# Glucose production from saccharides using layered transition metal oxide and exfoliated nanosheets as a water-tolerant solid acid catalyst†

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**The layered transition-metal oxide $HNbMoO_6$ is demonstrated to exhibit remarkable catalytic performance for the hydrolysis of saccharides such as sucrose, cellobiose, starch, and cellulose, attributable to water tolerance and the facile accessibility of saccharides into the strong acidic interlayer gallery of the solid.**

The urgent demand to reduce carbon dioxide emissions with respect to global warming has lead to the rapid development of the utilization of biomass as an alternative to fossil fuels. Many methods are currently being employed to transform biomass into practical fuels such as bioethanol, biodiesel, and bio-oil. The production of bioethanol is primarily conducted using food crops such as corn and sugarcane as biomass sources. However, the use of such biomass resources for fuel production competes with the need for food production. To avoid this problem, the utilization of cellulose-based biomass is therefore recognized as a key technology.[1–3] Polysaccharides such as starch and cellulose can be converted into monosaccharides such as glucose, a major platform for the synthesis of a variety of chemicals,[4] by a homogeneous acid-catalyzed reaction using sulfuric acid and/or by enzymatic reactions. However, the use of sulfuric acid is inefficient, generating large amounts of acid waste and incurring considerable energy consumption in the separation process. The development of a reusable and readily separable solid acid catalyst for the hydrolysis of saccharides is therefore considered essential in order to convert biomass into bioethanol and useful chemicals with the lowest environmental impact.[5]

Styrene-based sulfonic acid resins,[6] sulfonated mesoporous silicas,[7] zeolites[8] and cesium-heteropolyacid[9] are known to exhibit activity for the hydrolysis of disaccharides (maltose, sucrose, and cellobiose) and starch. However, to realize high conversion of saccharides, solid acids must have strong acidity, be water tolerant, and allow facile access of saccharides to active sites in the solid material. The present authors have studied layered transition-metal oxides and their derivatives as exfoliated nanosheet materials suitable for application as solid acid catalysts. These exfoliated nanosheet materials, such as $HTiNbO_5$, exhibit strong acidity and high catalytic performance for the hydrolysis of ester in water.[10] The nanosheet materials have large surface areas of up to 100 $m^2\ g^{-1}$, 100 times that of the parent layered oxide. Layered niobium molybdate ($HNbMoO_6$) was recently found to be highly active for several acid-catalyzed reactions,[11] achieving a turnover rate three times that of Nafion NR50 (a standard solid acid catalyst) for the Friedel–Crafts alkylation of benzyl alcohol. The high performance of the layered oxide is attributed to the facile intercalation of substrates in the strongly acidic interlayer gallery of the catalyst. $HNbMoO_6$ also exhibits high activity for hydration.[11] Exfoliated metal-oxide nanosheet materials and layered metal oxide are thus expected to be suitable for the hydrolysis of saccharides, providing both strong acidity and water tolerance.

In the present study, the hydrolysis of saccharides is performed using exfoliated nanosheet $HTiNbO_5$ and layered $HNbMoO_6$ (See ESI†). The catalytic performance of these catalysts are compared with that of a range of conventional solid acids, including ion-exchange resins (Nafion NR50 and Amberlyst-15), H-type zeolite (H-ZSM5; JRC-Z-5-90H, $Si/Al_2$ = 90), and niobic acid ($Nb_2O_5 \cdot nH_2O$). The activity of layered $HNbMoO_6$ and nanosheet $HTiNbO_5$ for the hydrolysis of sucrose was investigated by reacting 0.2 g of catalyst, 1.0 g of sucrose, and 20 mL of water at 353 K. The products were analyzed by high-performance liquid chromatography (HPLC) using a Shodex Asahipak NH2P-50 column. Fig. 1(A) shows the time course of sucrose hydrolysis over layered $HNbMoO_6$. The sucrose concentration decreased rapidly, accompanied by equivalent increases in glucose and fructose. Fig. 1(B) shows the time courses of glucose production over all of the solid acid catalysts tested. H-ZSM5 zeolite was inactive for this reaction, and niobic acid, although known to be water-tolerant,[12] did not achieve appreciable activity for this reaction. Nanosheet $HTiNbO_5$ exhibited comparable activity to Nafion NR50. The activity of layered $HNbMoO_6$, however, substantially exceeds the maximum performance of any of the other materials tested, achieving glucose yield of 82% within 30 min.

Table 1 summarizes the acid density and surface area of the tested solid acids, and the results of the hydrolysis of sucrose and cellobiose. The hydrolysis of cellobiose was carried out at 373 K using 0.2 g of catalyst, 1.0 g of cellobiose, and 10 mL of water. Cellobiose, a subunit of cellulose, consists of β-1,4-glycosidic bonds, which are much more stable than the α-1,2-glycosidic bonds comprising sucrose and thus more resistant to hydrolysis. Accordingly, the rate of glucose production by hydrolysis of cellobiose was significantly lower than for sucrose over all of the acid catalysts tested, including liquid sulfuric acid. Especially, solid acids with relatively weak acid sites like Amberlyst-15 and nanosheet $HTiNbO_5$ gave lower turnover frequency. Fructose and hydroxymethyl furfural (HMF) were not detected in all cases, indicating that further acid-catalyzed reactions (isomerization of glucose, dehydration of fructose) did not occur.

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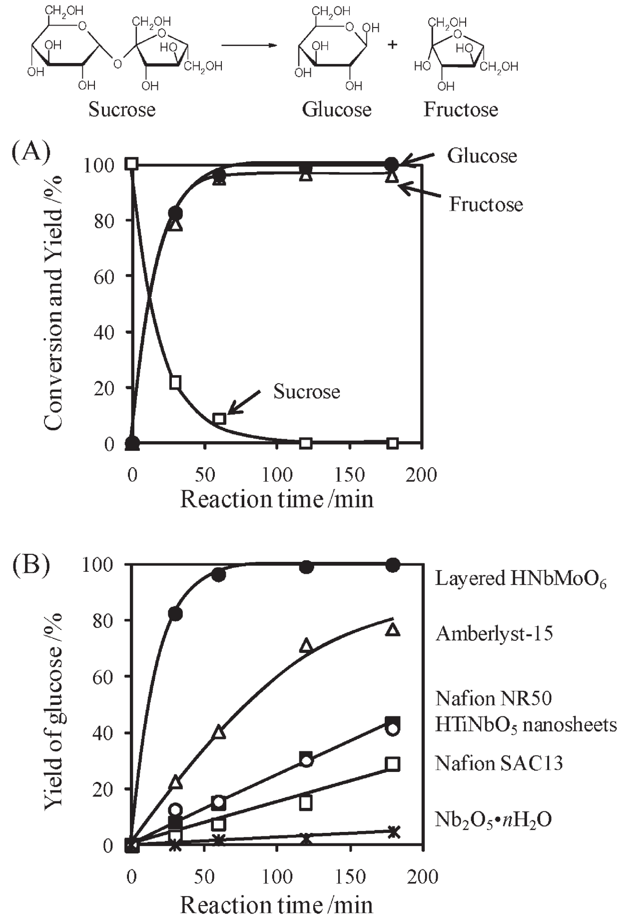

**Fig. 1** Time course of sucrose hydrolysis (A) over layered $HNbMoO_6$, and (B) over all solid acids tested (glucose production).

The layered $HNbMoO_6$ catalyst also exhibited the highest performance in this hydrolysis reaction, producing glucose at twice the rate of the ion-exchange resins and achieving a turnover frequency comparable to that of Nafion NR50. Notably, the turnover frequency of $HNbMoO_6$ was much higher than that of Amberlyst-15 and twice that of sulfuric acid. The turnover number of $HNbMoO_6$ was 1.6 after 3 hours (See ESI Fig. S1†). After 18 hours reaction, the glucose yield reached 40.8% and the corresponding turnover number was 6.3.

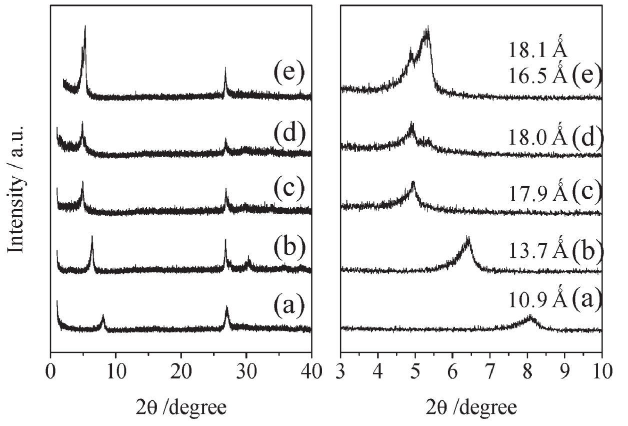

**Fig. 2** XRD patterns for (a) dehydrated $HNbMoO_6$, (b) hydrated $HNbMoO_6 \cdot nH_2O$ ($n$ = 1.23), and (c, e) $HNbMoO_6$ after immersion in aqueous solution containing (c) glucose, (d) sucrose, or (e) cellobiose.

The high catalytic activity of layered $HNbMoO_6$ for these reactions can largely be attributed to the intercalation ability of the material. $HNbMoO_6$ intercalates water, alcohol and ketone at room temperature, resulting in high activity for acid-catalyzed reactions such as Friedel–Crafts alkylation and acetalization.[11] $HNbMoO_6$ also appears to intercalate saccharides, which include many hydroxyl groups. This mechanism was investigated further by immersing 0.15 g of layered $HNbMoO_6 \cdot nH_2O$ (hydrated, $n$ = 1.23) in 3 mL of water containing 0.5 g of glucose, sucrose, or cellobiose. After stirring at room temperature for 1 h, the oxide was filtered and characterized by X-ray diffraction (XRD) measurements. The XRD patterns of $HNbMoO_6$ are shown in Fig. 2. The results indicate that the saccharide was successfully intercalated into the interlayer gallery. The basal spacing of the dehydrated sample was 10.9 Å, suggesting that the intercalation of saccharides is accommodated by expansion of 7.0–7.1 Å given the basal spacings of glucose and sucrose (17.9 and 18.0 Å, respectively). This expansion is considered to be the sum of the diameter of glucose (*ca.* 4 Å[13]) and water, indicating that hydrated $HNbMoO_6$ accommodates the insertion of saccharides. Two distinct peaks were observed for cellobiose, corresponding to basal spacings of 18.1 Å and 16.5 Å. The latter peak is presumably attributable to intercalated cellobiose, which has poor solubility in water and thus does not preserve water upon

**Table 1** Hydrolysis of sucrose and cellobiose over some solid acid catalysts

| | | | Hydrolysis of sucrose[a] | | Hydrolysis of cellobiose[b] | |
|---|---|---|---|---|---|---|
| Catalyst | BET surface area/$m^2$ $g^{-1}$ | Amount of acid/mmol $g^{-1}$ | Rate of glucose production/ mmol $g^{-1}$ $h^{-1}$ | Turnover frequency/$h^{-1}$ | Rate of glucose production/mmol $g^{-1}$ $h^{-1}$ | Turnover frequency/$h^{-1}$ |
| Layered $HNbMoO_6$ | 5 | 1.9[c] | 24.1 | 12.7 | 1.18 | 0.62 |
| $HTiNbO_5$ nanosheets | 153 | 0.4 | 2.2 | 5.7 | 0.05 | 0.12 |
| Amberlyst-15 | 50 | 4.8 | 6.6 | 1.4 | 0.51 | 0.11 |
| Nafion NR50 | <0.1 | 0.9 | 2.2 | 2.4 | 0.44 | 0.48 |
| Nafion SAC13 | 210 | 0.1 | 0.9 | 8.5 | 0.03 | 0.34 |
| $Nb_2O_5 \cdot nH_2O$ | 128 | 0.4 | 0.3 | 0.6 | 0 | 0 |
| H-ZSM-5 | 326 | 0.2 | 0.1 | 0.7 | 0 | 0 |
| $H_2SO_4$ | — | 20.4 | 45.6 | 2.2 | 6.73 | 0.33 |

[a] Reaction conditions: sucrose (1.0 g, 2.92 mmol), $H_2O$ (20 mL), catalyst (0.2 g), 353 K. [b] Reaction conditions: cellobiose (1.0 g, 2.92 mmol), $H_2O$ (10 mL), catalyst (0.2 g), 373 K. [c] Determined by $^{31}P$ NMR using trimethylphosphine oxide.[11]

intercalation. Elemental analysis revealed that the carbon contents (C(%, w/w)) of intercalated saccharides, which were prepared by washing the samples with water as shown in Fig. 2(c)–(e) were 0.44, 0.56 and 0.10 for glucose, sucrose and cellobiose, respectively. These values correspond to 1.75, 1.12 and 0.21 mol% of saccharides per mol of catalyst. For the FT-IR spectrum, several peaks attributed to glucose were clearly observed for the glucose-intercalated sample (See ESI Fig. S2†). The difference in intercalation ability of sucrose and cellobiose into $HNbMoO_6$ is considered to be another important factor influencing hydrolysis activity in addition to the difficulty of cleavage of β-1,4-glycosilic bonds. In these experiments, the amounts of intercalated saccharides seem to be small. This is due to weak interaction of such saccharides with the interlayer of $HNbMoO_6$. The intercalated saccharides are easily released from the interlayer space by water washing. Similar results have been reported in montmorillonite.[14]

The acidity of the interlayer gallery of $HNbMoO_6$, determined by $^{31}P$ magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy using trimethylphosphine oxide and $NH_3$-TPD,[11] is comparable to that of strongly acidic H-type zeolites (H-ZSM5[15] and H-MOR[16]). The high catalytic performance of layered $HNbMoO_6$ is therefore attributable to its strong acidity, water tolerance, and facile intercalation of saccharides.

Layered $HNbMoO_6$ was also applied for the hydrolysis of polysaccharide. Fig. 3 shows results for the hydrolysis of starch and cellulose over layered $HNbMoO_6$ and Amberlyst-15. In these reactions, 0.2 g of catalyst and 0.1 g of starch (Kanto, soluble) or cellulose (Avicel, Merck, microcrystalline) were added to 5 mL of water. The mixture was then heated at 373 K for 15 h for starch and 403 K for 12 h for cellulose. Layered $HNbMoO_6$ successfully catalyzed the hydrolysis of both starch and cellulose. The glucose yield over layered $HNbMoO_6$ was 21%, much higher than that over Amberlyst-15 (3.4%). Maltose (disaccharide of glucose connected by α-1,4-glycosilic bond) was not detected in the starch reaction. The increasing of the reaction time to 72 h for $HNbMoO_6$ gave 0.25 mmol (45%) of glucose and 0.14 mmol of HMF due to further acid-catalyzed reaction. The turnover number of $HNbMoO_6$ reached 1.44 for starch hydrolysis under optimal condition (See ESI Table S1†).

The total yield of products (glucose and cellobiose) was estimated to be 8.5% in the hydrolysis of cellulose, corresponding to 0.07 of TON. Preferential cellobiose production over $HNbMoO_6$ is probably due to the difference of intercalation behavior between glucose and cellobiose. We prolonged the reaction time to 72 h, resulting in 8.8 μmol of glucose and 0.25 mmol of HMF. Although the yield of glucose was decreased, turnover number was significantly increased to 0.67. Further improvement will be achieved by increasing the surface area of $HNbMoO_6$ and by dissolving cellulose in an ionic liquid such as 1-butyl-3-methylimidazolium chloride or 1-allyl-3-methylimidazolium chloride.[17]

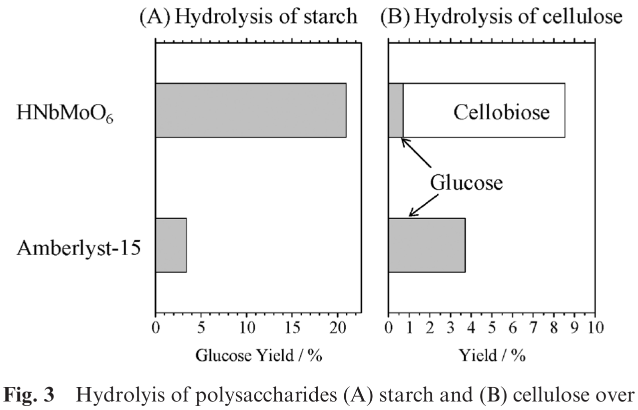

**Fig. 3** Hydrolyis of polysaccharides (A) starch and (B) cellulose over $HNbMoO_6$ and Amberlyst-15.

In summary, layered $HNbMoO_6$ was demonstrated to exhibit high catalytic performance as a solid acid catalyst for the hydrolysis of saccharides. The high activity of this material is attributed to the ease of intercalation into the substrate and the strong acidity of the interlayer gallery.

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