that crystallinity of cellulose in the cedar powder is significantly low. From these facts, we used the cellulose after the ball-milling treatment of 2 days in the following catalytic experiments.

Typical time-conversion profiles for $H_3PW_{12}O_{40}$, $Sn_{0.75}PW_{12}O_{40}$ and H_2SO_4 are shown in Fig. 6. As the reaction time increased, the cellulose conversion monotonically increased, while TRS selectivity decreased after 10 h, and consequently TRS yield reached a maximum value at 16 h.

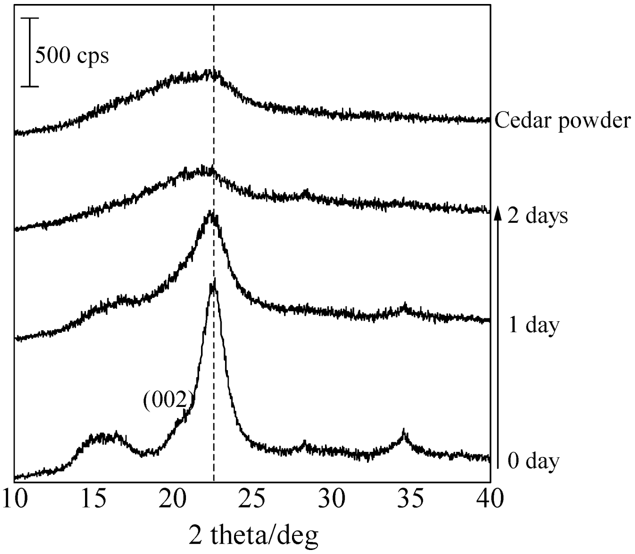

Fig. 4 XRD patterns of cellulose as a function of time of ball-milling and a XRD pattern of Japanese cedar wood powder (a lignocellulose).

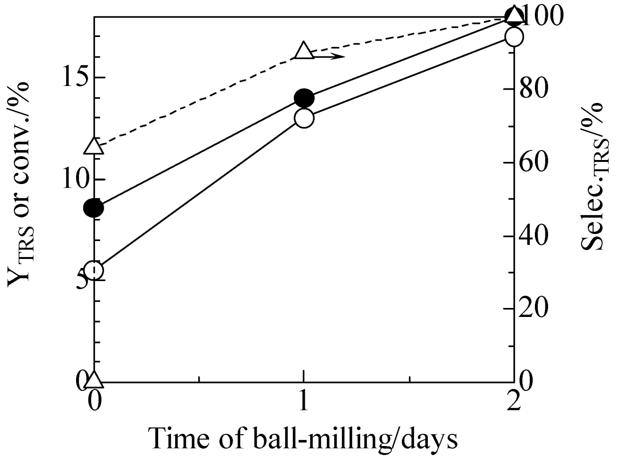

Fig. 5 Effect of ball-milling time of cellulose for (○) TRS yield, (●) cellulose conversion, and (△) TRS selectivity for cellulose hydrolysis by $H_3PW_{12}O_{40}$ ($H^+ = 18$ mol% with respect to molar quantity of the glucose unit in the cellulose) at 423 K for 24 h.

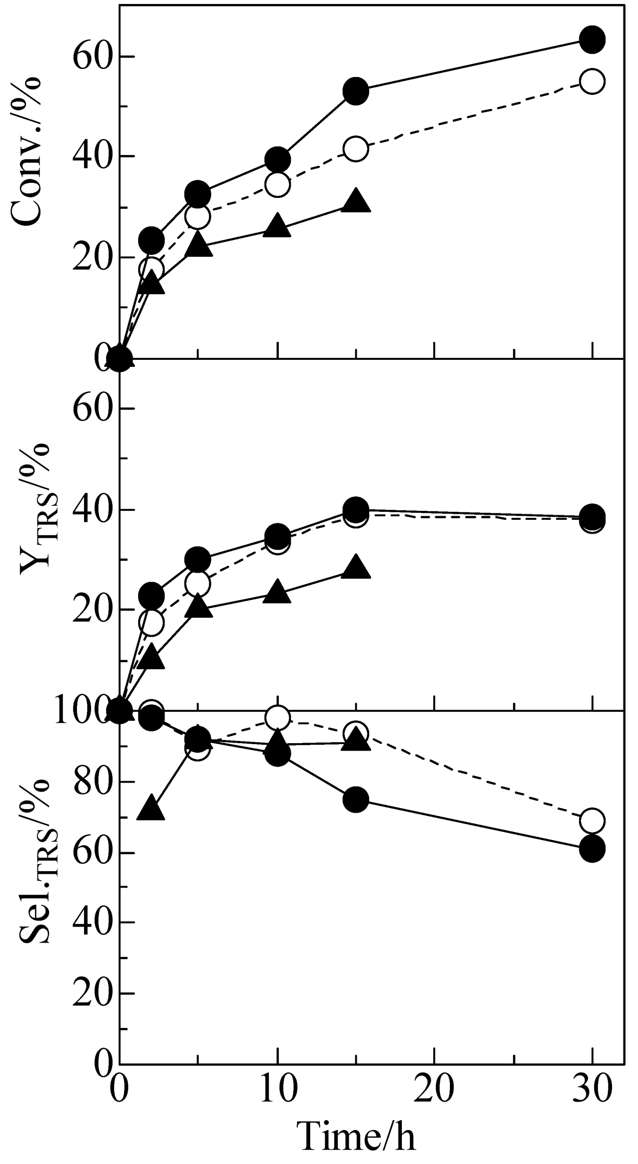

Fig. 6 Time course of cellulose hydrolysis by (○) $H_3PW_{12}O_{40}$, (●) $Sn_{0.75}PW_{12}O_{40}$, (▲) H_2SO_4 at 423 K. Conditions: cellulose (0.58 mmol), H_2O (6 mL), catalyst ($H^+ = 18$ mol% or $PW_{12}O_{40}^{3-} = 6$ mol%).

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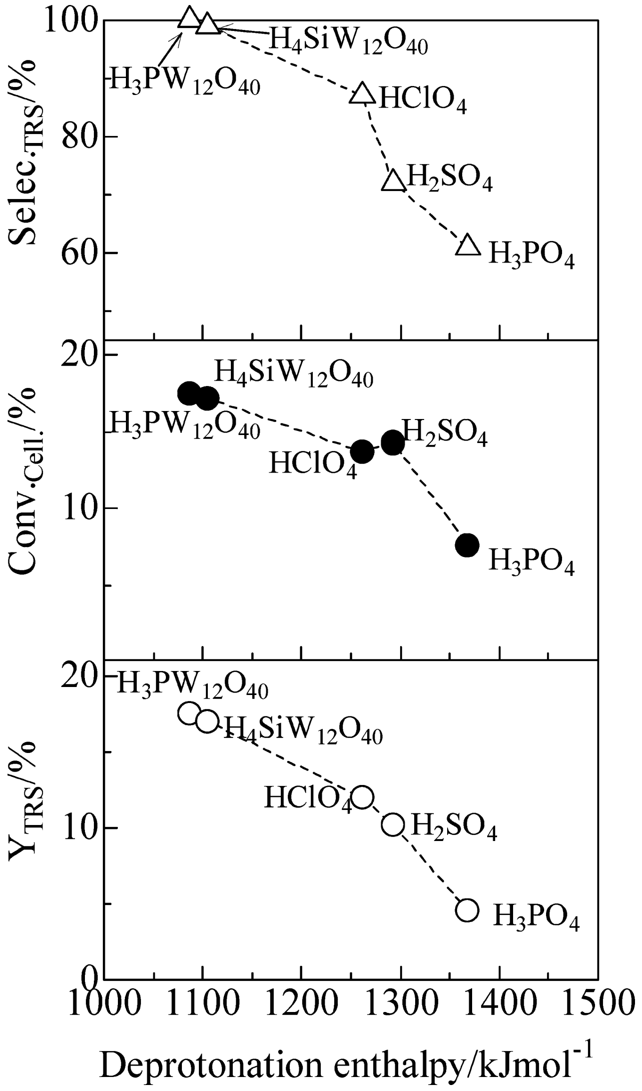

Fig. 7 Effect of the ratio of charge and ionic radius of the cation (M^{n+}) in $M_{n/3}PW_{12}O_{40}$ catalysts on (○) TRS yield, (●) cellulose conversion, and (△) TRS selectivity for cellulose hydrolysis at 423K for 2 h. Conditions are the same as in Fig. 5.

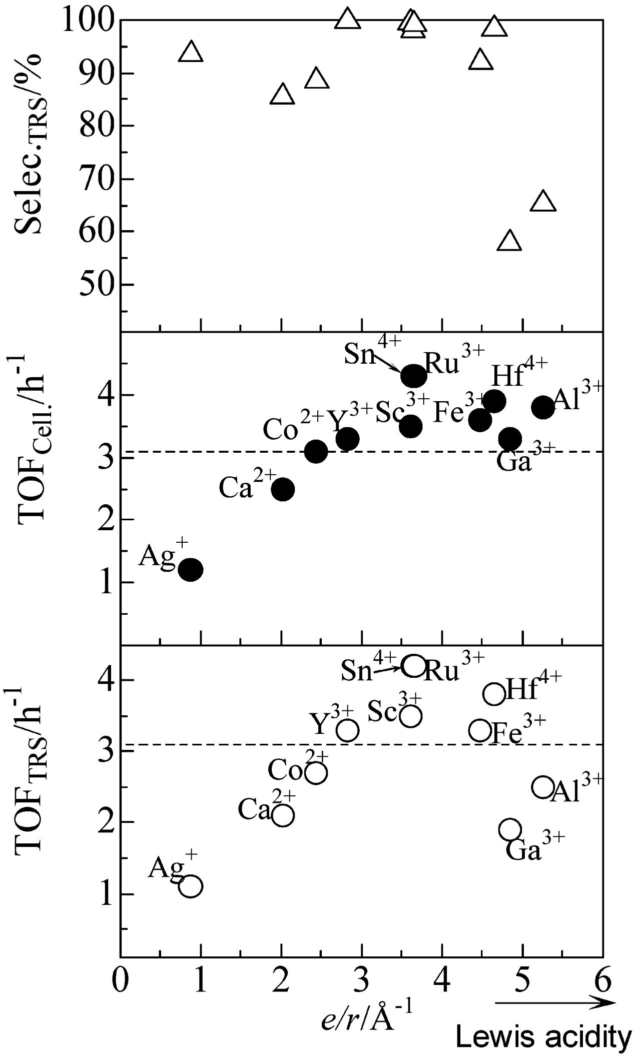

Fig. 8 Effect of the ratio of charge and ionic radius of the cation (M^{n+}) in $M_{n/3}PW_{12}O_{40}$ catalysts on (○) TRS yield, (●) cellulose conversion, and (△) TRS selectivity for cellulose hydrolysis at 423 K for 2 h. Conditions: cellulose (0.58 mmol), H_2O (6 mL), catalyst ($M_{n/3}PW_{12}O_{40}$ = 6 mol%). Dashed lines denotes TOFs for $H_3PW_{12}O_{40}$.

Table 2 compares the results for hydrolysis of cellulose in the initial period of the reaction (2 h). Among the Brønsted acids tested, the TRS yield changed in the following order: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > HClO_4 > H_2SO_4 > H_3PO_4$. It should be noted that the $H_3PW_{12}O_{40}$ catalyst showed higher TRS yield (18%) than conventional dilute H_2SO_4 catalyst (10%), previously reported Lewis acid catalyst, $LaCl_3$[10a] (4%), $Sc(CF_3SO_3)_3$ (4.9%) known as a water tolerant Lewis acid catalyst, and various heterogeneous acid catalysts, such as zeolite, acidic oxides and resin (3.1–4.7%). For the reaction with $H_3PW_{12}O_{40}$ catalyst, glucose yield was also analyzed by HPLC experiment. The glucose yield for $H_3PW_{12}O_{40}$ was 15%, corresponding to a glucose selectivity of 83%.

After the reaction, the reaction mixture (6 mL) was heated to remove water, and the concentrated solution (0.5 mL) was cooled by ice-cold water. Then, a part of the recrystallized $H_3PW_{12}O_{40}$ (about 50% of the first use) was separated from the mixture by a simple filtration, followed by drying in air at 80 °C. The recovered $H_3PW_{12}O_{40}$ catalyzed the reaction, though its activity in the second run was lower than that in the first run (24% TRS yield after 7 h).

To discuss the effect of Brønsted acidity on the activity and selectivity for this reaction, TRS yield, conversion and TRS selectivity are plotted in Fig. 7 as a function of DPE.[2,19] There are general tendencies that TRS yield, conversion and TRS selectivity decrease with increase in DPE. This indicates that a stronger Brønsted acid is more favorable for the hydrolysis of β-1,4 glycosidic bonds in cellulose. A separate experiment showed that 10% of glucose was decomposed when glucose (0.2 g) in 6 mL H_2O was heated after 6 h at 423 K (result not shown). The acid catalyst with stronger Brønsted acidity could result in the higher relative rate of acid-catalyzed cellulose hydrolysis with respect to non-catalytic decomposition of sugars, which could lead to the higher TRS selectivity.

Metal salts of $PW_{12}O_{40}{}^{3-}$ ($M_{3/n}PW_{12}O_{40}$) were tested for hydrolysis of cellulose. In the initial period of the reaction (t = 2 h),

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initial rates for TRS formation and cellulose consumption were estimated, and the turnover frequencies (TOF) per mole of $M_{3/n}PW_{12}O_{40}$ were estimated. As shown in Fig. 8, there were volcano type dependencies for TOFs for TRS formation and cellulose consumption, and the highest rates were observed for the catalyst with moderate Lewis acidity (e/r value), such as Sn^{4+} and Ru^{3+}. These catalysts show higher TOFs for glucose formation than $H_3PW_{12}O_{40}$. These tendencies are consistent with those observed for hydrolysis of cellobiose (Fig. 4).

Finally, catalytic properties of representative catalysts ($H_3PW_{12}O_{40}$ and $Sn_{0.75}PW_{12}O_{40}$) for the reaction of the lignocellulosic material, Japanese cedar wood powder was examined (Table 3). When the mixture containing the cedar powder (0.2 g) and catalyst ($H^+ = 18$ mol%, $PW_{12}O_{40}{}^{3-} = 6$ mol%) in H_2O (6 mL) was heated at 423 K for 24 h, the yield of TRS calculated based on the content of polysaccharides (76 wt%) was 32 and 27% for $H_3PW_{12}O_{40}$ and $Sn_{0.75}PW_{12}O_{40}$ respectively. These values were higher than the TRS yield (24%) for H_2SO_4 ($H^+ = 18$ mol%), demonstrating that the heteropolyacids-based catalysts are applicable for hydrolysis of lignocellulose.

Conclusion

Heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$) and polyvalent transition metal salts of $PW_{12}O_{40}{}^{3-}$ act as effective heterogeneous catalysts for the selective hydrolysis of cellobiose and cellulose to saccharides. For Brønsted acid catalysts, the activity for both reactions increases with decrease in the deprotonation enthalpies (DPE), indicating that stronger Brønsted acidity is more favorable in β-1,4 glycosidic bonds in cellobiose and cellulose. After the hydrolysis of cellulose, about 50% of $H_3PW_{12}O_{40}$ in the reaction mixture can be recrystallized, separated from the mixture by a simple filtration, and can be reused. For $M_{3/n}PW_{12}O_{40}$ of 11 kinds of metal ions (Ag^+, Ca^{2+}, Co^{2+}, Y^{3+}, Sn^{4+}, Sc^{3+}, Ru^{3+}, Fe^{3+}, Hf^{4+}, Ga^{3+} and Al^{3+}), highest rates were observed for the catalyst with moderate Lewis acidity (e/r value), such as Sn^{4+} and Ru^{3+}. For the hydrolysis of lignocellulose, $H_3PW_{12}O_{40}$ and $Sn_{0.75}PW_{12}O_{40}$ showed higher TRS yield than H_2SO_4.

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