Graphical Abstract

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.

Keywords: biomass, furfural, hydrogenation, layered double hydroxide, mixed metal oxide, cobalt

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. 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 similar 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 M³⁺ and M²⁺ 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. A couple of recent studies have been conducted with Co in the metallic phase, which have shown promise in the hydrogenation of furfural to furfuryl alcohol in liquid phase batch.^{35,36} Thermodynamically, Co and Mg oxides have vastly different reduction energies, Co oxide being more reducible than Mg, which causes varying interactions with Ni during the reduction phase of catalyst synthesis. An in-depth investigation was conducted on the metallic and oxide species present after reduction, which gave 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 N₂ atmosphere to limit its polymerization. Co(NO₃)₂·6H₂O (99% purity), Na₂CO₃ (99.5% purity), and ethylene glycol diethyl ether (98% purity) were purchased from Sigma Aldrich. Ni(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, and Mg(NO₃)₂·6H₂O were purchased from Alfa Aesar (98%-102%). NaOH (97% purity) was purchased from EMD. Lastly, 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 Na₂CO₃. 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 was empty, the mixture was heated to 60°C, and it was aged under vigorous stirring for 48 hours. After, the precipitant was filtered and washed with distilled water until the wash solution was at about pH of 7. The recovered solid was dried in an oven at 100°C overnight, and then it was calcined at 400°C with 50 mL/min flow of air with a ramp rate of 10°C/min and a hold time of 4 hours.

2.3 Characterization Techniques

Nitrogen physisorption was performed in a Micromeritics Tristar II at -196°C after the samples were pretreated at 200°C (150°C for uncalcined LDH materials) under vacuum for 12 hours. Chemisorption experiments including temperature programmed reduction (TPR) and pulse CO chemisorption were conducted on a Micromeritics AutoChem II 2920. For each TPR experiment, approximately 50 mg of sample was placed on top of a small bed of quartz wool in a quartz U-tube. In regards to the TPR experiment, the mixed metal oxide was pretreated in 20 mL/min of He (Airgas, UHP) at 200°C for 2 hours to remove preadsorbed species. The sample was then cooled to 50°C and 20 mL/min of 10% H₂ balance He was flown over the sample. The furnace was heated to 800°C at 5°C/min while under the flow of 10% H₂/He. The outlet gas passed through a liquid acetone/nitrogen trap, and then passed through a Thermal Conductivity Detector (TCD). Pulse CO experiments were conducted in a similar fashion with a few minor changes. Approximately 20 mg catalyst sample was diluted with 80 mg of SiC, and placed in the quartz tube held in place by quartz wool. During the reduction step the sample was heated to 500°C at 5°C/min and held for 1 hour. The sample was then cooled to 400°C where He began to flow for 30 min to remove all adsorbed species. Afterwards the sample was cooled to 30°C to begin pulse CO testing. Doses of 10% CO/He (Airgas) were passed over the sample and analyzed in the TCD. Once saturation was reached, He was flowed over the sample for 60 min to

remove physisorbed species. Finally a second round of pulses was conducted to verify if there were any physisorbed species adsorbed, which was taken into consideration when calculating the active metallic surface area.

Powder X-ray diffraction patterns (XRD) were collected using a Philips X-pert diffractometer using Cu K α radiation. X-ray Photoemission Spectroscopy (XPS) analysis was conducted using a Thermo K-Alpha spectrometer employing a monochromatic Al K α . The pressure inside the analytical chamber was approximately 5×10^{-8} Torr. The binding energies (BE) of all elements were tuned to the Ag 3d peak (368.2 eV) with an uncertainty of ± 0.2 eV. Samples for scanning transmission electron microscopy (STEM) imaging were prepared by dropping a methanol-catalyst mixture on a lacy carbon-coated Cu grid and allowing the methanol to evaporate. Images were collected on an aberration-corrected-Nion UltraSTEM100 at 100 kV and aberration corrected JEOL 2200FS STEM at 200 kV. Electron energy loss spectroscopy (EELS) was performed on the Nion while energy-dispersive X-ray spectroscopy (EDS) was performed on the JEOL. Elemental analysis was conducted at Georgia Tech Renewable Bioproducts Institute utilizing inductively coupled plasma optical emission spectroscopy (ICP-OES) by Perkin Elmer OPTIMA 7300 DV after dissolving the metal oxides by caustic fusion and acid digestion.

In situ X-ray absorption spectroscopy (XANES and EXAFS) was conducted at the Advanced Photon Sources (APS), Argonne National Lab (ANL) at beamline 12-BM. The data were obtained in transmission mode at the Ni K-edge (8333 eV) in the range of 8130-9190 eV, and the Co K-edge (7712 eV) in the range of 7510-8260 eV, both with a spot size of 0.5mm x 1.2mm. To perform the *in situ* reduction XAS experiments, the catalyst sample was diluted and ground with boron nitride, and then ~1 mg sample was loaded into a 1/16" quartz tube held in

place by quartz wool. The quartz tube was secured in a sample holder with a gas inlet and outlet, and a coil heater was centered along the catalyst. An XAS scan was taken before reduction at room temperature. Next the catalyst was heated to 500 °C at 5 °C/min and held for 1 h, all while under a 10 mL/min flow of 4% H₂/He. Transient scans were collected during the reduction. After the reduction was complete, the sample was cooled in He, and a final scan was collected at room temperature. The XAS data were processed and analyzed with Athena software including background removal, edge-step normalization, and Fourier transform.

2.4 Reaction Studies

Vapor phase reactions were performed in a 1/4" tubular stainless steel reactor located inside a furnace. The catalyst was pelletized (120-170 mesh) diluted with SiC (200-400 mesh) and loaded into the reactor between layers of SiC (46 mesh) and quartz wool. The catalyst was reduced *in situ* under 60 mL/min H₂ (Airgas, UHP) to 500 °C at 5 °C/min and held for one hour. Once the reduction was completed, the bed was cooled under N₂ (Airgas, UHP) to reaction temperature. Unless stated otherwise, reactions were conducted in a flow of 60 mL/min of H₂. Furfural was pumped into the vaporization zone at a rate of 5.5 mmol/h (~2.5 mol% ethylene glycol diethyl ether as internal standard). The furfural flow met heated H₂ (H₂/furfural approximately 25) in the vaporization zone, which was heated to approximately 165 °C. The vapor flowed through the catalyst bed at temperatures fixed in the range of 155 °C-175 °C, and then it flowed into an online Agilent 7890A GC through lines heated to approximately 180 °C to minimize condensation. Selectivity and conversion were determined by the internal standard method, and carbon balances closed within 5% unless stated otherwise. After the reaction or reduction was completed, the catalyst was passivated for one hour at room temperature under 1%

O₂/N₂ (Airgas) before removal from the reactor, separated from SiC, and stored under argon for further characterization studies.

3. Results and discussion

3.1 Catalyst Characterization

LDH materials were synthesized as the precursors to the mixed metal oxide catalysts due to the large variability of metal cations that can be introduced during synthesis. LDH precursors allow for synthesis of materials with fairly consistent physical properties even when various metals and metal ratios are used. Once these materials are calcined there is an emergence of high porosity and surface area, and additionally, high dispersion of metal oxides can be achieved. This suggests the potential for high interaction of the metallic species with oxide species once the mixed metal oxide is partially reduced compared to catalysts prepared by traditional wetness impregnation techniques. The physical properties of the catalysts are summarized in Table 1. The catalysts are named according to their metal molar ratio determined through ICP-OES, normalized to Al content.

Table 1: Physical properties of the catalysts

<u>Catalyst</u>	<u>ICP-Analysis</u>	<u>ICP-Analysis</u>	<u>Uncalcined</u>			<u>Calcined at 400°C</u>		
	Ni:M:Al ratio	Ni/M	BET Surface ² Area (m ² /g)	Pore Volume ³ (cm ³ /g)	Average Pore Diameter (nm)	BET Surface ² Area (m ² /g)	Pore Volume ³ (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

As shown in Table 1, the LDH derived synthesis yielded porous mixed metal oxides with relatively high BET surface areas ranging from 150 m²/g – 300 m²/g. In general, calcined Co samples had lower surface areas than Mg samples, and Co-Al had the lowest surface area of all the catalysts, which may be due to the larger ionic radius of Co²⁺ over Mg²⁺ and the potential for Co²⁺ to oxidize to Co³⁺.^{30,37} According to ICP-OES results, the synthesized Co catalysts did not reach the target molar ratios. Since Co has the ability to oxidize to the 3+ oxidation state, the

Figure 1: XRD patterns of each catalyst after calcination at 400°C

presence of large amounts of Co may have caused a charge imbalance that did not allow its full incorporation into the precursor hydrotalcite structure.³⁸

XRD patterns obtained for the uncalcined samples showed characteristic layered structures such as the (003) and (006) peaks (Figure S1), whereas the XRD patterns of the calcined catalysts shown in Figure 1 above, lack such sharp crystalline peaks. Interestingly, as the Co content increased, the intensity of the peaks decreased, which is similar to the phenomenon observed upon incorporation of Co into Mg-Al LDH materials.³⁹ Once the samples were calcined in air, the crystalline layered structures vanished and the XRD patterns contained only small, moderately broad peaks (Figure 1). The lack of sharp peaks in Figure 1 suggests the absence of large crystalline domains or clusters of metal oxides, which may help promote metal dispersion when reducing the catalysts.

The three diffraction lines approximately at 37.5°, 42.5°, and 62.5° are difficult to conclusively assign since various metal oxides and spinels in the compositional system have reflections that overlap with the broad peaks (Figure S2). The intensities of the Co sample peaks were severely diminished compared to the Mg samples, suggesting smaller domain sizes or a more amorphous structure. The absence of specific metal oxide domains may be explained by the homogeneous mixing of oxides that created a solid solution.^{23,40,41} These solid solutions caused reduction of nickel to be significantly more difficult than for samples containing large nickel oxide domains, such as those often prepared by impregnation methods, due to the dispersion of the NiO domains and intermixing with other oxide species. Therefore, H₂-TPR was a useful tool in determining the reduction profiles of the mixed metal oxides. The reduction behavior of each mixed metal oxide is displayed in Figure 2, and the total hydrogen uptake is given in Table S1.

The TPR profiles contained many different features due to the compositional complexity of the mixed metal oxides. Under these conditions, MgO and Al₂O₃ are unreducible, but Ni²⁺, Co³⁺, and Co²⁺ are reducible. Starting with the more complex TPR profiles, the Ni-Co-Al catalysts displayed larger hydrogen uptakes as the temperature increased. The addition of Co resulted in the emergence of a peak at lower temperatures (~250°C). This suggests that during calcination in air, Co₃O₄ domains evolved, and at lower temperatures, Co₃O₄ was reduced to CoO.⁴² The very broad uptake could result from a mixture of many different oxide species being reduced, including Ni²⁺ and Co²⁺. According to prior literature, the low temperature shoulder is due to the reduction of surface Ni²⁺ to Ni⁰, which is followed by the reduction of bulk Ni²⁺ to metallic Ni.^{23,25,43} Although XRD does not provide evidence for any spinel structures (NiAl₂O₄ or NiCo₂O₄), as the temperatures rise above 600 °C, the reduction of more recalcitrant (perhaps

highly embedded) Ni or Co species clearly occurred.^{44,45} As the Ni content was increased, the apex of the broad peak shifted slightly to lower temperatures, confirming that Ni oxide species required less thermal energy to reduce. Along with the shift in the broad peak, the Co_3O_4 peak shifted towards lower temperatures as well, which alludes to the potential of Ni assisting in the reduction of Co. Similar to the addition of Pt to $\text{Co}/\text{Al}_2\text{O}_3$, the more easily reducible Ni may assist in the reduction of cobalt oxide through H_2 dissociation and spillover.⁴² Therefore, not only does NiO reduce to metallic Ni, but it is possible that CoO is reduced to metallic Co under specific reduction conditions. Unfortunately, these TPR profiles cannot give a detailed depiction of the reduced species.

Figure 2: Temperature programmed reduction (TPR) profiles of each catalyst. Heating rate of $5^\circ\text{C}/\text{min}$

Consequently, spectroscopic studies were conducted to probe this, as discussed further below.

Unlike the Co samples, the Ni-Mg-Al catalysts showed significantly less hydrogen uptake due to the unreducible (under these conditions) MgO. Similar to the Co samples, there was a shift of the main peak to lower temperatures as there was an increase of Ni in the system. The Ni-Mg-Al profiles displayed a prominent lower temperature shoulder, alluding to more surface NiO species segregated from embedded NiO species. The potential for more segregated surface species allowed for production of larger Ni domains during reduction (see below). Overall, these

mixed metal oxides derived from LDH precursors create highly embedded oxide species, which yields higher reduction temperatures compared to samples prepared by wetness impregnation. For the vapor phase reaction studies, 500 °C was chosen as the pre-reduction temperature to create a bifunctional catalyst with the partial reduction of the reducible oxide species. Metallic Ni or Co is expected to act as the hydrogenation site, while the hydrophilic oxide support would facilitate adsorption of the highly oxygenated furfural molecule.

3.2 Catalytic Performance

Initial high furfural conversion testing (90%-99.5%) was completed using all the catalysts to compare selectivities and activities under conditions relevant to practical application. Further studies on several catalysts at low conversion proceeded the initial high conversion tests to compare intrinsic activity. Reactions were conducted at 155 °C, a pressure of about 1 atm, and a H₂/furfural molar ratio of 25. The major pathway for all reactions was hydrogenation of the aldehyde to produce furfuryl alcohol, followed by side or sequential products yielding products such as THFA, furan, and 2-methylfuran.

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

<u>Catalyst</u>¹	<u>Conversion</u>	<u>Activity</u>²	<u>Selectivity (%)</u>						
	%	$\frac{\text{mol}_{\text{conv}}}{\text{h} * \text{g}_{\text{cat}}}$	FA	THFA	Furan	2-MF	BOH	1,2-PD	Others ³
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-Al⁴	98	0.086±0.003	48.0	0.8	2.3	42.3	3.4	0.6	2.6

¹Reactions Conditions: 155°C and 1 atm with a furfural flow rate of 5.5mmol/hr and H₂/furfural = 25. Catalyst amount ranged between 35-135 mg. Values obtained after approximately 1 hour on stream. Error determination discussed in supplementary information. ³Others include 1-pentanol, 2-pentanol, and 1-butanol. ⁴ Carbon balance closure was within 10%. FA- furfuryl alcohol; THFA- tetrahydrofurfuryl alcohol; 2-MF- 2-methylfuran; BOH- 1-butanol; 1,2-PD- 1,2-pentandiol.

The major product obtained for each catalyst was furfuryl alcohol, which resulted from the hydrogenation of the aldehyde of furfural to an alcohol. In prior literature, it has been established that bifunctional catalysts that contain a reduced metal and an oxide such as Ir-ReO_x/SiO₂ are highly active and selective towards unsaturated aldehyde hydrogenation.²⁶

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

The oxide is suggested to adsorb the oxygen of the aldehyde and the zero valent metal hydrogenates the carbonyl over the “bifunctional” catalyst. The Ni mixed metal oxides reduced *in situ* may create similar bifunctionalities due to the formation of Ni and/or Co metallic phases embedded in a solid solution metal oxide support. The oxide support may allow for strong interaction of the aldehyde with the catalyst, while the reduced metal hydrogenates the carbonyl species. Furthermore, the LDH synthesis method allows for strong interactions between the oxide and the reduced metal due to the relative homogeneity of the starting mixed metal oxide. In general, the Ni-Co-Al catalysts produced slightly more furfuryl alcohol than the Ni-Mg-Al materials, and the major outliers were 2Ni-Al and Co-Al due to the large amounts of side products or sequential products formed.

Other products were formed through hydrogenation, decarbonylation, and hydrogenolysis pathways. Further hydrogenation through ring saturation occurred in all catalysts except Co-Al, potentially due to reduced Ni allowing for flat adsorption of furfuryl alcohol at low temperatures,

leading to reduction of the olefinic bonds.¹⁴ The second major side product was furan, resulting from decarbonylation of furfural, which has been shown to form over Ni catalysts at high temperatures.¹³ Prior studies revealed that furan production is due to the strong $\eta^2(\text{C},\text{O})$ adsorption of the aldehyde, which seems to be more predominant over the Mg catalysts.¹³ When Co was incorporated into the Ni mixed metal oxide, 2-methylfuran production increased slightly; moreover, Co-Al, which contained no Ni species, produced a significant amount of 2-methylfuran. Additional, minor ring-opening products were formed, including 1-butanol and 1,2-pentanediol, but were in insignificant amounts.

Activities per gram of catalyst are displayed in Table 2, and it can be seen that the 1.1Ni-0.8Co-Al catalyst showed the highest activity per gram. Further investigation at lower furfural conversions of 1.9Ni-Mg-Al, 1.4Ni-1.4Mg-Al, 1.1Ni-0.8Co-Al, 0.7Ni-1.1Co-Al, and 2Ni-Al were conducted to compare catalysts with various metal ratios under conditions that minimized side reactions and sequential reactions. Table 3 displays the activity per gram and per active site, as estimated by CO chemisorption (for chemisorption data, see table S2). Due to the potential for multiple CO species forming on the metallic surfaces, including monodentate and bidentate CO, it was assumed that each adsorbed CO corresponded to 1.5 active sites.⁴⁶⁻⁵⁰ The active site estimation by CO chemisorption may be slightly overstated for each catalyst due to potential titration of Lewis acid sites with CO, but previous literature has used CO adsorption to estimate metallic sites on similar catalysts based on LDH derived mixed metal oxides.^{30,51,52} The 1.4Ni-1.4Mg-Al catalyst gave slightly higher CO adsorption than both the 1.1Ni-0.8Co-Al and 2Ni-Al materials. Even though the dispersion and estimated particle size ranged between approximately 2.5%-5.5% and 18 nm-38 nm, respectively, these values are likely not a good representation of the morphology (Table S1) of the metal species. Mixed metal oxides derived from LDH

precursors yield highly embedded metallic species after reduction, which can yield lower exposed metallic surface areas.⁵³ Consequently dispersion will be understated in such materials, while particle diameter will be overstated.

Table 3: Activity and selectivity at low furfural conversion for selected catalysts

<u>Catalyst¹</u>	<u>Conversion</u> %	<u>Activity</u>		<u>Selectivity (%)</u>			
		$\frac{\text{mol}_{\text{conv}}}{\text{h} * \text{g}_{\text{cat}}}$	$\frac{\text{mol}_{\text{conv}}}{\text{hr} * \text{mol}_{\text{site}}}$	FA	THFA	Furan	2-MF
1.4Ni-1.4Mg-Al	14	0.20	550±10	80.7	3.5	15.8	-
1.1Ni-0.8Co-Al	25	0.44	1690±160	78.6	7.2	11.0	3.2
0.7Ni-1.1Co-Al	15	0.25	1020±100	79.1	7.8	8.6	4.4
1.9Ni-Mg-Al	17	0.29	550±10	76.0	10.5	13.5	-
2Ni-Al	16	0.29	1050±80	77.8	9.1	11.9	1.2

¹Reactions Conditions: 155°C and 1 atm with a furfural flow rate of 12 mmol/hr and H₂/furfural = 20. Catalyst amount was between 5-10 mg. Values obtained after approximately 1 h on stream. Assuming 1.5 sites per CO adsorbed, with error quantified through CO adsorption standard deviations.

Table 4: Activity and selectivity of the 1.1Ni-0.8Co-Al catalyst at various temperatures

<u>Catalyst¹</u>	<u>Conversion</u> %	<u>Activity</u> $\frac{\text{mol}_{\text{conv}}}{\text{h} * \text{g}_{\text{cat}}}$	<u>Selectivity (%)</u>				
			FA	THFA	Furan	2-MF	Others ²
1.1Ni-0.8Co-Al							
155 °C	25	0.44	78.6	7.2	11.0	3.2	-
165 °C	26	0.57	75.8	7.1	11.3	3.3	2.5
175 °C	27	0.61	74.3	6.5	11.8	4.6	2.8

¹Reactions Conditions: 1 atm with a furfural flow rate of 12 mmol/h and H₂/furfural = 20. Catalyst amount was ~5.5 mg. Values obtained after approximately 1 hour on stream. ²Others includes 1-butanol and butanal.

Others have reported the use of base metal catalysts for furfural hydrogenation as well. Reduced Cu impregnated on SiO₂ was employed for vapor phase hydrogenation of furfural and displayed high selectivity towards furfuryl alcohol (99%). Similarly, Ni impregnated on SiO₂ showed high selectivity towards THFA at a low temperature of 130 °C (94%).^{14,15,54} For furfural conversion to furfuryl alcohol, Tomishige et al. reported a TOF of 130 h⁻¹ at 130 °C using a 10 wt% Ni/SiO₂ catalyst, and Mérida-Robles et al. reported a TOF of 9.6 h⁻¹ for an 8 wt% Cu/SiO₂

catalyst at 170 °C. Although these studies were conducted at different temperatures, the site-time-yields (STYs) of both 1.1Ni-0.8Co-Al and 2Ni-Al demonstrate these materials to have promising activity for furfural hydrogenation (Table 3); however, improvements in selectivity by lowering decarbonylation products are needed to compete with the best catalysts.

Figure 3: XANES spectra at the Ni K-edge of the catalysts at room temperature both before and after reduction at 500 °C with 4% H₂ balance He and 10 mL/min. Inset graphs show Fourier Transformed EXAFS data for each catalyst;. a) 1.1Ni-0.8Co-Al. b) 1.4Ni-1.4Mg-Al

Low conversion testing also supported the observation at higher furfural conversions of higher activity (per gram catalyst) associated with the 1.1Ni-0.8Co-Al compared to all other catalysts tested at low conversion. Also, both Co catalysts showed higher activity per site compared to both Mg samples. The activity per site, as measured by CO chemisorption, showed an almost three times higher activity of the 1.1Ni-0.8Co-Al catalyst compared to 1.4Ni-1.4Mg-Al and 1.9Ni-Mg-Al samples. The 1.1Ni-0.8Co-Al catalyst had more than a 50% higher turnover frequency than 2Ni-Al, suggesting the addition of Co had a positive effect on activity, unlike Mg addition. In terms of selectivity, very little difference was observed compared to high conversion tests except for slightly higher furfuryl alcohol selectivities due to reduced sequential reactions. The 1.1Ni-0.8Co-Al catalyst was used at low conversion to investigate the effects of temperature on the reaction rate, with the results displayed in Table 4. Increasing the temperature increased the activity, as expected, while also changing the product distribution. Slightly greater amounts of furan and 2-methylfuran were produced with the increase in temperature, which has been noted in a previous report utilizing Ni catalysts.¹³

The use of TPR and XRD together did not allow for sufficient insight into the nature of the reduced metallic species. To this end, XAS and XPS were applied to further elucidate the states of Ni and Co. *In situ* XAS under reduction conditions similar to the reaction pretreatment was utilized to give insight into the bulk characteristics of the 1.4Ni-1.4Mg-Al and 1.1Ni-0.8Co-Al catalysts (Figures 3 and 4). XAS was conducted in a quartz tube that was heated to 500°C at 5°C/min and held for 1 hour, all while under 10 mL/min 4% H₂ (balance He). Scans were taken

throughout the reduction process, but only pre and post reduction conditions are presented here. The quality of the EXAFS spectrum can significantly diminish as temperature rises, especially temperatures above 600K, due to significant changes in the Debye-Waller factor, which adjusts for the thermal vibration effects.^{55–57} For this reason, room temperature spectra were used to allow for ease of EXAFS processing and comparison. Both the Ni K-edge and the Co K-edge were interrogated to determine if Co also reduced under the pretreatment conditions employed in this work. Figure 3 displays the Ni K-edge XAS results for both the 1.4Ni-1.4Mg-Al and 1.1Ni-0.8Co-Al samples at room temperature before and after reduction at 500°C.

Figure 4: In situ XANES of Co K-edge of the 1.1Ni-0.8Co-Al catalyst at room temperature both before and after reduction with 4% H₂ balance He flowing at 10 mL/min. Inset graph shows Fourier transformed EXAFS data of the same sample.

Qualitatively, both XANES spectra showed a shift in the white line to lower energies as well as a decrease in the intensity; however, the Mg catalyst showed a much more significant shift and reduction in intensity, suggesting larger amounts of NiO reduced to Ni⁰ in this catalyst.^{53,58} The pre reduction spectra for both the Co and Mg containing samples mimicked the

NiO spectrum due to the presence of the pre-edge feature at 8333 eV and the major peak at 8352 eV. After reduction for an hour at 500 °C, the pre-edge feature disappeared for the Mg catalyst and the appearance of a second edge started, similar to that of Ni foil.^{59,60} Moreover, when examining the derivative norm(E) (Figure S5) there was an increase in the peak at 8333 eV and a decrease in peaks at 8342 eV and 8346 eV, which was more characteristic of Ni foil reference. The Co catalyst displayed a smaller shift in the white line of the Ni k-edge, suggesting a simultaneous reduction of both Ni and Co. The Mg samples do not have that reduction competition since MgO and Al₂O₃ are not reducible under these conditions, allowing for significantly more reduction of the NiO species. In terms of the Co catalyst, there were still strong characteristic NiO features after reduction, including the small pre-edge feature at 8333 eV; therefore, there was clearly less reduction of Ni in the Ni-Co-Al catalyst, relative to the Ni-Mg-Al catalyst. Overall, both catalysts did not have 100% reduction of Ni²⁺ to Ni⁰, possibly due to the large amount of imbedded Ni²⁺ species in the well-mixed oxide as well as strong interactions with the oxide support, as supported by TPR results, unlike traditional impregnated Ni catalysts.¹⁴

EXAFS spectra displayed significant changes between the pre and post reduction catalyst samples, especially with the first two major scattering peaks. For both pre-reduction samples, two major peaks were present: a first peak at ~1.5 Å and a second peak at ~2.5 Å, corresponding to Ni-O and Ni-Ni (or Ni-Co) scattering, respectively.^{61,62} After pretreatment, each catalyst showed a large increase in the Ni-Ni (Ni-Co) peak, which suggested an increase in the coordination number and formation of metallic Ni particles or Ni-Co alloys. Although both samples showed an increase of the metal-metal peaks after reduction, the Mg sample also showed a slight shift to lower atomic scattering distances, suggesting a larger degree of

agglomeration of the Ni atoms. This larger agglomeration was potentially due to the larger amount of Ni atoms present on the surface of the mixed oxide, as shown by the larger shoulder at lower reduction temperatures in the TPR data.

Even though there was a large increase in the magnitude of the second peak of the Co sample, there was no shift in the second peak, which suggests less Ni agglomeration due to the Co addition. From TPR, it was suggested that Co begins mainly as a Co_3O_4 that was reduced to CoO at low temperatures. However, from the TPR data over these samples, at higher temperatures it was uncertain when CoO reduction began. The *in situ* XAS spectra of the Co-containing sample at the Co k-edge before and after reduction, as shown in Figure 4, do not display characteristics of significant metallic Co, as the post reduction white line mimics CoO from prior literature.⁶³ However, the EXAFS spectrum showed a small increase in the second scattering peak corresponding to Co-Co (Co-Ni), suggesting a slight increase in the coordination number, which could result from total reduction of some Co oxide species to metallic Co or development of alloyed, metallic CoNi domains.⁶⁴

Figure 5: XPS spectra of 1.1Ni-0.8Co-Al catalysts in the Co binding energy region. a) Pre-reduction; b) Post-reduction, after passivation.

XPS spectra of the catalysts before and after reduction in hydrogen further support the hypothesis that some Co oxide species were reduced to metallic Co, which may contribute to increased activity (Table 3) of the catalyst. XPS spectra shown in Figure 5 demonstrate the partial reduction of CoO to metallic cobalt. Peak deconvolution of the spectra, including multiplet splitting and Auger peaks, was conducted similar to prior literature using standard references analyzed on the same instrument.^{65–68} The experimental conditions were slightly different than those for the XAS experiments, since post-reduction XPS was conducted after the catalysts were passivated in 1% O₂ (balance N₂) for one hour, which was necessary to transfer the sample from the reactor to the XPS instrument. Deconvolution of the Co region revealed that the main species present before reduction was Co₃O₄, which was reduced to Co²⁺ and Co⁰ after reduction. This was noticeable mainly through the increase in the 2p_{3/2} satellite peak (786.7 eV), since many of the Co₃O₄ and Co²⁺ 2p_{3/2} peaks were similar. After reduction at 500°C and passivation at room temperature, the major species present was CoO, with a quantifiable amount of Co⁰ that caused the shoulder at lower binding energies. Even after passivation, by analyzing the 2p_{3/2} deconvolution approximately 15% Co⁰ species remained on the surface of the catalysts, hence adding to the metallic surface area of the catalyst.

Figure 6: HAADF-STEM image and FFT patterns showing a metallic core surrounded by an oxidized shell in the 1.1Ni-0.8Co-Al catalyst reduced at 500 °C for 1 h and then passivated at room temperature for 1 h in 1% O₂ balance N₂.

XPS conducted around the Ni binding energy region displayed reduction results that were consistent with those gleaned from the previously mentioned characterization techniques (TPR, XAS). After passivation of the 1.1Ni-0.8Co-Al sample, the amount of Ni⁰ on the surface was approximately 19% compared to the 1.4Ni-1.4Mg-Al sample, which had 14% Ni⁰. Although this may at first glance appear to differ with the results from XAS, which showed more extensive reduction, the post-reduction XPS results were from a sample that experienced a passivation step, which reoxidizes some of the reduced metal in the catalysts. When considering the combined results, the XPS and XAS of the 1.4Ni-1.4Mg-Al catalyst gave evidence of significant agglomeration of Ni, likely due to the presence of more Ni species on the surface after calcination compared to the 1.1Ni-0.8Co-Al sample. This would yield more accessible Ni⁰ species, which after passivation yielded less Ni⁰, as observed in the XPS results.

The combined spectroscopic studies demonstrated that there was the emergence of metallic Ni in the Ni-Mg-Al catalyst and both metallic Ni and Co species in the Ni-Co-Al sample.

However, these techniques were unable to determine the interactions between the two metallic species in the Ni-Co-Al catalyst. Aberration-corrected STEM allowed the morphology of both the reduced and unreduced catalysts to be probed, and EDS and EELS were conducted to complement the imaging. Figure 6 displays a HAADF-STEM image of a nanoparticle approximately 5 nm in size on the reduced 1.1Ni-0.8Co-Al sample, which had been reduced at similar conditions and then passivated for 1 hour in 1% O₂ (balance N₂) for sample transfer to the microscope. Two major domains can be distinguished in the nanoparticle through fast Fourier transform (FFT) analysis: the center domain contains either Ni and/or Co and the outer edge contains either NiO and/or CoO. Lattice analysis cannot discern if the particle is a mixture of Ni and Co or just an individual species; therefore, EELS and EDS were used to probe the compositions (Figure S8, S9, and S10). Both methods provide evidence that suggests a random mixture of Ni and Co species, which hints that upon reduction, NiCo alloys were produced when both metals were present in the sample. This EELS and EDS certainly support the emergence of NiCo alloys previously observed by the other techniques.

The hypothesis that bimetallic nanoparticle emerge after reduction may offer an explanation for the enhanced catalytic activity in the 1.1Ni-0.8Co-Al compared to both 2Ni-Al and 1.4Ni-1.4Mg-Al, where no bimetallic particles can be formed under the reduction conditions employed. The intimate mixing of each metal species may facilitate hydrogen spillover to CoO, which may allow CoO to reduce simultaneously, ultimately being a factor in the increase in activity. From XAS, XPS, and STEM results, the oxide species present after reduction were a mixture of NiO, CoO, and Al₂O₃, which may have been a more useful combination than NiO, MgO, and Al₂O₃. Lastly, it is interesting to note that the metallic species do not seem to

significantly change the overall furfuryl alcohol selectivity, but the nature of the oxide species does produce changes in the nature of the different side products observed.

4. Conclusions

Porous nickel mixed metal oxide catalysts were synthesized by calcination of LDH derived materials to investigate the effects of various oxophilic metal additions to the structure and reactivity of the Ni metal particles. LDH derived mixed metal oxides allowed for the comparison of various metal additions to Ni based catalysts on the conversion of furfural under vapor phase hydrogenation conditions. In the calcined mixed oxide materials a homogeneous solid solution was formed with no observed separation of oxide domains as shown by XRD, suggesting close interactions between the Ni and other metals. TPR profiles suggested complex reduction behavior in the materials due to the various reducible species present in the mixed metal oxides including surface NiO, bulk NiO, Co₃O₄, and CoO species. Under the reduction conditions employed, neither Ni nor Co were fully reduced, which is attributed to metallic particles embedded in an oxide structure, likely with strong metal-support interactions. At high furfural conversion in a flow reactor, furfuryl alcohol was the major product produced. The inclusion of different oxophilic metals (Co vs. Mg) in varied amounts influenced the product distribution (mildly) and activity (more significantly) of the catalysts. In general, Mg catalysts showed less activity per site and slightly higher furan production, while the Co catalysts showed higher activity per site and slightly higher 2-methylfuran production. At low conversions, the STY of the 1.1Ni-0.8Co-Al was more than three times that of the 1.4Ni-1.4Mg-Al catalyst and 50% greater than the catalyst with no metal addition (2Ni-Al). Through extensive spectroscopic characterization by XAS and XPS, the increase in activity was attributed to the increased homogeneity of the Ni-Co catalysts, which gave metallic domains associated with both Ni⁰ and

Co⁰. STEM and EELS characterization supported the hypothesis that NiCo alloys may have formed in the catalysts containing both metals. Further studies varying the calcination temperature and reduction temperature could potentially allow for tuning of the nature of the reduced species in the NiCo catalyst, further influencing the activity and product distribution.

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