

Acid-basic property of YNbO₄ for lactic acid formation from glucose in water

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Abstract: The Lewis acid/base property of YNbO₄ has been studied as a new bifunctional heterogeneous catalyst. Despite no basicity of pure niobium oxide, YNbO₄ combined Lewis acidity of Nb₂O₅ and Lewis basicity of Y₂O₃ in a single mixed metal oxide. These Lewis acid-base sites functioned as catalytically active sites for the Claisen-Schmidt condensation of benzaldehyde and acetylacetone in THF-DMF mixture and lactic acid formation from glucose or 1,3-dihydroxyacetone in water.

Keywords: Lactic acid, glucose conversion, Acid-base bifunctional catalyst, YNbO₄.

1. Introduction

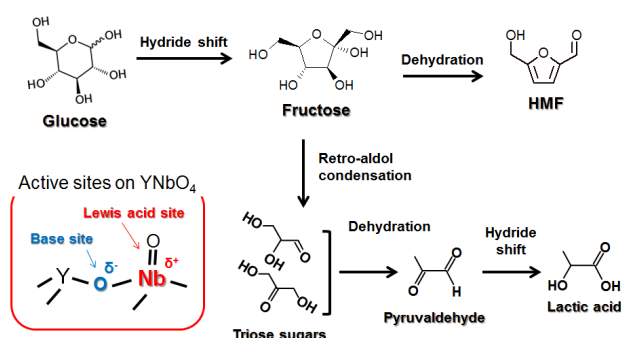


Figure 1. Possible reaction pathways for the conversion of glucose to HMF or lactic acid over a solid Lewis acid

Lewis acid and base catalysis of metallocates 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 effectively.² In the latter reaction, retro-aldol reaction of fructose to two triose sugars (1,3-dihydroxyacetone (DHA) and glyceraldehyde (GLA)) is a key step to produce desired lactates selectively. While Lewis acid sites on Nb₂O₅ and TiO₂ also

catalyze HMF formation from glucose in water,^{3,4} selective lactates formation from glucose or fructose cannot proceed on these catalysts at all. This could be explained by their Lewis acid and base properties that are not suitable for such a consecutive reaction consisting of isomerization, retro-aldol reaction, and dehydration (Figure 1). Because retro-aldol reaction is a base-catalyzed reaction, precise control of Lewis acidity and basicity of metal oxide catalyst 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 property of a niobium-based mixed oxide, YNbO₄, in water. Despite no basicity of pure Nb₂O₅, its mixed oxide with a secondary component of basic metal oxide such as Y is expected to have intrinsic Lewis acidity and basicity available for sugar conversion involving retro-aldol reaction (Figure 1).

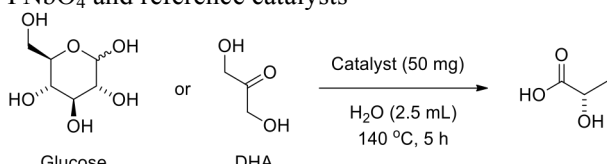
2. Experimental

[(NH₄)₃·Nb(O₂)₄] was adopted as a water-soluble precursor for the preparation of YNbO₄. Briefly, the peroxo complex dissolved in water was mixed with a solution containing yttrium nitrate at 273 K without stirring. The precipitate readily formed was aged at room temperature for several hours, recovered with vacuum filtration, and then dried at 80 °C in air for 3 h. The Claisen-Schmidt condensation of benzaldehyde and acetylacetone was carried out in a Pyrex round-bottom flask with THF (1.8 mL), DMF (0.2 mL), benzaldehyde (0.1 mmol), acetylacetone (0.15 mmol) and solid catalyst (100 mg) at 90 °C. Lactic acid formation from glucose was also carried out in a Pyrex glass vessel containing water (2.5 mL), glucose (20 mg), and solid catalyst (50 mg) at 140 °C. After 5 hour, products in the reaction mixture were evaluated with ¹H NMR and/or high performance liquid chromatography.

3. Results and discussion

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 effective basic site, YNbO_4 gave desired product with 30-35% yield for 5 h, which was comparable to that of MgO , a typical base catalyst. Basicity of YNbO_4 tends to decrease with calcination treatment: product yields of YNbO_4 calcined at 400 °C and 700 °C for 3 h exhibited 18% and 2%, respectively. These results indicate that YNbO_4 without calcination treatment at high temperature has basic sites effective for a typical base-catalyzed reaction. Basic property was investigated with FT-IR measurement with CHCl_3 as an acidic molecular probe, which demonstrated that adsorption of CHCl_3 results in the red-shift of original CH stretching mode due to hydrogen-bonding interaction of acidic CH bond in CHCl_3 with base site on YNbO_4 surface. In addition, new band for CHCl_3 bending mode was observed at 1240 cm^{-1} , indicating simultaneous interaction of H and Cl atom in CHCl_3 with Lewis base and Lewis acid site of YNbO_4 .

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



Catalyst	Acidity/basicity ^a	Substrate	Conversion ^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

These Lewis acid and base sites 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 (DHA and GLA), dehydration of triose sugars to pyruvaldehyde, and the hydride transfer of pyruvaldehyde into lactic acid (Figure 1). We applied YNbO_4 to lactic acid formation from glucose and DHA in water at 140 °C. 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 poor 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 was 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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