Acid-base catalysis of $YNbO_4$ for sugar conversion in water

Minjune Kim[1,2], Hideki Kato[3], Atsushi Fukuoka[1], Kiyotaka Nakajima[1,2]
[1]*Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, Japan*
[2]*JST Agency, ALCA program, 4-1-8 Honcho, Kawaguchi 332-0012, Japan*
[3] *IMRAM, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan*
*E-mail: nakajima@cat.hokudai.ac.jp

Lewis acid and base catalysis of metallosilicates and metal oxides has been extensively investigated for the conversion of biomass-derived sugars to versatile platform molecules such as 5-hydroxymethyl furfural and lactate derivatives. Sn-containing beta zeolite (Sn-β) converted glucose to fructose in water through the hydride transfer mechanism,[1] whereas heat treatment of glucose and Sn-β in methanol produces methyl lactate.[2] In the latter reaction, retro-aldol reaction of fructose to form two triose sugars, 1,3-dihydroxyacetone (DHA) and glyceraldehyde (GLA), is a key step to produce desired lactates selectively. While Nb_2O_5 and TiO_2 with Lewis acid sites can catalyze HMF formation from glucose in water,[3,4] selective lactates formation from glucose or fructose cannot be achieved due to the absence of Lewis base sites effective for the retro-aldol reaction (Fig. 1). Therefore, precise control of Lewis acid/base property of metal oxides would lead to the development of an effective solid catalyst for the conversion of glucose to lactate-based compounds. Here, we focus on Lewis acid/base catalysis of a niobium-based mixed oxide, $YNbO_4$, in water. Despite no basicity of pure Nb_2O_5, its mixed oxide with basic component oxide such as Y is expected to have intrinsic Lewis acidity and basicity available for sugar conversion (Fig. 1).

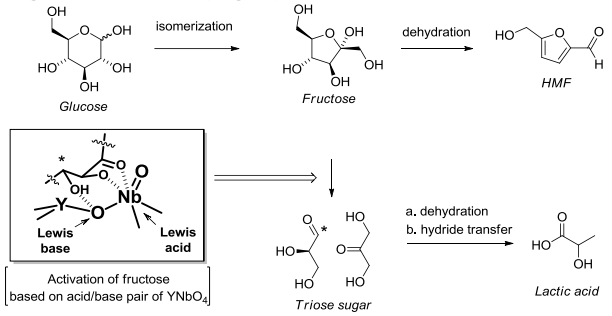
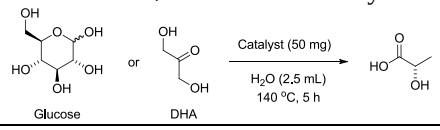


Fig. 1 Possible reaction pathways for lactic acid formation from glucose in water over a solid acid/base catalyst.

$YNbO_4$ can be synthesized by a simple precipitation method using water soluble precursors ($[(NH_4)_3{\cdot}Nb(O_2)_4]$ and $Y(NO_3)_3{\cdot}6H_2O$) in water. The precipitate readily formed was aged at room temperature for several hours, recovered with vacuum filtration, and then dried at 80 ºC in air for 3 h. Basic property of $YNbO_4$ was evaluated by the Claisen-Schmidt condensation as a test reaction. Although Nb_2O_5 showed no activity for the reaction, due to the absence of basic site, $YNbO_4$ gave desired product with 30-35% yield which was comparable to MgO, a typical solid base catalyst. In addition, FT-IR measurement with $CHCl_3$ as an acidic molecular probe demonstrated that adsorption of $CHCl_3$ on $YNbO_4$ results in the redshift of original C-H stretching mode. These results suggest that basic sites are formed on $YNbO_4$ and available as catalytically active sites.

Table 1. Lactic acid formation from DHA or glucose in water over $YNbO_4$ and reference catalysts



Catalyst	Acidity /basicity[a]	Substrate	Conv.[b] (%)	Yield[c] (%)
Nb_2O_5	BA+LA	Glucose	99.7	3.2
		DHA	>99.9	56
$YNbO_4$	LA+LB	Glucose	96.3	19.6
		DHA	>99.9	74
MgO	LA+LB	Glucose	99	17.5
		DHA	>99.9	37
Pyridine	LB	Glucose	24.2	1.8
		DHA	>99.9	4

[a] BA, Brønsted acid; LA, Lewis acid; LB, Lewis base; [b] Conversion of glucose or DHA, [c] Lactic acid yield

Lewis acid and base sites on $YNbO_4$ are fundamentally essential for lactic acid formation from glucose in water, because the reaction contains four elementary steps catalyzed by Lewis acid and/or base: the hydride transfer of glucose to fructose, retro-aldol reaction of fructose to triose sugars, dehydration of triose sugars to pyruvaldehyde (PVA), and the hydride transfer of PVA into lactic acid (Fig. 1). We applied $YNbO_4$ to lactic acid formation from glucose and DHA in water at 140 ºC. Almost no lactic acid formation from both substrates on pyridine means that Lewis base alone is not effective for the reactions. Nb_2O_5 with Brønsted and Lewis acid can produce lactic acid from DHA. Brønsted acid was reported to be ineffective for hydride transfer of pyruvaldehyde,[6] so that Lewis acid on Nb_2O_5 is responsible for the conversion of DHA to lactic acid. Despite low catalytic activity of Nb_2O_5, $YNbO_4$ with Lewis acid and base can produce lactic acid from glucose, as well as from DHA. These results could be due to Lewis acid and base sites that promote all elementary steps shown in Figure 1. Similar results were also obtained in the case of MgO with Lewis acid and base, suggesting that control of Lewis acidity and basicity is dominant for the development of an effective catalyst for lactic acid formation from glucose.

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