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Tin–Tungsten Mixed Oxide as Efficient Heterogeneous Catalyst for Conversion of Saccharides to Furan Derivatives

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The Sn–W mixed oxide prepared by calcination of the Sn–W mixed hydroxide precursor with Sn/W molar ratio of 2:1 at 800 °C (Sn–W oxide) acts as an efficient heterogeneous catalyst for the synthesis of 5-hydroxymethylfurfural (HMF) and furfural from various hexoses (including polysaccharides) and pentoses, respectively.

The utilization of lignocellulose biomass, which is renewable, carbon (CO_2) neutral, readily available, and compatible with the food supply, has attracted much attention as potential alternatives to fossil fuels.[1] Furan derivatives, in particular HMF, have been considered to be very important platform chemicals because they can easily be converted into biofuels and useful chemicals.[2] Although fructose can selectively be converted into HMF with various kinds of acid catalysts including homogeneous as well as heterogeneous ones,[3] the selective synthesis of HMF is mainly limited to fructose (ketose) and difficult from aldohexoses including glucose,[4,5] which is the most abundant saccharide. Natural lignocellulose is mainly composed of various aldohexoses (mainly glucose) and aldopentoses. Therefore, in order to utilize lignocellulose effectively, much more efficient and practical procedures should be developed from the standpoint of their performance (high yields and selectivities) and applicability to various aldoses. In addition, the development of heterogeneous catalysts is more desirable.[5]

Quite recently, we reported that Sn–W oxide prepared by calcination of a hydroxide precursor can act as an effective and reusable heterogeneous acid catalyst for C–C bond-forming reactions[6a] and alkyne hydration.[6b] It has been revealed by various characterization that strong Brønsted (97 µmol g^{-1}) and Lewis acid sites (37 µmol g^{-1}) are generated on Sn–W oxide.[6,7] In this study, we found that Sn–W oxide can catalyze both glucose isomerization and fructose dehydration and that various aldohexoses and aldopentoses can be converted into HMF and furfural, respectively.

First, the catalytic performance for glucose isomerization was compared among various acid and base catalysts (Table 1). Sn–W oxide showed catalytic activity for the isomerization in DMSO at 70 °C for 24 h, giving HMF and mannose in 2% and 15% yields, respectively, at 23% conversion of glucose. It is generally known that glucose isomerization is catalyzed by base (enolate formation)[5] or Lewis acid catalysts (hydride shift, in particular with Sn-based Lewis acid catalysts).[8] In the presence of Sn–W oxide with Lewis acid sites, glucose isomerization proceeded even under mild conditions to afford isomerized saccharides such as fructose and mannose in equilibrium. Then, the subsequent dehydration of fructose proceeded to afford HMF. No isomerization proceeded in the absence of the catalyst, or in the presence of SnO_2, WO_3, or a physical mixture of SnO_2 and WO_3. In the case of commonly utilized homogeneous Brønsted acid catalysts such as H_2SO_4 and $H_3PW_{12}O_{40}$, no isomerization proceeded, and disaccharides and anhydroglucoses were formed through inter- and intramolecular dehydration, respectively. Other heterogeneous acid catalysts such as sulfated zirconia, Amberlyst-15, Nafion NR-50, and acidic zeolites were not effective. No isomerization proceeded in the presence of Mg–Al hydrotalcite under the present conditions.

Table 1. Glucose isomerization by various catalysts[a]

Entry	Catalyst	Conv./%	Yield/%	
			HMF	Mannose
1	Sn–W oxide	23	2	15
2	Sn–W hydroxide	4	n.d.	n.d.
3	SnO_2[b]	7	n.d.	n.d.
4	WO_3[c]	13	n.d.	n.d.
5	$SnO_2 + WO_3$[d]	5	n.d.	n.d.
6	Amberlyst-15	8	n.d.	n.d.
7	Nafion NR-50	11	n.d.	n.d.
8	Sulfated zirconia	13	n.d.	n.d.
9	H-mordenite	4	n.d.	n.d.
10	H-Y	1	n.d.	n.d.
11	H_2SO_4	17[e]	n.d.	n.d.
12	$H_3PW_{12}O_{40}$	23[f]	n.d.	n.d.
13	Hydrotalcite[g]	1	n.d.	n.d.
14	None	2	n.d.	n.d.

[a]Reaction conditions: Glucose (1 mmol), catalyst (amount of acidic sites: 1.9 mol % with respect to glucose), DMSO (5 mL), 70 °C, 24 h. n.d.: not detected. [b]SnO_2 (200 mg). [c]WO_3 (200 mg). [d]SnO_2 (100 mg) + WO_3 (100 mg). [e]Disaccharides (14%) and anhydroglucoses (1%) were formed. [f]Disaccharides (12%) and anhydroglucoses (1%) were formed. [g]$Mg_6Al_2(OH)_{16}(CO_3)$ hydrotalcite (100 mg).

With regard to fructose dehydration (Table 2), various solid acid catalysts such as Sn–W oxide, sulfated zirconia, Amberlyst-15, Nafion NR-50, and acidic zeolites were effective, giving HMF in moderate to high yields (47–70%). Among solid acid catalysts examined, Sn–W oxide gave the highest yield of HMF, and the catalytic activity of Sn–W oxide was comparable to those of commonly utilized homogeneous Brønsted acid catalysts such as H_2SO_4 and $H_3PW_{12}O_{40}$. *Among catalysts examined, only Sn–W oxide showed activity for both glucose isomerization and fructose dehydration.*

Next, we turned out our attention to direct synthesis of HMF from glucose. The reaction conditions were optimized by changing temperature, solvent, and scale (Table S1).[7] Under the optimized conditions, the Sn–W oxide-catalyzed transformation of glucose efficiently proceeded to afford HMF in 48% yield

Table 2. Fructose dehydration by various catalysts[a]

Entry	Catalyst	Conv./%	HMF yield/%
1	Sn–W oxide	>99	70
2	Amberlyst-15	71	53
3	Nafion NR-50	94	68
4	Sulfated zirconia	>99	66
5	H-mordenite	76	47
6	H-Y	93	62
7	H_2SO_4	>99	68
8	$H_3PW_{12}O_{40}$	>99	81

[a] Reaction conditions: Fructose (1 mmol), catalyst (amount of acidic sites: 1.0 mol % with respect to fructose), DMSO (5 mL), 80 °C, 12 h.

Table 3. Conversion of various (poly)saccharides[a]

Entry	Substrate	Product	Yield/%
1	Glucose	HMF	48
2[b]	Glucose	HMF	44
3[c]	Fructose	HMF	70
4	Mannose	HMF	47
5	Galactose	HMF	45
6	Cellobiose	HMF	39
7	Sucrose	HMF	42
8[d]	Starch	HMF	41
9	Xylose	Furfural	52
10	Arabinose	Furfural	46

[a] Reaction conditions: Saccharides (1 mmol for monosaccharides, 0.5 mmol for disaccharides), Sn–W oxide (100 mg), THF/water (5 mL/1 mL), 120 °C, 18 h. [b] Reuse experiment. [c] Reaction conditions: Fructose (1 mmol), Sn–W oxide (100 mg), DMSO (5 mL), 80 °C, 12 h. [d] Starch (162 mg), 36 h.

(Table 3, Entry 1), and the yield was comparable to those of previously reported systems with heterogeneous catalysts.[5] This high performance is likely due to the coexistence of Lewis (for isomerization) and Brønsted (for dehydration) acid sites on Sn–W oxide. Sn–W oxide could be reused without an appreciable loss of its catalytic performance (Table 3, Entry 2). Besides glucose, various hexoses such as fructose, mannose, and galactose could be converted into HMF (Table 3, Entries 3–5). Notably, polysaccharides such as cellobiose, sucrose, and starch also gave HMF in moderate yields (Table 3, Entries 6–8). In addition, furfural could be obtained from pentoses such as xylose and arabinose (Table 3, Entries 9 and 10).

Quite recently, we reported an efficient procedure for saccharification of natural nonpurified lignocellulose biomass with highly negatively charged heteropolyacids.[9] For example, the saccharification of Japanese cedar sawdust efficiently proceeded in a $H_5BW_{12}O_{40}$ solution (0.7 M aqueous solution), giving a mixture of water-soluble saccharides in 80% isolated yield (total yields based on holocellulose) (Figure 1).[9] By the Sn–W oxide-catalyzed conversion of the saccharide mixture obtained, HMF and furfural were produced in 36% (based on hexoses) and 62% (based on pentoses) yields, respectively (Figure 1). Thus, 31% overall yield of furan derivatives was obtained from natural lignocellulose biomass by the present two-step procedure.

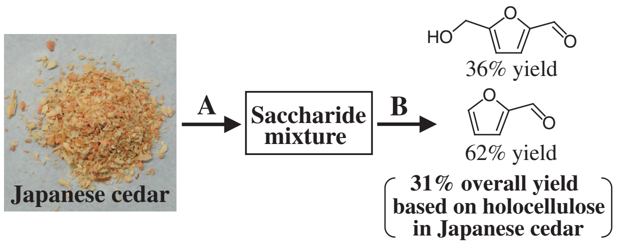

Figure 1. Two-step production of HMF and furfural from Japanese cedar sawdust. Reaction conditions **A**: Japanese cedar sawdust (100 mg), $H_5BW_{12}O_{40}$ solution (0.7 M aqueous solution, 2 mL), 60 °C (see Supporting Information in more detail). By the reaction, a mixture of glucose (53%), galactose (4%), mannose (11%), xylose (8%), arabinose (1%), and cellobiose (3%) was obtained. Reaction conditions **B**: Saccharides obtained, Sn–W oxide (18 mg), THF/water (5 mL/1 mL), 120 °C, 18 h.

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