

# Continuous Transfer Hydrogenation of Sugars to Alditols with Bioderived Donors over Cu–Ni–Al Catalysts

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The transfer hydrogenation of sugars to alditols with biobased alcohol donors was studied over hydrotalcite-derived  $Cu_{6-x}Ni_xAl_2$  catalysts prepared by coprecipitation at different pH and featuring variable Cu/Ni ratios. Their evaluation, after in situ activation in pure H<sub>2</sub> at 773 K, in the ethanol-assisted upgrading of glucose in a continuous-flow fixed-bed reactor identified the solid synthesized at pH 9–10 and with Cu/Ni = 1 as the best performer. Based on textural, structural, and

## Introduction

In the last two decades, the conversion of biobased feedstocks into commodity and platform chemicals has become a central area of research across multiple scientific disciplines.<sup>[1]</sup> Among the routes explored to transform (hemi)cellulose-derived C<sub>5</sub> and C<sub>6</sub> sugars,<sup>[2]</sup> reductive upgrading has recently gained increasing attention. This technology not only allows enhancing the stability of saccharide feedstocks in view of further processing along alternative value chains but also leads to industrially relevant products. Indeed, the polyols obtained from hexoses and pentoses find wide application in the food, pharmaceutical, cosmetic, and polymer sectors.<sup>[3]</sup> Specifically, sorbitol, xylitol, and arabinitol, that is, the hydrogenation products of glucose, xylose, and arabinose, respectively, have been included by the US Department of Energy within the 12 top addedvalue chemicals that can be attained from biomass.<sup>[4]</sup>

The reduction of glucose and xylose has been studied over Ni,<sup>[5,6]</sup> Ru,<sup>[7,8]</sup> Co,<sup>[6,9]</sup> Pd,<sup>[6]</sup> and Pt<sup>[10,11]</sup> catalysts. Ru-containing systems have displayed the best performance, reaching almost 100 and 98% sorbitol and xylitol yields in batch mode, respectively, and being recyclable in successive runs. Nevertheless, the high market price of ruthenium represents a hurdle for a prospective large-scale implementation of these solids. Considering more economical metals, catalysts such as Raney-Ni have a limited industrial scope because metal leaching strongly impacts their lifetime.<sup>[5e]</sup> Recently, Zhang et al.<sup>[12]</sup> reported that a ternary Cu–Ni–Al catalyst achieved a sorbitol selectivity of 93% at a glucose conversion of 73% after 3 h at 393 K and 30 bar  $H_2$ . This result highlights the benefits, already demon-

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redox analyses, this is related to an enhanced intermetallic interaction. Upon screening alternative donors, a sorbitol yield as high as 67% was achieved with 1,4-butanediol. The catalytic system displayed a stable behavior during 48 h on stream and proved suitable to hydrogenate also fructose, mannose, xylose, and arabinose to the corresponding polyols (yields up to 65%), thus standing as a more sustainable and economical alternative to Ru-based catalysts for sugar reductive upgrading.

strated in various works,<sup>[13]</sup> of using a hydrotalcite precursor for attaining high dispersion and excellent metal interaction and thus generating efficient multimetallic hydrogenation catalysts. Still, in spite of the promising sorbitol yield, the stability of this material was not evaluated.

The use of a hydrogen donor instead of molecular hydrogen can be instrumental in view of developing a more industrially viable hydrogenation process. This would circumvent safety-related issues, for example, storage and handling of pressurized hazardous gases, and alleviate the environmental footprint, that is, saving of the energy required for H<sub>2</sub> production, especially if not obtained from renewable sources. So far, transfer hydrogenation has been attempted only using furfural as the substrate in the presence of formic acid<sup>[14]</sup> or alcohols.<sup>[15]</sup> Whereas the former donor has shown to undermine the stability of catalytic materials owing to its corrosiveness and reduce the efficiency of the transformation through decomposition with the concomitant formation of CO<sub>2</sub>, alcohols have the advantage to be largely available biobased substrates. Besides, they form upon dehydrogenation carbonyl compounds that can serve as feedstock or auxiliary chemical for the preparation of valuable products.

Herein, we explored the application of hydrotalcite-derived Cu-Ni-Al catalysts for the transfer hydrogenation of glucose in the presence of ethanol using a continuous-flow fixed-bed reactor. An optimal catalytic system was attained identifying the most adequate coprecipitation pH and the relative amount of copper and nickel in the solid, and selecting suitable reaction conditions in terms of temperature and contact time. Thereafter, other biobased alcohols such as methanol, 1,4-butanediol, and glycerol were evaluated as hydrogen donors and the stability of the catalyst assessed in a prolonged catalytic run. Finally, the technology developed was extrapolated to the transfer hydrogenation of other relevant sugars substrates, including fructose, xylose, mannose, and arabinose.



## **Results and Discussion**

#### Properties of precursors and activated catalysts

Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> precursors were prepared by coprecipitation at different pH values (7–8, 9–10, or 11–12). The application of distinct basic conditions in the synthesis of these materials was motivated by a reported correlation between the coprecipitation pH value and the particle size of Cu–Ni hydrotalcites. The latter property was assumed to have an impact on the characteristics of the bimetallic phase obtained upon reduction.<sup>[16]</sup> Along this line, additional samples featuring a variable relative amount of copper and nickel, that is, Cu<sub>6-x</sub>Ni<sub>x</sub>Al<sub>2</sub> with x=0-6, were synthesized according to the same method.

As determined by X-ray fluorescence (XRF) spectroscopy (Table 1), the relative bulk concentrations of the metals in the

Table 1. Characterization	data	of	the	hydrotalcite	precursors	and	of	the	activated
catalysts.									

Sample <sup>[a]</sup>	S <sub>BET</sub> [m <sup>2</sup> a <sup>-1</sup> ]	Cu <sup>[b]</sup> [at.%]	Ni <sup>[b]</sup> [at.%]	Al <sup>[b]</sup> [at. %]	Cu/Ni
		[		10	
$NI_6AI_2(OH)_{16}CO_3$	154	-	81	19	-
CuNi <sub>5</sub> Al <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub>	140	14	66	20	0.2
$Cu_3Ni_3Al_2(OH)_{16}CO_3^{[c]}$	3	38	41	21	0.9
Cu <sub>3</sub> Ni <sub>3</sub> Al <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub>	141	39	41	20	1.0
$Cu_3Ni_3Al_2(OH)_{16}CO_3^{[d]}$	7	39	41	20	1.0
Cu <sub>5</sub> NiAl <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub>	131	67	13	20	5.2
Cu <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub>	126	80	-	20	-
Ni <sub>6</sub> Al <sub>2</sub>	214	_	81 (62)	19 (38)	_
CuNi <sub>5</sub> Al <sub>2</sub>	225	14	66	20	0.2
Cu <sub>3</sub> Ni <sub>3</sub> Al <sub>2</sub> <sup>[c]</sup>	50	38	41	21	0.9
$Cu_3Ni_3Al_2$	107	39 (21)	41 (40)	20 (38)	1.0 (0.5)
Cu <sub>3</sub> Ni <sub>3</sub> Al <sub>2</sub> <sup>[d]</sup>	125	39	41	20	1.0
Cu <sub>5</sub> NiAl <sub>2</sub>	102	67 (38)	13 (15)	20 (47)	5.2 (2.5)
$Cu_6Al_2$	106	80 (28)	-	20 (72)	-

[a] Coprecipitation at pH 9–10 unless specified otherwise. [b] Bulk compositions determined by XRF and surface compositions (in parenthesis) determined by XPS. [c] Coprecipitation at pH 7–8. [d] Coprecipitation at pH 11–12.

precursors generally are in good agreement with those of the coprecipitation solution. Interestingly, whereas conducting the synthesis at pH 7-8 and 11-12 led to materials with very low surface areas, the use of pH 9–10 attained solids with  $S_{BET} =$ 125–155  $m^2 q^{-1}$ , regardless of the metal composition (Table 1). The X-ray diffraction (XRD) patterns (Figure 1 a) of the Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> samples prepared at the intermediate and high pH revealed the unique presence of reflections specific to the hydrotalcite structure (JCPDS 37-630). As previously reported, the diffraction lines at 11.7, 23.3, and  $61.6^{\circ}$  assigned to the (003), (006), and (113) planes, respectively, are symmetric, whereas those at 35.0, 39.0, and 47.2°, indexed as (012), (015), and (018), respectively, are asymmetric.<sup>[12]</sup> The diffractogram of the ternary material precipitated at pH 7-8 evidences the formation of a poorly crystalline main phase with similar basal reflections to those of the other two samples, but sensibly shifted to smaller  $2\theta$ . Accordingly, it is assumed that this phase may comprise a hydrotalcite with a different interlayer spacing from those precipitated at higher pH. Three additional narrow and weak reflections are visible at 12, 24, and 29°  $2\theta$ , which possibly indicate the presence of minor amounts of Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub> (JCPDS 75-1779), Ni<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub> (JCPDS 14-0117), and CuCO<sub>3</sub> (JCPDS 27-0150).<sup>[16]</sup> The layered morphology of the solids prepared at middle and high pH is visible by scanning electron microscopy (SEM), but that of the material obtained at low pH cannot be clearly appreciated (Figure 2a-c). In line with the total surface areas of the materials, this analysis indicates that the former two solids are composed of compact and large-sized particles and dense aggregates with rather large layers, respectively, whereas the hydrotalcite obtained at pH 9-10 exhibits agglomerates featuring smaller particles and abundant voids. This trend in particle dimensions appears in contrast to the work by Naghash et al.<sup>[17]</sup> which showed that decreasing the copre-

> cipitation pH from 10 to 7 reduced the particle size because of the lower rate of nucleation and agglomeration in the presence of a lower concentration of hydroxide ions. This discrepancy might be related to the different composition of the solids (only Ni or Cu and Ni in their hydrotalcites, the latter having a distinct Cu/Ni ratio compared to our case), coprecipitation temperature, and aging time. Overall, our results indicate that the low pH is unsuitable to obtain a pure hydrotalcite and that nucleation dominates over growth at the intermediate pH and vice versa at the high pH. Based on the performance of the catalysts obtained from these precursors (vide infra), the pH of 9-10 was further applied for the synthesis of the materials with variable Cu/Ni ratios. With regard to those, the progressive enrichment of the precursor either in copper or nickel led to minor changes in the diffractograms (Figure 3 a). The hydrotalcite remained as the exclusive crystalline phase for all materials but the reflections became broader and less intense at higher Ni contents. This is in line with previous observations that a more significant presence of nickel leads to a less crystalline hydrotalcite-like material.[17]

The reducibility of the catalyst precursors was studied by temperature-programmed reduction with hydrogen (H<sub>2</sub>-TPR). As CO<sub>2</sub> evolves from the solids up to a temperature of approximately 680 K (not shown), the analyses were conducted by using limestone to absorb this gas, additionally to the molecular sieves used to trap water, and thus ensure that the profiles obtained can be exclusively ascribed to metal reduction. As shown in Figure 1 c, for the solids obtained at a coprecipitation pH 9-10 and 11-12, a single reduction peak with a low-temperature shoulder was observed in the 500-670 K region, which is attributed to the reduction of copper species followed by that of nickel species. Hydrogen spillover from metallic Cu is known to favor the nucleation of Ni<sup>0</sup> and thus to enable the reduction of oxidic nickel at temperatures below 700  $K^{\rm [13c]}_{\rm }$  The fact that the maximum of the reduction feature occurs at approximately 70 K higher temperature for the materials synthesized at pH 7-8 and 11-12 likely relates to the bigger size of



**Figure 1.** Characterization of the  $Cu_3Ni_3Al_2(OH)_{16}CO_3$  precursors precipitated at different pH by a) XRD and c)  $H_2$ -TPR. b) XRD patterns of the  $Cu_3Ni_3Al_2$  catalysts obtained after their activation in  $H_2$  at 773 K.

the particles in these solids. Considering the H<sub>2</sub>–TPR profiles of the  $Cu_{6-x}Ni_xAl_2(OH)_{16}CO_3$  materials (Figure 3 c), the following observations could be made. The reduction of copper species in  $Cu_6Al_2(OH)_{16}CO_3$  determined a broad peak that spans be-

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**Figure 2.** SEM images of  $Cu_3Ni_3Al_2(OH)_{16}CO_3$  hydrotalcites coprecipitated at pH a) 7–8, b) 9–10, and c) 11–12, and TEM pictures of d)  $Cu_5NiAl_2$  after activation and of e)  $Cu_3Ni_3Al_2$  after activation and f) after use in a 5 h catalytic test.

tween 490 and 600 K and the progressive replacement of copper by nickel produced a gradually sharper peak with maximum at higher temperature (580-610 K). These changes in shape and location of the signals likely indicate an augmenting interaction between the two metals determining a more pronounced assistance of copper to the reduction of nickel. This seems to be maximized for the material containing equimolar amount of the two redox metals. The very broad and weak reduction between 600 and 1000 K additionally identified in the profile of the copper-lean CuNi<sub>5</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub> sample indicates that part of nickel is reduced without the aid of copper at higher temperatures. The reduction of the Ni<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub> hydrotalcite occurred in the broad range of 650-1100 K and was characterized by low- (650-770 K) and high- (700-1100 K) temperature peaks assigned to the reduction of surface and bulk species, respectively. The formation of metallic phases was corroborated by XRD analysis of the solids after reduction in H<sub>2</sub> flow at 773 K for 30 min in the reactor system (Figures 1 b, 3 b).<sup>[18]</sup> The main reflection at 44°  $2\theta$  in the patterns of the Cu– Ni-Al systems prepared at variable pH, which is located at higher and lower angles compared to main diffraction lines of pure metallic copper and nickel, suggests the presence of a homogeneous, substitutional Cu-Ni alloy. This is substantiated by the known mutual solubility of the two transition metals in the solid state and by previous characterization of bimetallic Cu-Ni particles.<sup>[19]</sup> A minor amount of Cu in form of an individual metallic phase was also detected. Furthermore, CuO (JCPDS 48-1548, reflections at 36 and 39°) and NiO (JCPDS 71-1179, reflections at 38 and 63°) were observed, which were likely generated upon passivation of the catalysts prior to exposure to air for the XRD analysis to avoid burning. This was confirmed by the negligible hydrogen consumption observed in H<sub>2</sub>-TPR experiments over Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> catalysts reduced according to the conditions applied in situ in the reactor (not shown). The



Figure 3. Characterization of the  $Cu_{6-x}Ni_xAl_2(OH)_{16}CO_3$  precursors by a) XRD and c) H<sub>2</sub>-TPR, and of the b)  $Cu_{6-x}Ni_xAl_2$  catalysts obtained after their activation in H<sub>2</sub> at 773 K by XRD.

smaller amount of oxides present in the activated solid coprecipitated at low pH might be explained by its low surface area (50 m<sup>2</sup>g<sup>-1</sup>, Table 1). Single Cu or Ni metallic phases were identified for Cu<sub>6</sub>Al<sub>2</sub> and Ni<sub>6</sub>Al<sub>2</sub>, as expected. In Cu<sub>5</sub>NiAl<sub>2</sub>, Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub>, CHEMCATCHEM Full Papers

and CuNi<sub>5</sub>Al<sub>2</sub> catalysts, besides for the intermetallic compounds, CuO and NiO were formed in proportional amount to the relative quantity of Cu and Ni introduced. As visualized by transmission electron microscopy (TEM) (Figure 2d, e), both Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> and Cu<sub>5</sub>NiAl<sub>2</sub> comprise metal nanoparticles with a broad size distribution.

X-ray photoelectron spectroscopy (XPS) of the activated  $Cu_6Al_2$ ,  $Ni_6Al_2$ ,  $Cu_5NiAl_2$ , and  $Cu_3Ni_3Al_2$  catalysts (Table 1) evidenced that their surface composition significantly differs from their bulk composition. In the case of the  $Ni_6Al_2$  sample, the surface is enriched in Al. For the copper-containing binary or ternary materials, the surface contains substantially less Cu and more Al and especially Ni, as reported elsewhere.<sup>[13c]</sup>

### Glucose transfer hydrogenation

The in situ reduced Cu–Ni–Al hydrotalcites were tested in the transfer hydrogenation of glucose with ethanol in a continuous-flow fixed-bed reactor set up at 423 K and a contact time of 5.6 min (Scheme 1). The glucose conversion and sorbitol



**Scheme 1.** Continuous-flow fixed-bed reactor setup used for the transfer hydrogenation of sugars. The mechanism of transfer hydrogenation of glucose in the presence of 1,4-butanediol is depicted in the left panel.

yield measured after 5 h on stream are displayed in Figure 4a, b. Fructose, mannose, and mannitol were detected as byproducts. The Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> catalyst obtained by coprecipitation at different pH could be ranked as: pH 9-10>pH 11-12>pH 7-8. Based on the characterization results described above, the superior performance of the first catalyst is attributed to the favorable combination of a higher surface area (Table 1) and an easier reducibility and better interaction between Cu and Ni (Figure 1 c) in this solid. A linear increase in sorbitol yield was observed upon replacing Cu by Ni up to the Cu<sub>4</sub>Ni<sub>2</sub>Al<sub>2</sub> composition. These results confirm the more suitable redox properties of intermetallic Cu-Ni compounds, which can be generated in progressively higher amount upon increasing the relative nickel content. Upon further raising the nickel concentration, the sorbitol yield was first only moderately enhanced (Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub>) and then leveled off at a lower value (Cu<sub>2</sub>Ni<sub>4</sub>Al<sub>2</sub> and Cu<sub>1</sub>Ni<sub>5</sub>Al<sub>2</sub>). The superiority of Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> is attributed to the pres-



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**Figure 4.** Performance of a) the Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> catalysts obtained by coprecipitation at variable pH and of b) Cu<sub>6-x</sub>Ni<sub>x</sub>Al<sub>2</sub> catalysts in glucose transfer hydrogenation. Influence of c) the temperature and d) the contact time on the catalytic properties of the Cu<sub>3</sub>Ni<sub>x</sub>Al<sub>2</sub> catalyst obtained by coprecipitation at pH 9–10. The glucose conversion levels and sorbitol yields were measured after 5 h on stream. Conditions: 90 mM glucose in ethanol/H<sub>2</sub>O=80:20, T=423 K, and  $\tau$ =5.6 min, unless specified otherwise in (c) and (d).

ence of bimetallic species featuring the best interaction between Cu and Ni (Figure 3 c). As the Ni<sub>6</sub>Al sample exhibited the same low performance of the Cu<sub>6</sub>Al<sub>2</sub> sample and the amount of Cu-Ni alloy appears similar in Cu<sub>5</sub>Ni<sub>1</sub>Al<sub>2</sub> and Cu<sub>1</sub>Ni<sub>5</sub>Al<sub>2</sub> (Figure 3 b), the better catalytic properties of the Ni-rich compared to the Cu-rich catalyst might be explained by its greatly larger surface area (225 vs. 102 m<sup>2</sup>g<sup>-1</sup>, Table 1). Reaction conditions such as temperature and contact time were optimized using the best catalyst, that is, Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub>. The influence of the first parameter was assessed in the 413-443 K range (Figure 4c). At the lowest temperature, very low glucose conversion and high sorbitol selectivity were observed. As expected, higher activity levels were attained at higher temperatures. At 443 K, the sorbitol selectivity strongly decreased as a result of the pronounced occurrence of side reactions, as confirmed by the rising number of peaks in the chromatograms of the outlet mixtures. The initially selected temperature of 423 K appeared to determine a good balance between activity and selectivity and was employed in all subsequent catalytic tests. Concerning the contact time (Figure 4d), lower sorbitol yields (20%) were measured at shorter times, and longer times boosted the yield up to 57%. To attain even more relevant catalytic results, alternative bioderived hydrogen donors were evaluated under the optimized conditions, namely, methanol, glycerol, and 1,4-butanediol (Figure 5). The C1 and C3 hydrogen sources appeared



**Figure 5.** Glucose conversion and sorbitol yield measured after 5 h on stream over the Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> catalyst obtained by coprecipitation at pH 9–10 in the presence of different hydrogen donors. Conditions: 90 mM glucose in donor/H<sub>2</sub>O = 80:20, T = 423 K, and  $\tau$  = 11.2 min.

unsuitable for the process, leading to very low glucose conversion and, in turn, sorbitol yield. Oppositely, the diol demonstrated a moderately better donor than ethanol (sorbitol yield of 61%). The reason for the superiority of this molecule likely traces back to the transformation undergone upon reaction conditions. Although for methanol, ethanol, and glycerol, the corresponding carbonyl compounds were obtained by dehy-

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drogenation,  $\gamma$ -butyrolactone was mainly formed from 1,4-butanediol. The generation of this cyclic ester requires a dehydrogenation followed by cyclization and a second dehydrogenation (Scheme 1). Accordingly, 2 instead of only 1 equivalent of hydrogen are released per equivalent of donor. Notably,  $\gamma$ -butyrolactone also holds a greater relevance than 4-hydroxybutanal in industry, and thus makes the overall process more appealing. A sorbitol/ $\gamma$ -butyrolactone ratio of 2.8 was experimentally determined, which is only moderately higher than the theoretical ratio of 2. Accordingly, a comparatively smaller fraction of the donor that reacted was only dehydrogenated to the aldehyde, which was indeed detected in the HPLC chromatograms, and did not undergo the subsequent lactonization. In view of the attractiveness of this catalytic system, measurements were repeated by using a greater catalyst mass (1.5 g) to increase the degree of conversion. When transforming 92% of glucose, a sorbitol yield of 67% could be attained. Remarkably, sorbitol was produced over Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> with a three times greater space time yield (0.061 vs. 0.019  $g_{sorbitol} h^{-1} g_{cat}^{-1}$ ) than that of a commercial 5 wt.% Ru/C catalyst tested under identical conditions. Additionally, it was found that the reference system mostly transformed the cyclic intermediate obtained from 1,4-butanediol, that is, tetrahydrofuran-2-ol, into the less industrially significant tetrahydrofuran through hydrogenolysis rather than the preferred  $\gamma$ -butyrolactone through dehydrogenation. Based on measurements at variable temperature (Figure 6), an apparent activation energy of 95 kJ mol<sup>-1</sup> was es-



**Figure 6.** Arrhenius plot for the transfer hydrogenation of glucose in the presence of 1,4-butanediol over the Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> catalyst obtained by coprecipitation at pH 9–10. Conditions: 90 mM glucose in 1,4-butandiol/H<sub>2</sub>O = 80:20, and  $\tau$  = 3.7 min.

timated for the transfer hydrogenation process over our system. This value is comparable to the activation energy found for the direct hydrogenation of glucose on Ru/C  $(84 \text{ kJ} \text{ mol}^{-1})$ .<sup>[20]</sup> Therefore, it may be plausible that the hydrogenation of the sugar and not the dehydrogenation of the donor is rate determining.

In view of evaluating the stability of the  $Cu_3Ni_3Al_2$  catalyst, the outlet stream of the reactor of a 5 h test was analyzed by inductively coupled plasma optical emission spectroscopy CHEMCATCHEM Full Papers

(ICP–OES). The amounts of copper and nickel found correspond to a loss of 0.4 and 0.3% of the original metals content, respectively. This minor depletion strongly contrasts with the significant instability of Raney-Ni.<sup>[5e]</sup> The robustness of our catalyst was further assessed in a 48 h catalytic run performed in the presence of the most suitable diol donor. After an initial slight deactivation over the first 5 h on stream, the sorbitol yield remained virtually unaltered in the remainder of the test (Figure 7). To rationalize the slight activity loss at the first



**Figure 7.** Evolution of the sorbitol yield during a 48 h glucose transfer hydrogenation test over the Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> catalyst obtained by coprecipitation at pH 9–10 in the presence of 1,4-butanediol. Conditions: 90 mm glucose in 1,4-butanediol/H<sub>2</sub>O=80:20, T=423 K, and  $\tau$ =11.2 min.

stages of the run, the used catalyst was characterized by various techniques. CHN analysis indicated a carbon content of 4.3 wt.% after the first 5 h and of 5.7 wt.% after 48 h on stream. N<sub>2</sub> sorption evidenced a slight decrease in the surface area for the catalyst used for 5 h compared to that of the activated material (100 vs.  $107 \text{ m}^2 \text{g}^{-1}$ ). Additionally, XRD analysis revealed that the main reflection comprising the intermetallic compound, and that of metallic Cu to a minor extent, became more intense and sharper, indicating that larger particles of (bi)metallic phase were produced during this time (Figure 8). A moderate agglomeration of the metal particles is also corroborated by TEM (Figure 2 f). Based on these observations, coking and/or adsorption of byproducts and sintering are supposed to play a predominant role in the stabilization period of the catalyst.

#### Extrapolation to other hexoses and pentoses

To broaden the scope of application of transfer hydrogenation with our  $Cu_3Ni_3Al_2$  catalyst, other relevant hexoses and pentoses substrate were tested using 1,4-butanediol as the hydrogen donor (Table 2).

In all cases, polyols were attained with high yields (60–66%). Interestingly, epimerization–hydrogenation products could be detected, indicating that our hydrotalcite-derived material is also able to catalyze the isomerization of these sugars. Generally, they were formed in trace amounts, except for the case of fructose, in which mannitol comprised the predominant reduc-







Figure 8. XRD patterns of the  $Cu_3Ni_3Al_2$  catalyst obtained by coprecipitation at pH 9–10 after activation and after use in the reaction for 5 h on stream.

<b>Table 2.</b> Catalytic data for the transfer hydrogenation of differenthexoses and pentoses over the $Cu_3Ni_3Al_2$ catalyst in the presence of1,4-butanediol at 423 K.							
Substrate	Conv. [%]	Sorbitol yield [%]	Mannitol yield [%]	Xylitol yield [%]	Arabinitol yield [%]		
glucose fructose	87 85	61 16	- 60	-	-		
mannose xvlose	92 85	13	62 _	- 60	- 10		
arabinose	90	-	-	8	66		

tion product. Typical hydrogenation catalysts reported so far in literature have yielded an even mixture of sorbitol and mannitol from this  $C_6$  saccharide.<sup>[21]</sup>

## Conclusion

An efficient continuous process for the conversion of C<sub>6</sub> and C<sub>5</sub> carbohydrates to their corresponding alditols was attained over hydrotalcite-derived Cu<sub>6-x</sub>Ni<sub>x</sub>Al<sub>2</sub> catalysts by using bioderived hydrogen donors. Different catalysts were prepared by varying the coprecipitation pH and Cu/Ni ratio. Cu<sub>3</sub>Ni<sub>3</sub>Al<sub>2</sub> synthesized at a coprecipitation pH of 9-10 displayed the highest activity and selectivity in converting glucose to sorbitol in the presence of ethanol. The superiority of this catalyst stems from the fact that the metallic phase formed after reduction showed an optimal interaction between copper and nickel compared to the other catalysts. The use of 1,4-butanediol instead of ethanol led to the highest sorbitol yield (67%). The higher efficacy of this donor relates to its transformation into  $\gamma$ -butyrolactone, which involves a lactonization and two dehydrogenations, thereby overall releasing a double amount of hydrogen. Despite a slight initial deactivation, explained by moderate coking and sintering, the catalyst remained stable during 48 h on stream. Finally, this new catalytic technology was successfully transposed to the reductive upgrading of other sugar substrates, including fructose, mannose, xylose, and arabinose and thus represents an attractive alternative system to the costly ruthenium-based catalysts.

## **Experimental Section**

## Catalysts

 $Cu_{6-x}Ni_xAl_2$  catalysts precursors (x=0-6) were prepared by coprecipitation according to a hydrotalcite synthesis method previously described.<sup>[12]</sup> Briefly, an aqueous solution (50 cm<sup>3</sup>) comprising 0.14-0.8 м of Cu(NO<sub>3</sub>)<sub>2</sub>·3 H<sub>2</sub>O (Sigma–Aldrich, 99%), 0.14–0.8 м of  $Ni(NO_3)_2{}{}^{\bullet}6\,H_2O$  (ABCR, 98%), and 0.26  ${}^{\rm M}$  of  $Al(NO_3)_3{}^{\bullet}9\,H_2O$  (Aldrich Fine Chemicals, 99%) were added dropwise to a 0.14 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (50 cm<sup>3</sup>) under vigorous stirring. The pH value, continuously monitored by a probe, was kept constant between 7-8, 9-10, or 11-12 by the dropwise addition of a 4 м NaOH aqueous solution. The resulting pale-blue slurry was transferred into a round-bottom flask and aged at 333 K for 2 h. The solid product was then filtered, thoroughly washed with deionized water, and dried under vacuum at 333 K for 24 h. Thereafter, the catalyst precursor was activated in situ in the fixed-bed reactor in which the catalytic tests were conducted by heating at 773 K (15 Kmin<sup>-1</sup>) for 30 min under a pure  $H_2$  flow (75 cm<sup>3</sup> min<sup>-1</sup>). A commercial 5 wt.% Ru/C catalyst (Sigma-Aldrich) was used as the reference material.

#### Characterization

XRF spectroscopy was performed by using an Orbis Micro-EDXRF analyzer equipped with a 35 kV Rh anode and a silicon drift detector. XPS was conducted by using a Physical Electronics (PHI) Quantum 2000 X-ray photoelectron spectrometer with monochromatic Al K $\alpha$  radiation, generated from an electron beam operated at 15 kV and 32.3 W, and a hemispherical capacitor electron-energy analyzer equipped with a channel plate and a position-sensitive detector. The samples were firmly pressed onto indium foil patches, which were then mounted onto a sample platen and introduced into the spectrometer. The analysis was conducted at  $8\times$  $10^{-9}$  mbar, with an electron take-off angle of  $45^{\circ}$ , and operating the analyzer in the constant pass energy mode. Elemental concentrations were calculated from the photoelectron peak areas after Shirley background subtraction and applying the built-in PHI sensitivity factors. The metal (Cu, Ni) content in the outlet stream of the reactor was determined by ICP-OES using a Horiba Ultra2 instrument equipped with a photomultiplier tube detector. The amount of carbon-containing species deposited on the catalysts after reaction was determined by elemental analysis using a LECO CHN-9000 instrument. Nitrogen sorption at 77 K was performed using a Quantachrome Quadrasorb SI analyzer. Prior to the measurements, samples were degassed under vacuum (10<sup>-1</sup> mbar) at 573 K for 3 h. Powder XRD patterns were measured by using a PANalytical X'Pert Pro-MPD diffractometer with Ni-filtered Cu K $\alpha$  radiation ( $\lambda$  = 0.1541 nm). Data were recorded in the 5–70°  $2\theta$  range with an angular step size of  $0.05^{\circ}$  and a counting time of 7 s per step. H<sub>2</sub>-TPR was performed by using a Thermo TPDRO 1100 unit equipped with a thermal conductivity detector and a trap consisting of molecular sieves and limestone to absorb the water and CO<sub>2</sub> formed in the process. A 25 mg sample of catalyst precursor was loaded into the quartz microreactor (i.d. 11 mm) heated at 423 K (5 Kmin<sup>-1</sup>) for 30 min in He (20 cm<sup>3</sup>min<sup>-1</sup>) and then cooled to 373 K under the same gas flow. The analysis was performed admitting 5 vol.% H<sub>2</sub>/He (20 cm<sup>3</sup>min<sup>-1</sup>) and ramping the temperature from 373 to 1273 K at 10 Kmin<sup>-1</sup>. SEM was performed by using a Zeiss Gemini 1530 FEG microscope on Pt-coated samples (2 nm).

#### **Catalytic testing**

Catalytic tests were performed by using a homemade continuousflow reactor setup comprising 1) an HPLC pump (Jasco PU-980) to feed the liquid reaction mixture, 2) a mass flow controller (Brooks 5850E Series) to feed hydrogen for the activation of the catalyst precursors, 3) a stainless-steel tubular reactor with a pre-column (Swagelok SS-T4-S-035, o.d. 1/4 inch, i.d. 4.6 mm) heated in a tubular oven, and 4) a backpressure regulator (Swagelok, LH2981001) (Scheme 1). The catalyst precursor (0.2-1.5 g) diluted with quartz (particle size = 0.25-0.36 mm) in a 3:1 weight ratio was loaded into the reactor and activated as described above. After cooling down to the reaction temperature (413-443 K), the pressure regulator was set at 15 bar and the reaction was started turning off the  $\mathrm{H}_{2}$ flow and admitting a liquid feed (0.1–0.4 cm<sup>3</sup>min<sup>-1</sup>) composed of an aqueous solution (20 wt.%) and of an alcohol donor (80 wt.%) consisting in methanol (ABCR, 99.9%), ethanol (Fluka, 99.8%), glycerol (ABCR, 99%), or 1,4-butanediol (Sigma-Aldrich, 99%) containing overall 90 mм of glucose (ABCR, 99%), fructose (ABCR, 99%), mannose (ABCR, 99%), xylose (Sigma-Aldrich, 99%), or arabinose (ABCR, 99%). Liquid samples were taken periodically during the 5-48 h tests. The components in these samples were isolated by HPLC using an Agilent 1260 Infinity system equipped with a Biorad Aminex HPX-87C column heated at 353 K and with a refractive index detector (Agilent G1362A) set at 303 K, using Millipore water (0.45 cm<sup>3</sup> min<sup>-1</sup>) as the eluent. Quantification was achieved by integration of their respective peaks, using the sugar substrates and sorbitol (ABCR, 98%), mannitol (ABCR, 99%), arabinitol (ABCR, 99%), and  $\gamma$ -butyrolactone (Acros, 99%) as references. The conversion was calculated as the number of moles of sugar reacted per mole of sugar fed, the polyol selectivity as the number of moles of polyol formed per mole of sugar reacted, and the polyol yield as the product between sugar conversion and polyol selectivity. As no significant change in bed size was observed upon in situ activation and the activated catalyst possessed only moderately reduced surface area, only the formation of gaseous hydrogen in the process was taken into account in the determination of the contact times in the tests. Accordingly, liquid holdups determined by the correlation of Larachi et al.<sup>[22]</sup> for trickle-bed reactors were included in the calculation.

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**Keywords:** alcohols · aldehydes · biomass · hydrogenation · copper-nickel interaction

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# **FULL PAPERS**

**Finding the right partner:** Hydrotalcitederived Cu–Ni–Al materials efficiently catalyze the continuous transfer hydrogenation of C<sub>6</sub> and C<sub>5</sub> sugars with biobased alcohols as hydrogen donors with yields of up to 67%. This technology comprises a safer and cheaper alternative to direct hydrogenation over Ru catalysts.



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Continuous Transfer Hydrogenation of Sugars to Alditols with Bioderived Donors over Cu–Ni–Al Catalysts