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Vapor phase hydrogenation of furfural over nickel mixed metal oxide catalysts derived from layered double hydroxides

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ABSTRACT

The hydrogenation of furfural is investigated over various reduced nickel mixed metal oxides derived from layered double hydroxides (LDHs) containing Ni-Mg-Al and Ni-Co-Al. Upon reduction, relatively large Ni(0) domains develop in the Ni-Mg-Al catalysts, whereas in the Ni-Co-Al catalysts smaller metal particles of Ni(0) and Co(0), potentially as alloys, are formed, as evidenced by XAS, XPS, STEM and EELS. All the reduced Ni catalysts display similar selectivities towards major hydrogenation products (furfuryl alcohol and tetrahydrofurfuryl alcohol), though the side products varied with the catalyst composition. The 1.1Ni-0.8Co-Al catalyst showed the greatest activity per titrated site when compared to the other catalysts, with promising activity compared to related catalysts in the literature. The use of base metal catalysts for hydrogenation of furanic compounds may be a promising alternative to the well-studied precious metal catalysts for making biomass-derived chemicals if catalyst selectivity can be improved in future work by alloying or tuning metal-oxide support interactions

1. Introduction

In an effort to reduce society's dependency on oil as a feedstock, conversion of biomass into chemicals and fuels continues to be a promising route towards feedstock sustainability [1]. Different challenges emerge in biomass refining compared to petroleum refining due to the over-functionalized and highly oxygenated compounds derived from common forms of biomass such as lignocellulose [2,3]. Furfural, which can be produced through the dehydration of xylose or via fast pyrolysis of biomass, is a lignocellulose derivative that can be converted into a wide variety of chemicals and fuels [4,5]. Some of the important chemicals include furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, furan, and 1,5-pentanediol (Scheme 1). Typically, furfural conversion utilizes heterogeneous catalysts due to the higher stabilities and ease of separation of these materials compared to homogeneous catalysts [6].

Industrially, chromium based catalysts have been heavily used for conversion of furfural to various chemicals. However, due to the environmentally hazardous nature of many oxidized chromium species, other metals may be preferred [7–11]. To date, many studies utilizing catalysts derived from a single metal species supported on a relatively inert material such as silica have been reported for furfural reduction. Specific examples include reports utilizing a variety of different transition metals, including Pt, Pd, Ir, Ni, and Cu [12–20]. Unfortunately, many monometallic catalysts suffer from lack of selectivity and therefore, the addition of a secondary metal has been used to greatly improve the properties of the first metal. One particularly successful approach has been to combine a reducible metal with a more oxophilic metal to create catalytic domains that offer the potential for multi-point interactions with the oxygenated furfural molecule [21–25]. The degree of reduction of the metal(s) plays a key role in creating a bifunctional catalyst surface with the reducible and oxophilic metal pair [2].

Among the array of bimetallic/bifunctional catalysts used for furfural hydrogenation, Ir-ReO_x catalysts have demonstrated high selectivity towards furfuryl alcohol, with some authors proposing that the ReO_x orients furfural on the surface, while Ir subsequently hydrogenates the aldehyde [26,27]. Since typically these bifunctional catalysts contain precious metals that may not be economically attractive for large scale use, we sought to utilize non-precious metals to create mixed metal-oxide domains simi-

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Table 1
Physical properties of the catalysts.

Catalyst	ICP-Analysis		Uncalcined			Calcined at 400 °C		
	Ni:M:Al ratio	Ni/M	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
2Ni-Al	2.0:0:1	–	129	0.47	14.6	239	0.61	12.8
1.3Ni-0.5Co-Al	1.3:0.5:1	2.6	113	0.54	19.4	196	0.67	16.5
1.9Ni-Mg-Al	1.9:1:1	1.9	137	0.45	9.3	288	0.50	8.9
1.1Ni-0.8Co-Al	1.1:0.8:1	1.4	108	0.57	21.4	175	0.59	16.3
1.4Ni-1.4Mg-Al	1.4:1.4:1	1.0	128	0.51	15.6	236	0.39	10.6
0.7Ni-1.1Co-Al	0.7:1.1:1	0.6	93	0.41	21.1	163	0.46	12.0
0.9Ni-1.9Mg-Al	0.9:1.9:1	0.5	148	0.41	10.9	236	0.51	10.3
Co-Al	0:1:1	–	62	0.33	28	160	0.32	8.5

Table 2
Selectivities and activities for each catalyst under reaction conditions yielding nearly complete conversion of furfural.

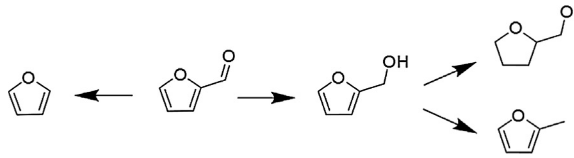
Catalyst[a]	Conversion	Activity[b]	Selectivity (%)						
	%	$\frac{mol_{conv}}{h \times g_{cat}}$	FA	THFA	Furan	2-MF	BOH	1,2-PD	Others[c]
2Ni-Al	94	0.098 ± 0.002	58.2	21.1	11.7	5.6	1.2	1.4	0.8
1.9Ni-Mg-Al	95	0.124 ± 0.002	65.0	13.1	18.2	1.1	2.0	0.6	0.0
1.3Ni-0.5Co-Al	99	0.100 ± 0.001	70.0	11.8	11.0	4.1	1.8	1.3	0.0
1.4Ni-1.4Mg-Al	94	0.081 ± 0.007	68.6	10.2	19.0	0.4	1.3	0.0	0.5
1.1Ni-0.8Co-Al	98	0.140 ± 0.002	71.8	9.9	8.9	5.3	2.2	0.9	1.0
0.9Ni-1.9Mg-Al	92	0.037 ± 0.003	66.7	13.1	16.9	0.7	1.6	0.4	0.6
0.7Ni-1.1Co-Al	91	0.124 ± 0.003	75.6	6.6	6.8	6.4	2.2	1.2	1.2
Co-Al[d]	98	0.086 ± 0.003	48.0	0.8	2.3	42.3	3.4	0.6	2.6

[a] Reactions Conditions: 155 °C and 1 atm with a furfural flow rate of 5.5 mmol/hr and H_2/furfural = 25. Catalyst amount ranged between 35 and 135 mg. Values obtained after approximately 1 h on stream. FA–furfuryl alcohol; THFA–tetrahydrofurfuryl alcohol; 2-MF–2-methylfuran; BOH–1-butanol; 1,2-PD–1,2-pentanediol.

[b] Error determination discussed in supplementary information.

[c] Others include 1-pentanol, 2-pentanol, and 1-butanal.

[d] Carbon balance closure was within 10%.



Scheme 1. Reaction pathways of the major products from furfural conversion on Ni based catalysts [13].

lar to those mentioned above. More specifically, Ni has previously been shown to be a good hydrogenation catalyst for furfural [14]. To this end, Ni was chosen as the reducible metal, and other oxophilic metals were included into the support matrix. Most studies conducted with two metal systems for furfural conversion containing Ni have focused on bimetallics or alloyed catalysts including NiFe, NiPd, and NiSn systems [12,28,29]. Two recent reports have shown the promise of Ni bifunctional catalysts by demonstrating that both Ni phyllosilicates and Ni-Al mixed metal oxides conduct C—O hydrogenolysis of HMF due to acid sites adjacent to Ni nanoparticles [24,25]. In this work, nickel-containing layered double hydroxides (LDH) derived from hydrotalcites have been used to create highly dispersed, porous, and thermally stable mixed metal oxides. LDH derived mixed metal oxides provide useful characteristics in the field of catalysis due to their wide versatility [30–33]. LDH materials derived from hydrotalcite structures have a balance of M^{3+} and M^{2+} cations, which allows for a variety of metals to be incorporated into the structure while maintaining high metal dispersity, high thermal stability, and sufficient porosity. Few studies have been conducted to investigate furanic compound hydrogenation utilizing LDH derived catalysts, and no in-depth spectroscopy has been reported [23,25,34]. In this study, two other metals, Co and Mg, were mixed with Ni and Al through a co-precipitation method. Two recent studies reporting catalysts with Co in the metallic phase have shown that the catalysts are effective in the hydrogenation of furfural to furfuryl alcohol in liquid phase batch reactions [35,36]. Thermodynamically, Co and Mg oxides have vastly different reduction energies, with Co oxide being more reducible than Mg, which causes varying interactions with Ni during the reduction phase of catalyst synthesis. In this work, an in-depth investigation was conducted on the metallic and oxide species present after reduction, which gives insight into the catalytic behavior of the materials in the gas phase hydrogenation of furfural.

2. Experimental

2.1. Materials and chemicals

Furfural (99% purity, ACS Grade) was purchased from Sigma Aldrich and stored in inert N_2 atmosphere to limit its polymerization. $Co(NO_3)_2 \cdot 6H_2O$ (99% purity), Na_2CO_3 (99.5% purity), and ethylene glycol diethyl ether (98% purity) were purchased from Sigma Aldrich. $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$ were purchased from Alfa Aesar (98–102% purity). NaOH (97% purity) was purchased from EMD. All chemicals were used as received without any further purification.

2.2. Catalyst synthesis

Ni-M-Al (M-Co, Mg) mixed metal oxides with varying Ni:M ratios of 1:2, 1:1, 2:1, while trying to maintain (Ni + M)/Al = 0.25, were prepared in the following manner. Solution A contained 0.6 M of the metal nitrates corresponding to the molar ratio of metal cations. Solution B contained 1 M solution of NaOH, and solution C contained 0.3 M solution of Na_2CO_3. Using a peristaltic pump Solution A and Solution B were added dropwise into Solution C, contained in a flat-bottom flask, at approximately 5 mL/min under vigorous stirring and room temperature. A pH meter was placed in the solution, and a Labview program maintained the pH at approximately 10 by adjusting the flow of Solution B. Once Solution A had