Tuning the Acid/Metal Balance of Carbon Nanofiber-Supported Nickel Catalysts for Hydrolytic Hydrogenation of Cellulose

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Carbon nanofibers (CNFs) are a class of graphitic support materials with considerable potential for catalytic conversion of biomass. Earlier, we demonstrated the hydrolytic hydrogenation of cellulose overreshaped nickel particles attached at the tip of CNFs. The aim of this follow-up study was to find a relationship between the acid/metal balance of the Ni/CNFs and their performance in the catalytic conversion of cellulose. After oxidation and incipient wetness impregnation with Ni, the Ni/CNFs were characterized by various analytical methods. To prepare a selective Ni/CNF catalyst, the influences of the nature of the oxidation agent, Ni activation, and Ni loading were investigated. Under the applied reaction conditions, the best result, that is, 76% yield in hexitols with 69% sorbitol selectivity at 93% conversion of cellulose, was obtained on a 7.5 wt% Ni/CNF catalyst prepared by chemical vapor deposition of CH4 on a Ni/γ-Al2O3 catalyst, followed by oxidation in HNO3 (twice for 1 h at 383 K), incipient wet impregnation, and reduction at 773 K under H2. This preparation method leads to a properly balanced Ni/CNF catalyst in terms of Ni dispersion and hydrogeneration capacity on the one hand, and the number of acidic surface-oxygen groups responsible for the acid-catalyzed hydrolysis on the other.

Introduction

In the framework of carbohydrate-based biorefinery schemes, the search for catalytic processes for converting cellulose has been intense. A particularly promising reaction in water is the one-pot hydrolytic hydrogenation of cellulose to sugar alcohols. Although discovered decades ago, this chemistry was recently reinvestigated for a wide range of heterogeneous catalysts. Among the screened candidates are supported noble-metal catalysts, such as Pt/γ-Al2O3, Pt/carbon black, Pt/H-ZSM-5, Pt/MCM-48, Ru/activated carbon, Ru/C, or Pt catalysts in combination with heteropolyacids (HPAs), Ru/H-USY zeolites with trace amounts of HCl, Ru/CNTs, Ru/Cs2P2W9O34, [RuCl(CO)H(PPh3)3]/KOH in 1-butyl-3-methylimidazolium, RhNi/MC, and combinations of Pt/C, Pd/C, or Ru/C with dilute HCl, H3PO4, or H2SO4. Catalytic hydrolysis of cellulose to ethylene glycol by using Ni-W/C/AC, Ni-W/SBA-15, WC supported on mesoporous carbon, or Ru/C in the presence of WO3 has been studied as well.

In 2010, two groups reported almost simultaneously the use of nickel as a less expensive alternative metal catalyst for the transformation of cellulose into C6 sugar alcohols. Ding et al. focused on a bifunctional nickel phosphide catalyst (16% NiP/AC), yielding up to 48% sorbitol under optimized reaction conditions (498 K, 6 MPa H2 added at RT). Mechanistically, hydrolysis of cellulose into glucose is proposed to be catalyzed by the acidity formed by excess phosphide, followed by nickel-catalyzed hydrogenation of glucose to sorbitol. In parallel, we investigated the catalytic conversion of cellulose over as-synthesized carbon nanofibers (CNFs) with nickel particles at the tip of the fibers. When compared with conventional carbon materials, aggregates of CNFs present interesting properties, such as enhanced mechanical strength and filterability, high hydrothermal stability, controllable surface chemistry, and reduced mass transfer limitations associated with the presence of mesopores and a high surface area. The combination of these features makes them suitable candidates for applications as catalyst supports in biomass-related reactions. Accordingly, when using as-prepared CNF-supported nickel catalysts (Ni/CNFs) for the conversion of cellulose, yields of sorbitol in the range of 30–50% were obtained under mild reaction condi-
Results and Discussion

Preparation and characterization of Ni/CNFs

Catalytic CVD of methane over a 20 wt% Ni/γ-Al2O3 catalyst, calcined and reduced at 873 K, results in CNFs of the fishbone type with the graphene layers inclined with respect to the central fiber axis.[22] From N2 physisorption isotherms, a relatively large and accessible surface area of 102 m2 g−1 was found with a total pore volume of 0.16 cm3 g−1 and a micropore volume of 0.01 cm3 g−1. A combined SEM and Raman spectroscopy study showed an average fiber diameter of 60 nm with an in-plane crystallite size of 21 nm. More detailed morphological and structural characteristics of the CNFs have been previously published.[22]

To introduce different amounts of acidic groups and anchoring sites for the Ni particles, the CNFs were heated at reflux once or twice for 1 h in either concentrated HNO3 or 1:1 mixtures of HNO3/H2SO4. The methodology is based on previous reports,[38b,40] which documented the influence of both oxidation agents on the texture of fishbone-type CNFs and the number of oxygen-containing surface groups. Herein, acid–base titration of the CNF suspensions in water, NH3 temperature-programmed desorption (NH3-TPD), and temperature-programmed decomposition were used to investigate the amount, strength, and stability of the acidic groups. The results (Table 1), in correlation with the catalytic behavior of the Ni/CNFs, are discussed in the next sections. Regarding the effect of oxidation on the textural properties, three representative N2 physisorption isotherms of the untreated, the HNO3-, and the HNO3/H2SO4-oxidized CNFs are shown in Figure 1a. The presence of hysteresis loops is attributed to the condensation of N2 between the open spaces of the entangled CNFs at high relative pressure.[41] While the observed increase in mesopore volume indicates a less dense macrostructure, Ros et al. previously associated the larger surface area to an altered surface roughness of the oxidized CNF surface.[38b]

Nickel was deposited on the oxidized CNFs by incipient wetness impregnation with an aqueous solution of nickel nitrate, followed by drying and reduction under a flow of H2. To find balanced acid and hydrogenation activity of the catalysts, the influence of metal loading was investigated by using different concentrations of the Ni precursor. ([Ni2+] = 0.17–0.95 mmol L−1). As measured by ICP-AES, the actual Ni loadings of the resulting Ni/CNFs varied from 2.6 to 10.4 wt%. The dispersion of the Ni particles was determined by using pulse CO

Table 1. Acid treatment method, nominal and actual Ni loading, reduction temperature, physicochemical features, Ni dispersion, and amount of Ni surface atoms of various Ni/CNF catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid treatment</th>
<th>Ni uptake[a]</th>
<th>Ni loading[b]</th>
<th>Reduction T</th>
<th>S BET [m2 g−1]</th>
<th>Pore V [cm3 g−1]</th>
<th>Acid density[c]</th>
<th>Ni dispersion[d]</th>
<th>Ni surface atoms[e]</th>
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<td>773</td>
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<td>0.00 (0.32)</td>
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<td>0.02 (0.06)</td>
<td>1.8</td>
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<tr>
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<td>7.6</td>
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<td>0.02</td>
<td>1.9</td>
<td>12.7</td>
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<tr>
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<td>973</td>
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<td>0.33</td>
<td>&lt;0.01</td>
<td>0.5</td>
<td>6.6</td>
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[a] Nominal Ni loading on the CNF support. [b] Quantitative elemental analysis of the actual Ni loading performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). [c] Determined by acid–base titrations. Values in parentheses refer to the corresponding acid densities of the unloaded CNFs after oxidation treatment. [d] Calculated from the actual Ni loading and the amount of Ni surface atoms. [e] Determined by pulse CO titration experiments.
chemisorption measurements (Table 1) and TEM. Figure 2 shows an example of a TEM micrograph of a 7.5 wt % Ni/CNF catalyst, indicating a rather broad distribution of the Ni particle sizes centered around 16 nm. The impregnation and subsequent reduction of oxidized CNFs yield Ni dispersions ranging from 0.5 to 3.6 %. For the Ni/CNF catalysts, the amount of accessible Ni surface atoms is listed in Table 1.

The reduction behavior of the Ni/CNFs was studied by H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}-TPR) of the catalyst precursor after deposition of the Ni compound onto the CNF support by incipient wetness impregnation and subsequent drying in air.

**Figure 1.** a) \text{N}_2\text{ physisorption isotherms at 77 K of the parent CNFs grown by CVD of methane over a \text{Ni}/\gamma-\text{Al}_2\text{O}_3 catalyst (-----) and after oxidation in either \text{HNO}_3 (-----) or a 1:1 mixture of \text{HNO}_3/\text{H}_2\text{SO}_4 (-----). The isotherms can be classified as type IV isotherms with type B hysteresis loops. b) H\textsubscript{2}-TPR profile of the catalysts precursor after deposition of Ni onto the HNO\textsubscript{3}-treated CNF support by incipient wetness impregnation and subsequent drying in air.

**Figure 2.** TEM micrograph and the corresponding histogram of the Ni particle size distribution of a 7.5 wt % Ni/CNFs catalyst prepared by impregnation of Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O onto HNO\textsubscript{3}-oxidized CNFs followed by H\textsubscript{2} reduction at 773 K.

**Figure 3.** Changes with time of the conversion of cellulose (Δ) and yields of sorbitol (○), erythritol (×), and mannitol (△). Reaction conditions: ball-milled Avicel cellulose (1 g), water (50 mL), 6 MPa initial H\textsubscript{2} pressure at RT, 463 K, 24 h, with 7.5 wt % Ni/CNF catalyst (0.5 g) prepared by oxidation (twice in HNO\textsubscript{3}, for 1 h), followed by incipient wetness impregnation and reduction at 773 K.

**Typical product spectrum**

The hydrolytic hydrogenation of cellulose with Ni/CNFs was studied at 463 K and 6 MPa H\textsubscript{2} added at RT (see the Experimental Section). Prior to the catalytic reactions, the reactivity of Avicel cellulose towards dissolution and catalytic hydrolysis was enhanced by ball-milling\textsuperscript{[1,22]} Detailed characterization data (such as SEM, XRD, \textsuperscript{11}C cross polarization magic angle spinning (CP-MAS) NMR spectroscopy, and FTIR spectroscopy) of the ball-milled cellulose samples have been provided elsewhere\textsuperscript{[22,43].}

Figure 3 shows the cellulose conversion changes in time over an optimized 7.5 wt % Ni/CNF catalyst, prepared by the liquid-phase oxidation of the CNFs in HNO\textsubscript{3}, incipient wetness impregnation, and reduction at 773 K. At 93 % cellulose conversion, yields of 64 % sorbitol and 7 % mannitol were obtained, which are significantly higher than those previously reported under identical conditions for untreated CNFs with Ni particles at the tip of the fibers (50 % sorbitol and 5 % mannitol at 92 % conversion)\textsuperscript{[20].}
Generally, the experimental sorbitol/mannitol product ratio ranged from 5 to 10. Whereas sorbitol and mannitol are known to be produced through the hydrogenation of glucose and mannose, the literature attributes the formation of mannose to the acid-catalyzed C2 epimerization of glucose.\[^{[40]}\] Although not always mentioned,\[^{[46]}\] a multitude of byproducts can be formed during the metal-catalyzed cracking of cellulose. For example, in the presence of the 7.5 wt% Ni/CNF catalyst, we identified small amounts of 1,4-sorbitan (3.6%), glycerol (3.5%), 1,2-butanediol (2.8%), xylitol (1.8%), and trace amounts (< 1%) of 1,2-propanediol, isosorbide, 1,2-hexanediol, and ethylene glycol. The dehydrogenation of sorbitol to isosorbide follows an intramolecular dehydration step to generate 1,4-sorbitan intermediates and subsequent dehydrogenation to isosorbide.\[^{[44]}\] On the other hand, ethylene glycol, glycerol, 1,2-propanediol, and other low-molecular-weight polyols were earlier shown to originate from metal-catalyzed hydrolysis.\[^{[47]}\] While the carbon balance in the liquid phase accounted for more than 90% of the initial number of carbon atoms, it is interesting to note that a product analysis of the gaseous effluent showed only small amounts of CH\(_4\) (0.3%) and CO\(_2\) (0.1%). The remaining gap in the carbon balance should be attributed to the formation of water-soluble cello-oligomers.\[^{[45]}\]

**Effect of the nature of the oxidation agent for support treatment**

The most important characteristics of the four catalyst samples used in this section are given in entries 1–4 of Table 1. Prior to Ni deposition, CNFs were oxidized by heating at reflux once or twice for 1 h in either concentrated HNO\(_3\) or 1:1 (HNO\(_3\)/H\(_2\)SO\(_4\)) mixtures.\[^{[40, 46]}\] The results from acid–base titrations, denoted in parentheses in Table 1, demonstrate that the number of acidic sites on the surface of the CNFs depends on both the oxidation agent and the treatment time. It has been shown that the concentration of nitronium ions (i.e., the active nitrating species) is higher for HNO\(_3\)/H\(_2\)SO\(_4\) mixtures than for concentrated HNO\(_3\) \[^{[40, 46]}\].

\[
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}^+ \tag{1}
\]

\[
2\text{HNO}_3 \rightarrow \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O} \tag{2}
\]

Indeed, results from X-ray photoelectron spectroscopy (XPS) analyses given in Table 2 show a much higher O/C peak area ratio when the CNFs were treated in HNO\(_3\)/H\(_2\)SO\(_4\) mixtures. Deconvolution of the O 1s region resulted in about 4–5% oxygen-containing species with a binding energy (E\(_b\)) of 535.1 eV, which could be assigned to carboxylic acids.\[^{[47]}\]

After impregnation with Ni, CO chemisorption results indicate that, for an identical reduction temperature (773 K), the oxidation agent has a pronounced effect on the dispersion of the Ni particles. Using only HNO\(_3\), Ni dispersions of about 2% could be obtained, while with HNO\(_3\)/H\(_2\)SO\(_4\)-treated CNFs, the dispersion values were consistently lower (Table 1). Because the HNO\(_3\)/H\(_2\)SO\(_4\)-treated CNFs seem to have lost all of the acidic groups, the impact of impregnation and reduction of the Ni/CNFs requires some clarification. The higher agglomeration degree of Ni on the HNO\(_3\)/H\(_2\)SO\(_4\)-treated CNFs is correlated to the decomposition of less stable surface oxygen groups during the reduction stage, which facilitates the mobility and agglomeration of the Ni particles on the CNF surface.\[^{[43]}\] This effect was observed in the XPS spectra by a strong decrease of the O 1s/C 1s peak area ratio from 0.122 to 0.043 after reduction of the Ni/CNFs. A similar conclusion was drawn in studies by Calvillo et al. on the preparation of Pt/CNFs with HNO\(_3\) and HNO\(_3\)/H\(_2\)SO\(_4\) mixtures.\[^{[48]}\]

As seen in Figure 4, the investigated oxidation variables significantly influence the overall conversion of cellulose and selectivity towards the products formed in the hydrolytic hydrogenation reaction. For the sake of clarity, only the amounts of sorbitol, mannitol, erythritol, and C\(_2\)-C\(_4\) hydrolysis products are plotted. At first glance, HNO\(_3\) is more suitable as an oxidation agent for the preparation of Ni/CNFs, resulting in enhanced yields of sorbitol and mannitol. In case of HNO\(_3\)/H\(_2\)SO\(_4\)-treated CNFs, the lower hexitol selectivities are partly due to strong sintering of Ni particles, which reduces the active metal surface for catalytic hydrogenation of the released glucose. However, only a different hydrogenation activity cannot adequately explain the observed differences in product selectivity and cellulose conversion. In Figure 4, the considerable difference between the conversion of cellulose, as measured by

![Figure 4. Comparison of the conversion and product yields of different Ni/CNF catalysts for the hydrolytic hydrogenation of cellulose.](image-url)
total organic carbon (TOC) analysis of the aqueous phase, and the sum of chromatographically identified products suggests significant changes in the formation of cello-oligomers, depending on the oxidation agent.

Differences are even more compelling among the chromatograms shown in Figure 5, representing relative amounts of β-1,4-glucan fragments determined after 24 h of reaction by using high-performance anion-exchange chromatography with pulsed amperometric detection (HPEAC-PAD; see the Experimental Section). Recently,[10] the dissolution–conversion of ball-milled Avicel cellulose in water at 463 K and 5 Mpa H₂ has been demonstrated to generate up to 80% cello-oligomers even in the absence of any catalyst. From Figure 5 it is clear that the reaction of cellulose with nonacidic Ni/CNFs results in a more than twofold greater β-1,4-glucan formation than acidic compounds. In qualitative terms, hydrolysis of the cello-oligomers to glucose seems to be the rate-determining step when using nonacidic Ni/CNF catalysts. However, by introducing small amounts of thermally stable Brønsted acid sites (i.e., up to 0.03 mmol H⁺ per g of catalyst) through pre-oxidation of the CNFs with HNO₃, the reaction rates for hydrolysis of β-1,4-glucans to glucose are observed to be much higher, thereby yielding significantly less cello-oligomers and more hexitols in the product spectrum (Figure 4 vs. Figure 5).

**Effect of catalyst reduction temperature**

Having identified HNO₃ as the most effective oxidation agent, we examined the effect of reduction temperature on the properties and catalytic activity of the Ni/CNFs. From entries 5–9 in Table 1, it can be derived that, while the specific surface area and pore volume remain approximately constant, the dispersion of the Ni particles decreases significantly with increasing reduction temperature. After 1 h reduction at 973 K (heating rate 5 K/min⁻¹), the Ni dispersion calculated from CO chemisorption even drops to 0.5% (Table 1, entry 9). The sintering process of carbon-supported Ni particles during a reduction treatment has long been recognized.[38] Studies by Baker have shown a relationship between the mobility of Ni particles on a graphite surface and the Tamman temperature of the metal.[39] In the current investigation, it can be speculated that the reasons for the relatively high susceptibility to Ni agglomeration/growth are related to the weak interaction of the Ni precursor with the CNF support,[38b] as well as to the higher actual temperature at the CNF surface due to the heat released by catalytic gasification.[41]

As reported above, heat treatment of the Ni/CNFs under a reducing atmosphere also leads to the removal of the oxygen-containing surface groups. In Table 1, a clear trend can be observed in the decrease of acid density of the Ni/CNFs with increasing reduction temperature. After reduction at 573 K, the acid density of the catalyst amounted to 0.12 mmol H⁺ per g, while for the samples reduced at 873 and 973 K less than 0.01 mmol g⁻¹ of residual Brønsted acidity remained. The loss of acidity from the Ni/CNFs was confirmed by ammonia temperature-programmed desorption (NH₃-TPD) after NH₃ adsorption at 473 K (Figure 6). Regardless of the low signal to noise ratio, it is clear that the amount of NH₃ desorbed from the Ni/CNFs has significantly decreased after reduction at higher temperatures. The NH₃-TPD profile associated with the sample reduced at 773 K reveals the presence of two desorption peaks. While the low-temperature peak centered at 400 K arises from weakly held NH₃ molecules (probably hydrogen bonded), the broad signal in the temperature range between 420 and 800 K is assigned to the presence of stronger Brønsted acid sites.

To unravel the nature of the surface oxygen complexes responsible for this acidity, the functionalized Ni/CNFs were further investigated by temperature-programmed decomposition in He with simultaneous analysis of CO and CO₂ evolution (Figure 7). The literature available on chemical activation of carbon materials reports seven possible types of oxygen-containing groups on the surface of CNFs (i.e., carboxylic acids, lactones, phenols, carbonyls, ethers, carboxylic anhydrides, and quinone groups).[38b] In general, the most acidic groups are thermally transformed into CO₂, whereas less acidic and more stable ones decompose into CO.[38] Although there is no general consensus on the assignment of the peaks in Figure 7 to specific functionalities, the profiles indicate a drastic decrease...
in the number of surface groups with increasing reduction temperature. From the results in Figure 7 and in agreement with earlier work,\textsuperscript{40,51} we conclude that only few acidic surface groups remain upon treatment of the Ni/CNFs at 973 K. It should be noted that the sample reduced at 973 K still gives desorption of CO and CO\textsubscript{2} at temperatures below 973 K, diagnostic of the formation of surface-oxygen complexes upon air exposure during catalyst handling after the reduction step.\textsuperscript{52}

From the results given in Table 3, a maximum in the catalytic activity is found for the Ni/CNFs reduced at 773 K, with a cellulose conversion reaching 91\% and a hexitol yield of 58\%. For reduction temperatures going from 553 to 773 K, the enhancement in hexitol formation indicates an improved balance between the acid and hydrogenation functions (see below). Based on the XPS spectra of these materials, it is instructive to note that the ratio of Ni\textsuperscript{0} species ($E_{b} = 852.6$ eV) to Ni\textsuperscript{2+} ($E_{b} = 854.6$ eV) increases from 8.92 to 19.81 after reduction at 553 and 773 K, respectively.\textsuperscript{53} However, although the ratio further increases to 24.76 for Ni/CNFs activated at 973 K, the observed yield to hexitols drops to 42\%. This trend can be explained by the lower dispersion of the bigger Ni particles hampering efficient participation in the hydrogenation and by the lack of hydrolytic activity on the CNF surface with an acid density below 0.01 mmol H\textsuperscript{+} per g.

### Effect of Ni loading

In a final set of experiments, we addressed the effect of Ni loading (2.6–10.4 wt\% Ni) on the catalytic performance of Ni/CNFs pre-reduced at 773 K. Values of the actual Ni loading as measured with ICP-AES are listed in Table 4. Up to 10.4 wt\% Ni, the metal loading barely affects the dispersion, and thus, the size distribution of the Ni particles. NH\textsubscript{3}-TPD spectra and N\textsubscript{2} physisorption data closely resemble those of the Ni/CNFs reduced at 773 K described above and are therefore not shown. The acid densities, listed in Table 4, are almost insensitive to Ni loading, which enables a straightforward study of the metal function.

From the results given in Table 4, for up to 7.5 wt\% Ni, the hexitol yield increases with increasing Ni loading. While in the case of 2.6 and 3.8 wt\% Ni, relatively low yields of sorbitol and mannitol were detected, higher Ni loadings shift the product spectrum towards enhanced hexitol yields. At low Ni loadings, the poor selectivities can be tentatively explained by the acid and metal functions being out of balance, leading to a loss of glucose through thermal and acid-catalyzed degradation reactions.\textsuperscript{10} Indeed, up to 2\% glucose formation was evidenced in contrast, at Ni loadings higher than 7.5 wt\%, several hydrolysis reactions of the C–C bonds in sorbitol become increasingly important and complicate the overall chemistry. To address this issue, results from a comparison of sorbitol stability after 24 h reaction time are given in Table 5, taking three Ni/CNFs with 2.6, 6.5, and 10.4 wt\% Ni as representative catalysts. The results indicate a reduced sorbitol stability in the presence of 10.4 wt\% Ni/CNFs, yielding a higher fraction of C\textsubscript{2}–C\textsubscript{5} molecules. Erythritol, 1,2-butanediol, glycerol, 1,2-propanediol, and ethylene glycol were the predominant hydrolysis products irrespective of the Ni loading. Collecting all arguments

### Table 3. Effect of the reduction temperature of the Ni/CNF catalysts on the conversion of cellulose and product yields\textsuperscript{[a]}

<table>
<thead>
<tr>
<th>Reduction temperature [K]</th>
<th>Conversion [%]</th>
<th>Hexitols</th>
<th>Yield [%]</th>
<th>Sorbitol</th>
<th>C\textsubscript{2}–C\textsubscript{5} prod.</th>
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\textsuperscript{[a]} Reaction conditions: ball-milled Avicel cellulose (1 g), Ni/CNF catalyst (0.5 g), water (50 mL), 6 M \textit{H}\textsubscript{2} pressure at RT, 463 K, 24 h.

### Table 4. Effect of the Ni loading on the properties of Ni/CNFs\textsuperscript{[a]} the conversion of cellulose, and product yields\textsuperscript{[b]}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ni loading [wt%]</th>
<th>Acid density [mmol g\textsuperscript{−1}]</th>
<th>Ni dispersion [wt%]</th>
<th>Ni surface atoms [μmol g\textsuperscript{−1}]</th>
<th>Conversion [%]</th>
<th>Hexitols</th>
<th>Sorbitol</th>
<th>C\textsubscript{2}–C\textsubscript{5} prod.</th>
<th>Yield [%]</th>
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\textsuperscript{[a]} Prepared by oxidation (twice in H\textsubscript{2}O, for 1 h), incipient wet impregnation with varying concentrations of the Ni precursor ([Ni\textsuperscript{2+}] = 0.01–0.05 g mL\textsuperscript{−1}), and reduction at 773 K. \textsuperscript{[b]} Reaction conditions: ball-milled Avicel cellulose (1 g), Ni/CNFs (0.5 g), water (50 mL), 6 MPa initial H\textsubscript{2} pressure at RT, 463 K, 24 h.
shows that an optimally balanced Ni loading is crucial for the selective conversion of cellulose because an excessive Ni loading favors C–C bond cleavage and inhibits hydrogenation.

As an addendum to the study of cellulose conversion, we also evaluated the use of Ni/CNFs for direct catalytic hydrogenation of glucose, using a pseudo-first-order kinetic approximation to probe the effect of Ni loading on the hydrogenation rate, as successfully applied in earlier work. Batch experiments were performed at 398 K and 6 MPa H₂ pressure to avoid glucose caramelization. This is not an issue when starting from cellulose as a substrate, provided that, once small concentrations are formed by acid-catalyzed hydrolysis, glucose is rapidly hydrogenated. For the reactions shown in Figure 8, the Ni/CNF catalysts show a consistently high selectivity to sorbitol. For example, in case of the 10.4 wt % Ni/CNF catalyst, the yields of sorbitol reach values up to 96%.

The product mixture also contained small amounts of gluconic acid (1.3%), which is a side product formed by the Cannizzaro reaction of glucose. From the Arrhenius plot extracted from the pseudo-first-order reaction rates in the temperature range of 378–398 K, an apparent activation energy of about 52 kJ mol⁻¹ was obtained. This value is appreciably higher than the activation energy of H₂ diffusion in liquids (12–21 kJ mol⁻¹), indicating that the catalytic hydrogenation experiments were performed in the kinetic regime. As shown in the inset in Figure 8, a nearly linear correlation is observed between the pseudo-first-order reaction rate constants for sorbitol formation and the amount of Ni surface atoms of the Ni/CNFs. These results clearly establish a linear dependence of the hydrogenation activity of the Ni/CNFs on the availability of surface metal sites.

**Evaluation of the catalyst acid/metal balance**

The experimental data set thus far obtained has been used to rationalize the acid/metal balance requirements of the Ni/CNFs for hydrolytic hydrogenation of cellulose to hexitols. Inspiration for the applied methodology was found in related literature available on the evaluation of bifunctional catalysts for hydrogenolysis of alkanes. Taking the characterization results reported in Tables 1 and 4, the ratio of the acid density to the number of Ni surface atoms (n_a/n_M) was used to monitor the balance between the hydrogenation and the acid functions. The applicability of this parameter can be assessed by studying Figure 9, in which the n_a/n_M values and the corresponding hexitol yields are presented.

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![Figure 8](image8.png) **Figure 8.** Effect of Ni loading on the catalytic hydrogenation of glucose to sorbitol at 398 K; 2.6, 3.8, 7.5, 10.4 wt% Ni. Reaction conditions: glucose (1 g), Ni/CNF catalyst (0.5 g), water (50 mL), 6 MPa initial H₂ pressure at RT, 463 K, 24 h.

![Figure 9](image9.png) **Figure 9.** Relationship between the n_a/n_M ratio and the observed hexitol yields for the Ni/CNF catalysts discussed: effect of nature of oxidation agent for support treatment (○), effect of catalyst reduction temperature (●), and effect of Ni loading (▲).

Considering the inevitable experimental error in this type of reactions, the observed relationship appears to be relatively good. The reduced hexitol yields (42–53%) generated for non-acidic Ni/CNFs (n_a/n_M = 0) suggest the need for acid sites on the CNF surface in the catalytic depolymerization of cellulose and other subsequent hydrolysis reactions. When the acid density is high enough to establish a proper balance between the two catalytic functions (0.7 < n_a/n_M < 1.1), the hexitol yield reaches a maximum of nearly 80%. For lower values, a further increase in the amount of Ni surface atoms renders the sugar alcohols more susceptible to C–C bond hydrogenolysis; hence, lowering the C₆ product selectivity. For increasingly higher values of this ratio, it is more likely that glucose is subjected to another acid-catalyzed degradation reaction rather than being hydrogenated to hexitols.

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</table>

[a] Reaction conditions: sorbitol (1 g), Ni/CNF catalyst (0.5 g), water (50 mL), 6 MPa initial H₂ pressure at RT, 463 K, 24 h.

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**Table 5.** Sorbitol conversion on Ni/CNF catalysts.

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Conclusions
A series of well-characterized Ni/CNFs were tested for the hydrolytic hydrogenation of cellulose to C6 sugar alcohols. Variations in the nature of the oxidation agent for support treatment (HNO3 vs. 1:1 mixtures of HNO3/H2SO4), the Ni activation procedure (different reduction temperatures), and Ni loading enabled us to tune the dispersion of the Ni particles, as well as the number of oxygen-containing surface groups. The catalytic results presented herein not only give insight into the optimal preparation conditions of bifunctional Ni/CNFs for cellulose to xehitol conversion, but also advance a diagnostic tool to evaluate the balance between the hydrogenation and the acid functions. In the investigated range of conditions, the 7.5 wt% Ni/CNFs with a relatively high amount of Ni surface atoms (26.9 μmol g−1) and low density of Brønsted acid sites (0.02 mmol g−1) prepared by an oxidative activation of fish-bone-type CNFs in HNO3, incipient wetness impregnation, and a reduction up to 773 K under H2 showed the highest xehitol yields of up to 76% at a cellulose conversion of 93%.

Experimental Section
Catalyst preparation: For the catalytic growth of CNFs, 20 wt% Ni/CNFs were prepared by wet impregnation of alumina (Puralox, 155 m2 g−1) with an aqueous solution of nickel nitrate ([Ni2+] = 0.17–0.95 mM). After drying at 373 K, the catalyst precursor was calcined for 5 h in static air at 873 K (heating rate 5 K·min−1). Prior to fiber growth, the Ni-catalyst precursor (1 g) was reduced for 1 h under a flow of H2 (50 mL·min−1) at 873 K (heating rate 5 K·min−1). Next, the CNFs were grown by CVD of CH4 (80 mL·min−1) at 873 K for 3.5 h. Typically, a CNF yield of 6 g was obtained. A more detailed description of CNF growth can be found elsewhere.22 For a typical activation of the CNFs by surface oxidation and removal of Ni, a suspension of CNFs (6 g) in HNO3 (120 mL; 65%) was heated at 383 K under vigorous stirring. After 1 h, the oxidized CNFs were filtered, washed with distilled water, and dried overnight at 373 K. Ni was deposited on the oxidized CNFs by using the incipient wetness impregnation technique. Briefly, the desired amount of Ni(NO3)2·6H2O was dissolved in distilled water (2 mL) and added dropwise to the CNFs (1 g). Next, the samples were dried at 333 K for 12 h, heated under N2, to 773 K (heating rate 5 K·min−1), and reduced for 1 h under a flow of H2 (100 mL·min−1).

Catalyst characterization: Brunauer–Emmett–Teller specific surface areas (SBET) and pore volumes of the catalysts were calculated from N2 physisorption data obtained at 77 K by using a Micromeritics Adsorption/Desorption analyzer. Some spectra were decomposed with Origin Pro 8 software (OriginLab). H2-TPR profiles were obtained in the same apparatus by using MS detection under the following conditions: sample weight 100 mg, heating rate 10 K·min−1, flow rate 12 mL·min−1, and 5 vol% H2 in N2. Prior to reduction, the samples were dried at 373 K. For temperature-programmed decomposition experiments, about 50 mg of the sample was placed in the sample holder and degassed under a flow of He (20 mL·min−1). The temperature was increased from 298 to 1373 K (heating rate 10 K·min−1); and the partial pressures of CO and CO2 were recorded by using a mass spectrometer.

XPS was performed on a 55X 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromated microfocused Al X-ray source (powered at 20 mA and 10 kV). The sample powder pressed in small stainless-steel troughs of 4 mm diameter was placed on an insulating ceramic insulator carousel. The pressure in the analysis chamber was around 10−6 Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The analyzed area was approximately 1.4 mm2, and the pass energy was set at 150 eV. In these conditions, the full width at half maximum of the Au 4f7/2 peak of a clean gold standard sample was about 1.6 eV. A flood gun set at 8 eV and a Ni grid placed 3 mm above the sample surface were used for charge stabilization. Data treatment was performed by using the CasaXPS program (Casa Software). Some spectra were decomposed with the least-squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtrac- tion of a nonlinear baseline.

Catalyst testing: The conversion of cellulose was studied in batch mode in a 100 mL Parr autoclave equipped with a mechanical stirrer, a liquid sampling tube, gas inlet and outlet tubes, a thermocouple, a rupture disc, and an electric heating jacket. The autoclave was loaded with cellulose (1 g) and the reduced catalyst (0.5 g) in distilled water (50 mL). After flushing the reaction mixture with N2, 6 MPa of H2 was added to the autoclave and the temperature was raised to 463 K. To operate in the kinetically controlled regime, the stirrer speed was set at 700 rpm. The short heating time (15 min) and the accurate temperature control ensured stable conditions during the reaction. Experiments with glucose were performed at 398 K and a H2 pressure of 6 MPa added at RT.

Product analysis: Samples of the reaction mixture (ca. 1 mL) were withdrawn periodically, centrifuged, filtered over a 0.45 μm PTFE
filter, and analyzed by HPLC (Agilent 1200 Series, Varian Metacarb 67C column (300 x 6.5 mm), mobile phase: 0.5 mL min$^{-1}$ of water), equipped with a refractive index detector. The product yield was calculated as follows: yield (%) = (weight of polyol/weight of cellulose charged in reactor). Conversions of cellulose were determined by TOC analysis of the liquid phase, as reported earlier.[22]

Water-soluble cell-oligomers were analyzed by HPAEC-PAD performed on a Dionex ICS-3000 chromatography system (Dionex Corporation, Sunnyvale, CA, USA). The product mixture was diluted (1:200 in water) and filtered (Millepore, Millipore, Carrigtwohill, Ireland) before injection on a CarboPac PA-100 anion-exchange column (250 x 4 mm). The mobile phase was composed of A (H$_2$O), B (200 mM NaOH), and C (400 mM NaOAc in 100 mM NaOH). Water-soluble cell-oligomers were separated by running a linear gradient of A/B/C changing from 50:50:0 to 12.5:12.5:75 within 25 min at a flow rate of 1 mL min$^{-1}$, followed by 25-30 min elution with a 100% C solution. The column temperature was maintained at 303 K.

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