

Efficient Xylose Dehydration to Furfural over Lewis Acid Catalysts in Biphasic Water and Toluene

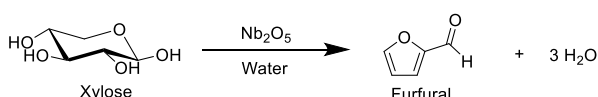
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Biomass derived sugars are readily available as raw materials and can be transformed by chemocatalytic routes into useful compounds *e.g.* HMF and furfural with an aim toward the production of industrial chemicals.^[1] An industrial process for furfural synthesis from xylose have been established using H₂SO₄ as a Brønsted acid catalyst.^[2] However, one serious drawback of this process is the use of liquid acid, which is inevitably accompanied by energy-inefficient separation of the catalyst from the reaction mixture or the removal of inorganic salt by-products such as gypsum by neutralization treatment. Herein, we have investigated the sustainable conversion of xylose into furfural over a stable and reusable solid acid catalyst, Nb₂O₅, because the combination of intrinsic Brønsted and Lewis acidity on the surface of Nb₂O₅ is potentially effective for furfural production (Scheme 1).^[3]



Scheme 1. Conversion of xylose to furfural in water over Nb₂O₅.

Nb₂O₅ was received from CBMM (Companhia Brasileira de Metalurgia e Mineração, BET surface area = 132 m² g⁻¹) and used without pretreatment. Catalytic reactions were typically performed in a pressure-resistant quartz reactor using 100 mg of solid catalyst, 0.5–1 mmol of xylose, and 2–5 mL of water at 383–413 K. After the reactions, the resultant solutions were diluted 10–30 times with water and then analyzed using high performance liquid chromatography (HPLC; Nexera X2, Shimadzu, Aminex HPC-87H column, 308 K, 5mM H₂SO₄) with refractive index photodiode array detectors.

Table 1 summarizes the acid site densities and catalytic activities of Nb₂O₅ and homogeneous catalysts at 393 K. HCl and Sc(OTf)₃ were adopted as Brønsted and Lewis acids for comparison. Nb₂O₅ gave a xylose conversion of 93% and 48% selectivity toward furfural over 3 h (Entry 1). Despite a high density of Brønsted acid sites, xylose conversion over HCl was below 40% (Entry 2), which revealed that typical Brønsted acids are less active for this reaction at 393 K. There was no decrease in the original conversion and selectivity

over Nb₂O₅, even after deactivation of the Brønsted acid sites by ion-exchange treatment with sodium cations (Entry 3), which indicates that the Lewis acid sites of Nb₂O₅ are responsible for the formation of furfural. Sc(OTf)₃ with a high density of Lewis acid also exhibited high xylose conversion (95%), but the selectivity toward furfural was low (18%) (Entry 4).

Table 1. One-pot synthesis of furfural from xylose using Lewis and Brønsted acid catalysts.

	Catalyst	Acidity /mmol g ⁻¹		Conv. (%)	Sel. (%)
		LAS ^a	BAS ^b		
1	Nb ₂ O ₅ ^c	0.03	0.14	93	48
2	HCl	-	9.90	31	39
3	Na ⁺ /Nb ₂ O ₅	0.03	-	89	45
4	Sc(OTf) ₃	2.00	-	95	18
5^d	Sc(OTf) ₃	2.00	-	79	38
6^d	Nb ₂ O ₅	0.03	0.14	92	46

Reaction conditions: 75 mg xylose (0.5 mmol); 5 mL water; 100 mg catalyst (S/C = 0.75); T = 393 K; t = 3 h. ^aLewis acid sites., ^bBrønsted acid sites. ^cAmounts of Lewis acid and Brønsted acid sites on hydrated Nb₂O₅ were estimated by pyridine-adsorption experiments with Fourier transform infrared spectroscopy (FTIR). ^d0.1 M HCl solution was used as a solvent instead of water.

Lewis acid catalysis of Nb₂O₅ is different from that of a typical Lewis acid such as Sc(OTf)₃, which is also suggested from entries 3, 5, and 6 of Table 1. When HCl was added to the Sc(OTf)₃ system, the selectivity toward furfural was significantly improved from 18% to 38% (Entry 5). In contrast, no effect was observed by deactivation of the Brønsted acid sites on Nb₂O₅ (Entry 3) and the addition of HCl to the Nb₂O₅ system (Entry 6). These results indicate that the unique catalysis over Nb₂O₅ can be explained by neither the cooperative action of Brønsted and Lewis acid sites nor by the simple catalysis over a water-tolerant Lewis acid. Isotope-labeling experiment confirmed that furfural is formed through step-wise dehydration.

In situ extraction of furfural from aqueous solution into an organic phase was applied to avoid catalytic degradation and polymerization of the products. The addition of toluene as extracting solvent in reaction mixture greatly improved furfural selectivity from 48% to 72% without decrease in xylose conversion (> 95%). No apparent decrease in original activity was observed even after three reuses of Nb₂O₅ catalyst in the biphasic reaction system. Facile recovery and high reusability of Nb₂O₅ in the biphasic system is essential for the development of an environmentally benign and efficient process for the production of furfural

REFERENCES

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