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# Efficient Epimerization of Aldoses Using Layered Niobium Molybdates

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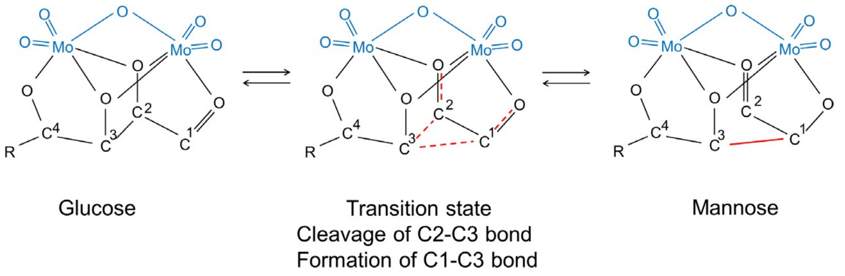
Both non-acidic $LiNbMoO_6$ and strongly acidic $HNbMoO_6$ efficiently catalyze the epimerization of sugars including glucose, mannose, xylose, and arabinose in water. The reactions over these oxides reached almost equilibrium within a few hours where yields of corresponding epimers from glucose, xylose, and arabinose were 24–29%. The layered mixed oxides functioned as heterogeneous catalysts and could be reused without loss of activity, whereas bulk molybdenum oxide $MoO_3$ was completely dissolved during the reaction. A $^{13}C$ substitution experiment showed that the reaction proceeds through a 1,2-rearrangement mechanism. The surface Mo octahedra were responsible for the activity. The layered $HNbMoO_6$ could also afford mannose from cellobiose through hydrolysis and successive epimerization.

The selective transformation of sugars into desired products using heterogeneous catalysts has recently received much attention because the catalysts have high reaction rates and can be readily separated from the products for reuse.[1–5] To date, a variety of solid acid and base catalysts have been developed for the selective transformation of glucose into valuable chemical intermediates such as levoglucosan,[6] 5-hydroxymethylfurfural,[7–9] and lactic acid[10–12] through dehydration, isomerization, the retro-aldol reaction, and rehydration. The catalysts also proved effective in the transformation of xylose[13–15] and arabinose.[16,17]

Epimerization involves a carbon skeleton rearrangement reaction, which consists of cleavage of the bond between carbons C2 and C3 and subsequent formation of a new bond between carbons C1 and C3 (Scheme 1). Epimerization is of significance for the synthesis of rare sugars and pharmaceuticals.[18,19] The reaction allows the direct transformation of D-glucose to D-mannose, D-xylose to D-lyxose, and L-arabinose to L-ribose. These transformations can also be attained through sequential isomerizations, such as glucose-to-fructose-to-mannose;[20] however, the selectivity to epimers is usually very low owing to the involvement of intermediate isomers and equilibrium limitations.



**Scheme 1.** Reaction mechanism of Mo-catalyzed epimerization of glucose. Adapted from Ref. [22].

This carbon rearrangement reaction is known as the Bílik reaction, first discovered over homogeneous Mo-based catalysts in acidic aqueous solution where a binuclear molybdate–glucose complex was proposed as the transition state (Scheme 1).[21,22] Homogeneous molybdate catalysts including molybdic acid and heptamolybdate can catalyze the glucose–mannose epimerization as well as the xylose–lyxose epimerization in acidic aqueous solutions.[23] Recently, a polymer-supported Mo catalyst[24] and Mo-based polyoxometalates[25] were found to exhibit high activity for epimerization of carbohydrates in water according to the same reaction mechanism.[22]

Another example of an efficient heterogeneous catalyst for epimerization of carbohydrates is Sn-beta zeolite.[26] The selective formation of epimers from glucose, xylose, and arabinose was achieved in sodium tetraborate-containing aqueous,[26,27] or methanol solutions,[28] although aqueous isomerization into fructose proceeded preferentially without any additives. The reaction mechanism of epimerization over Sn-beta zeolite[29] as well as metal oxalates including V, Mo, and W[30] was investigated using density functional theory. The selective epimerization in the presence of sodium tetraborate is ascribed to the formation of a glucose–borate complex that inhibits the competitive isomerization.

Herein, epimerization of sugars in water was examined using two crystalline layered niobium–molybdenum mixed oxides, $LiNbMoO_6$ and $HNbMoO_6$. This is the first example of epimerization of sugars in water using heterogeneous mixed oxides. These NbMo oxides consist of layers formed by randomly placed $MO_6$ (M=Nb and Mo) octahedra with $Li^+$ or $H^+$ in the interlayers (Figure 1). The protonated niobium molybdate can

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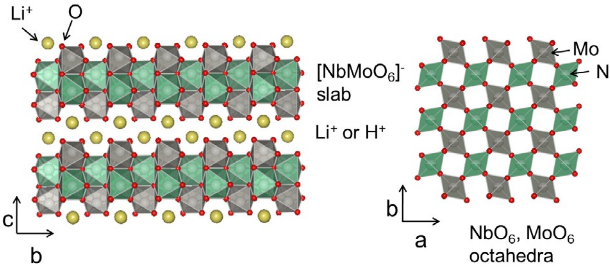

**Figure 1.** Structure of layered niobium molybdate.

be obtained by proton-exchange of $LiNbMoO_6$ where crystal structure remains unchanged. The protonated $HNbMoO_6$ is highly acidic, and can function as a solid acid catalyst.[31] The layered $HNbMoO_6$ is easily prepared by proton exchange of the precursor $LiNbMoO_6$, which is obtained by calcination of a stoichiometric mixture of $Li_2CO_3$, $Nb_2O_5$, and $MoO_3$ at 853 K (See the Supporting Information for details).

Figure 2 shows the time courses of transformation of glucose and mannose over layered $LiNbMoO_6$ in water. The concentration of glucose decreased with the increase of mannose, and after 0.5 h, the concentrations of each sugar reached a plateau (Figure 2a). A similar trend was observed for the transformation of mannose, in which mannose was rapidly converted to glucose (Figure 2b). For both cases, the final concentrations of glucose and mannose were almost the same, indicating that the reaction was reversible and proceeded to completion in the presence of $LiNbMoO_6$. In addition, no formation of fructose was observed. Thus, layered $LiNbMoO_6$ was found to catalyze the glucose–mannose epimerization efficiently.

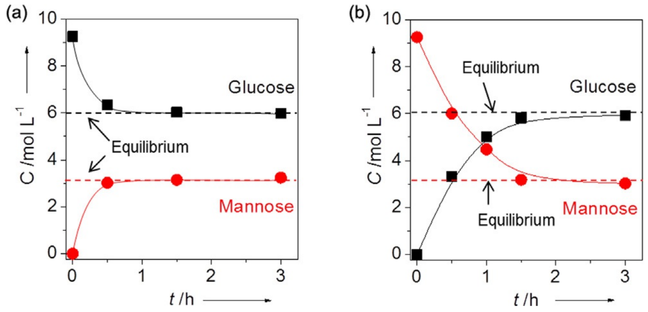

**Figure 2.** Time courses of epimerization of (a) glucose and (b) mannose over layered $LiNbMoO_6$. Reaction conditions: glucose (50 mg, 0.28 mmol), catalyst (50 mg), $H_2O$ (3 mL), 373 K.

**Table 1.** Transformation of monosaccharides over a variety of catalysts in water.[a]

| Entry | Catalyst | Substrate | Conv. [%] | Selectivity [%] | |
|---|---|---|---|---|---|
| | | | | Epimer | Isomer |
| 1 | $HNbMoO_6$ | Glucose | 33, 30,[b] 32[c] | 88, 84,[b] 88[c] | 0 |
| 2 | | Mannose | 67 | 96 | 0 |
| 3 | | Xylose | 31 | $>99$ | 0 |
| 4 | | Arabinose | 31[d] | 76[d] | 0 |
| 5 | $LiNbMoO_6$ | Glucose | 26 | 91 | 0 |
| 6 | | | 19[e] | 98[e] | 0 |
| 7 | | Mannose | 65[f] | $>99$[f] | 0 |
| 8 | | Xylose | 33[d] | $>99$[d] | 0 |
| 9 | | Arabinose | 30[f] | 64[f] | 0 |
| 10 | $Li_{0.85}Nb_{0.85}Mo_{1.15}O_6$ | Glucose | 32[e] | 86[e] | 0 |
| 11 | $Li_{1.15}Nb_{1.15}Mo_{0.85}O_6$ | | 16[e] | 96[e] | 0 |
| 12 | $LiNbWO_6$ | | $<1$ | 0 | 0 |
| 13 | Amberlyst-15 | | $<1$ | 0 | 0 |
| 14 | Mg-Al hydrotalcite[g] | | 21 | 4 | 72 |
| 15 | $Nb_2O_5\cdot nH_2O$ | | 2 | 0 | 42 |
| 16 | $SnO_2$ | | 1 | 0 | 0 |
| 17 | $TiO_2$ | | 1 | 0 | 0 |
| 18 | $WO_3$ | | $<1$ | 0 | 0 |
| 19 | $MoO_3$ | | 49 | 55 | 0 |

[a] Reaction conditions: substrate (300 mg, 1.67 mmol), catalyst (10 mg), water (3 mL), 393 K, 1.5 h. Equilibrium conversions of glucose, mannose, xylose, and arabinose are theoretically calculated to be 30, 70, 33, and 31 %, respectively.[35] [b] 2nd run. [c] 3rd run. [d] 3 h. [e] Glucose (50 mg, 0.28 mmol), catalyst (50 mg), water (3 mL), 353 K, 0.5 h. [f] 4.5 h. [g] Mg/Al = 3.

Table 1 lists the results of the transformation of glucose over a variety of catalysts in water. The reaction was carried out in 3 mL of 1.67 M sugar solution with a slight amount of catalyst (10 mg) at 393 K. The protonated niobium molybdate, $HNbMoO_6$, selectively afforded mannose (Table 1, entry 1). The yield of mannose was 29%, which is almost the equilibrium yield. The catalyst could be reused at least three times without loss of activity (entry 1). No apparent leaching of Mo was confirmed by inductively coupled plasma atomic emission spectrometry (ICP-AES) ($<0.01$ ppm). The lithium form of niobium molybdate, $LiNbMoO_6$ also gave mannose as mentioned above (entry 5). No fructose was formed over either $HNbMoO_6$ or $LiNbMoO_6$. This indicates that the selective epimerization was catalyzed over these niobium molybdates regardless of the solid acidity. A sulfonated polystyrene-based ion exchange resin, Amberlyst-15, which is a representative Brønsted acid catalyst, did not convert glucose in water (entry 13). An anionic clay, Mg–Al hydrotalcite $[Mg_6Al_2(OH)_{16}CO_3\cdot nH_2O]$, which is a common Brønsted base catalyst, selectively gave fructose through isomerization (entry 14).[32] An amorphous niobium oxide hydrate, $Nb_2O_5\cdot nH_2O$, which was recently reported as a water-tolerant Lewis acid catalyst,[33] also afforded fructose (entry 15). Other metal oxides such as $TiO_2$, $WO_3$, and $SnO_2$ were inactive (entries 16–19). In contrast, molybdenum oxide could convert glucose and yielded mannose, although the oxide was completely dissolved during the reaction (entry 18). From these results, it can be deduced that Lewis acids and Brønsted bases do not produce mannose in water. As will be discussed, the reaction also cannot be attributed to the Brønsted acid sites within the interlayers of $HNbMoO_6$. Rather the surface Mo octahedra in the niobium molybdates are the likely active sites for the reaction. The niobium tungstate, $LiNbWO_6$, that is isostructural to $LiNbMoO_6$ showed no activity (entry 12). The niobium molybdates with different amounts of Mo, $Li_{0.85}Nb_{0.85}Mo_{1.15}O_6$, $LiNbMoO_6$, and $Li_{1.15}Nb_{1.15}Mo_{0.85}O_6$, were synthesized[34] and tested for the glucose epimerization (entries 6, 10, and 11). It was found that the activity increased with increase of the Mo content.

The transformation of other monosaccharides, such as mannose, xylose, and arabinose, was also investigated using $HNbMoO_6$ and $LiNbMoO_6$ (entries 2–4, 7–9). Both niobium molybdates afforded the corresponding epimers selectively. The conversions of glucose, xylose, and arabinose over $HNbMoO_6$ were around 30% with remarkable selectivity toward the corresponding epimers. The theoretical equilibrium product ratios from Gibbs free energy calculations were estimated to be 70:30, 67:33, and 69:31 for glucose/mannose, xylose/lyxose, and arabinose/ribose epimerizations, respectively,[35] indicating that these reactions reached equilibrium with $HNbMoO_6$. The epimerization reactions over $LiNbMoO_6$ also reached equilibrium by prolonging the reaction time from 0.5 h to 3 or 4.5 h (entries 7–9).

The manner in which the epimerization of glucose over $HNbMoO_6$ proceeded was further elucidated by using $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy (Figure 3) using a method previously reported.[22] Using D-(1-$^{13}$C)glucose and $D_2O$ as the solvent, the shift in position of the C1 carbon was followed. Before the reaction, two signals were observed at 95.8 and 92.0 ppm that corresponded to the C1 carbon of the β-pyranose and α-pyranose configurations of glucose.[36] After the reaction two new signals appeared at 71.1 and 70.6 ppm, which were assigned to the C2 carbon of the β-pyranose and α-pyranose configurations of mannose. No signals for the C1 carbon of mannose (94.6 and 95.1 ppm) were observed. These results demonstrated that a 1,2-rearrangement occurred for epimerization of glucose over $HNbMoO_6$ in water.

The XRD patterns of $LiNbMoO_6$ and $HNbMoO_6$ before and after immersion in the glucose-containing aqueous solutions are shown in Figure S1 in the Supporting Information. A shift of the (001) peak, which corresponds to expansion of the basal spacing, was observed for $HNbMoO_6$ after the immersion, which is a result of intercalation of glucose into the interlayers of $HNbMoO_6$ as shown in a previous study.[37] In contrast, the (001) peak remained unchanged for $LiNbMoO_6$. Considering that both layered oxides catalyzed the epimerization in a similar manner, the active sites of $LiNbMoO_6$ for the reaction are attributable to the Mo octahedra at the surface, not the Mo octahedra within the interlayer. The unit cell parameters of $LiNbMoO_6$ were reported as $a=b=0.4785$ nm and $c=0.925$ nm.[38] One Mo atom is located in the *ab*-plane in the unit cell, and the surface density of Mo octahedra is calculated to be 7.6 $\mu$mol m$^{-2}$. The BET surface area of $LiNbMoO_6$ used in this study was 5 m$^2$ g$^{-1}$. Thus, the amount of surface Mo octahedra in 50 mg of $LiNbMoO_6$ was 1.9 $\mu$mol, much lower than 170 $\mu$mol calculated by the molecular formula. This value was used for calculation of the turnover frequency (TOF).

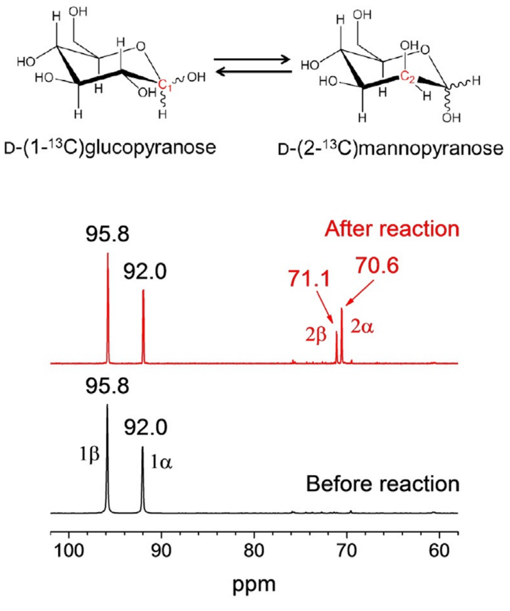

**Figure 3.** $^{13}C$ NMR spectra taken before and after epimerization of D-(1-$^{13}$C)glucose using $HNbMoO_6$ in $D_2O$. Reaction conditions: D-(1-$^{13}$C)glucose (300 mg, 1.67 mmol), $HNbMoO_6$ (10 mg), $D_2O$ (3 mL), 393 K, 1.5 h.

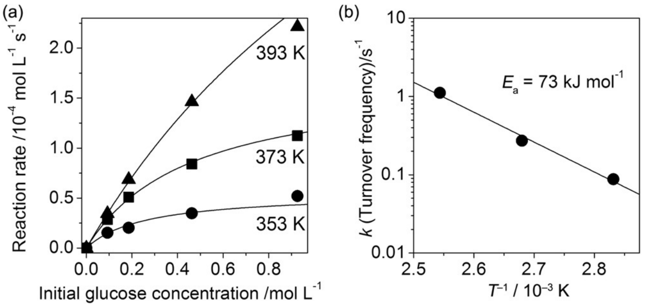

**Figure 4.** (a) Reaction rate versus initial glucose concentrations using $LiNbMoO_6$ at 373 K. Reaction conditions: glucose (0.28–2.8 mmol), $LiNbMoO_6$ (50 mg), water (3 mL), 373 K. (b) Arrhenius plots for epimerization of glucose over $LiNbMoO_6$.

Figure 4a shows the reaction rate versus the initial concentration of glucose for the epimerization over $LiNbMoO_6$. The reaction rate gradually levelled off with increase of initial concentration of glucose. This behavior is typical of Langmuir–Hinshelwood kinetics, $r=(S)kKC_0/(1+KC_0)$ where $r$ is the reaction rate (mol L$^{-1}$ s$^{-1}$), $(S)$ is the concentration of active sites (mol L$^{-1}$), $k$ is the rate constant (s$^{-1}$), $K$ is the adsorption equilibrium constant (L mol$^{-1}$), and $C_0$ is the initial glucose concentration (mol L$^{-1}$). On the basis of mole of active sites, the reaction rate $r'$ [mol s$^{-1}$ (mol-active sites)$^{-1}$] $= r$ (mol L$^{-1}$ s$^{-1}$)$\times$(3$\times$10$^{-3}$ L)/(1.9$\times$10$^{-6}$ mol) is also shown in Figure S2. Based on the kinetics, the rate constants over $LiNbMoO_6$ at 353, 373, and 393 K were estimated to be 0.09, 0.27, and 1.1 s$^{-1}$. These values are identical to TOFs at saturation coverage, $KC_0 \gg 1$, since TOF$=r/(S)$ is equal to $k$. The TOFs were higher than those over Mo-based polyoxometalates, such as $H_3PMo_{12}O_{40}$, $Sn_{0.75}PMo_{12}O_{40}$, and $Ag_3PMo_{12}O_{40}$.[25] Figure 4b also shows Arrhenius plots for the epimerization. The apparent activation energy, $E_a$ was 73 kJ mol$^{-1}$, which is much lower than that of a homogeneous molybdate catalyst (126 kJ mol$^{-1}$)[23] and Mo-based polyoxometalates (96–99 kJ mol$^{-1}$),[25] and comparable to that of Sn-beta zeolite in methanol (70 kJ mol$^{-1}$).[28] The reaction mechanism is similar to Scheme 1 because Mo is crucial for the activity. However, Mo–O–Nb bonding is dominant for the layered NbMo oxides. Thus, one possible explanation for the lower activation energy of the layered NbMo oxide than that of a homogeneous Mo catalyst is likely attributed to the Mo–O–Nb structure.

Previous studies demonstrated that the layered $HNbMoO_6$ can function as an efficient solid acid catalyst for a variety of acid-catalyzed reactions such as Friedel–Crafts alkylation,[31] esterification,[39] hydrolysis,[37] and cyclodehydration,[40] and this was attributed to facile intercalation of the reactant within the interlayers holding strong acid sites. Table 2 compares the results for the aqueous transformation of cellobiose over acidic $HNbMoO_6$, the non-acidic $LiNbMoO_6$, and strongly acidic ion-exchange resin, Amberlyst-15. Because of acid-catalyzed hydrolysis of cellobiose, Amberlyst-15 selectively yielded glucose. The non-acidic $LiNbMoO_6$ produced neither glucose nor mannose. In contrast, the acidic $HNbMoO_6$ afforded both glucose and mannose. The TOF of $HNbMoO_6$ for hydrolysis of cellobiose on the basis of the amount of acid sites was 0.25 $h^{-1}$, ten times higher than that of Amberlyst-15 (0.03 $h^{-1}$). The one-pot transformation of cellobiose to mannose proceeded by hydrolysis on the interlayers and by epimerization on the surface Mo octahedra.

**Table 2.** Transformation of cellobiose using $HNbMoO_6$, $LiNbMoO_6$, and Amberlyst-15.[a]

| Catalyst | Acid amount [mmol $g^{-1}$] | Conv. [%] | Selectivity [%] Glu[b] | Man[c] | HMF[d] | TOF [$h^{-1}$] |
|---|---|---|---|---|---|---|
| $HNbMoO_6$ | 1.9 | 32 | 47 | 29 | 8 | 0.25 |
| $LiNbMoO_6$ | 0 | 0 | 0 | 0 | 0 | 0 |
| Amberlyst-15 | 4.8 | 6 | >99 | 0 | 0 | 0.03 |

[a] Reaction conditions: cellobiose (50 mg, 0.15 mmol), catalyst (50 mg), water (3 mL), 393 K. 3 h. [b] Glucose. [c] Mannose. [d] 5-Hydroxymethylfurfural.

In summary, both $LiNbMoO_6$ and $HNbMoO_6$ were found to catalyze epimerization of monosaccharides including glucose, mannose, xylose, and arabinose in water. The surface Mo octahedra were responsible for the activity. The TOF was higher or comparable to those of Mo-based polyoxometalates and Sn-beta zeolite and the apparent activation energy was lower. The one-pot transformation of cellobiose to mannose was achieved using $HNbMoO_6$ through hydrolysis and successive epimerization.

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