

Selective Bifunctional Catalytic Conversion of Cellulose over Reshaped Ni Particles at the Tip of Carbon Nanofibers

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Although cellulose, as an abundant and renewable resource, offers a promising alternative for the production of biofuels and platform chemicals,^[1] there have thus far only been a few studies that have reported its aqueous-phase conversion into polyols by solid chemocatalysts.^[2–5] The principal reason is that these polymeric biomolecules with a semicrystalline structure cannot penetrate the pores of conventional heterogeneous catalysts. Advances in the conversion of cellulose therefore require the design of efficient multifunctional catalysts with sterically accessible sites.^[6] Herein, we demonstrate that sugar alcohols can be selectively produced from cellulose in a one-pot catalytic process over reshaped Ni particles at the tip of carbon nanofibers.

One elegant strategy to valorize cellulose into polyols is inspired by a previous report on starch conversion.^[7] One-pot catalytic approaches of this kind rely on proton-catalyzed hydrolysis of the glycoside bonds, followed by fast metal-catalyzed hydrogenation of the released glucose units into sorbitol. A high sorbitol yield is only guaranteed if hydrolysis is the rate-limiting step (preventing undesirable glucose degradation). The first reports on the application of such bifunctional catalysis to cellulose fractions appeared in the pioneering work of Fukuoka and Dhepe.^[2] They demonstrated the selective conversion of cellulose into sugar alcohols by using supported precious-metal catalysts at elevated temperatures. Pt and Ru gave the highest hexitol yields. For example, Pt/ γ -Al₂O₃ catalyzed the conversion of cellulose to yield 25% and 6% of sorbitol and mannitol, respectively. Alternatively, on a Ru/C catalyst Luo et al. reported yields of 30% and 10% of sorbitol and mannitol, respectively.^[3] Most notably, in such studies less-expensive Ni catalysts consistently exhibit inferior performances towards sugar alcohol production (Supporting Information,

Table S1),^[2,4–5] in agreement with their known unselective hydrogenolysis behavior.^[8]

The main difficulty in using conventional heterogeneous catalysts for bulky cellulose substrates is the limited accessibility of the active catalytic sites. Their performance seems to be governed by the restricted space inside the pore systems, preventing polymeric biomolecules from penetrating to the metal sites.^[6] To overcome this incompatibility between substrate and catalyst, the present study uses carbon nanofibers instead of porous solids to support Ni at the tip of the carbon filaments. In a typical synthesis, the Ni-containing carbon nanofibers (Ni/CNF) were formed by catalytic vapor deposition (CVD) of methane over a catalyst consisting of Ni nanoclusters supported on γ -alumina (Puralox, 155 m²g⁻¹).^[9] The textural properties of the catalysts were investigated by scanning electron microscopy (SEM) and N₂ physisorption.

As can be seen in Figure 1 a, the obtained sample of carbon nanofibers grown over supported nickel (Ni/CNF) showed an entangled “spaghetti-like” morphology with a fiber diameter of (60 ± 40) nm. The agglomerated carbon nanofibers showed a mesoporous structure, with a Brunauer–Emmett–Teller (BET) specific surface area of 76 m²g⁻¹ and a total pore volume of 0.16 cm³g⁻¹. Representative transmission electron microscopy

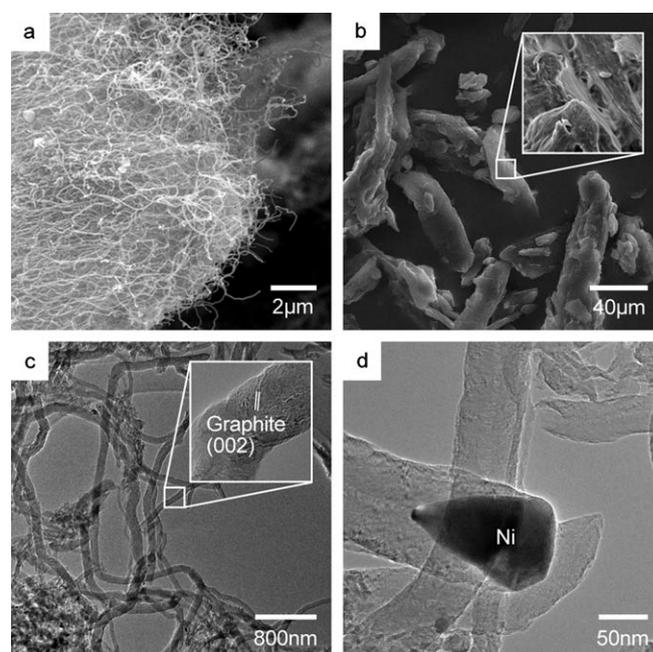


Figure 1. Typical SEM images of a) carbon nanofibers grown over Ni catalysts, and b) microcrystalline cellulose. TEM images show c) a detail of the fishbone stacking of graphene layers in the nanofibers, and d) a pear-shaped Ni particle at the tip of a carbon nanofiber.

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(TEM) images reveal elongated pear-shaped Ni nanoclusters with an aspect ratio of approximately 1.6, on the tips of the carbon nanofibers (Figure 1 d). The latter consisted of a fish-bone alignment of graphene layers along the fiber axis (insert in Figure 1 c). Raman spectroscopy can not only give structural information about the incorporation of defects and disordering in the alignment of the graphene sheets, but its characteristic D (disorder-induced) and G (graphitic) bands also allow the determination of the graphitic crystallite size.^[10] For example, for a 3 wt% Ni/CNF catalyst, the integral intensity ratio I_D/I_G was 1.8, corresponding to an in-plane crystallite size L_a of 21.4 nm. This value agrees very well with high-resolution TEM observations (Supporting Information, Figure S1 f and S4). The dispersion of the Ni particles, which had sizes similar to the diameters of the carbon nanofibers, was determined by CO chemisorption to be no more than 0.2%. It should be noted that the Ni metal particles were partly enveloped by graphene layers.

With these well-characterized Ni/CNF catalysts in hand, batch experiments were selected for the one-pot catalytic conversion of microcrystalline cellulose (Sigma–Aldrich, Avicel PH-101; Figure 1 b). Impregnated Ni on γ -Al₂O₃ (Ni/Al₂O₃) and Ni on activated carbon (Ni/AC) were also evaluated for comparison, and the results are summarized in Table 1. Entry 1 shows that even in the absence of any catalyst, a high conversion into oligosaccharides was obtained, confirming the acid hydrolysis of cellulose by in situ-produced H⁺ ions.^[3] With the reference Ni/Al₂O₃ catalyst, cracking of cellulose resulted in only minor yields of ethylene glycol and sorbitol (entry 2). The catalytic performance of Ni/AC (entry 3) is comparable to that reported by Ji et al. with a low sorbitol selectivity of 3.8% at 69% conversion.^[4] Using the title Ni/CNF catalyst, the yield of hexitols could be significantly increased. After 24 h reaction with microcrystalline cellulose at 483 K, the sorbitol and mannitol yields were 30% and 5%, respectively, at 87% cellulose conversion (entry 7). In view of the literature on the bifunction-

al conversion of cellulose into sugar alcohols, it is surprising that the less-expensive Ni/CNF catalysts were as efficient as supported precious metal catalysts such as Pt/Al₂O₃^[2] and Ru/C.^[3]

To assess the effect of the external hydrogen pressure on the overall conversion process, reactions were carried out at initial pressures of 2, 4, and 6 MPa and a constant temperature of 503 K (entries 4, 5, and 6). The yield of sorbitol progressively increased as the H₂ pressure increased from 2 to 6 MPa. In addition, by fine-tuning the Ni loading on the carbon nanofibers during their growth process, the yield of sugar alcohols could be significantly improved (entries 5, 8, and 9).

With respect to the mechanism of this reaction, we propose the involvement of acid-catalyzed hydrolysis by in situ-produced H⁺ ions, followed by fast hydrogenation of glucose over supported Ni nanoclusters. While previous studies have focused on processing of cellulose with porous materials,^[2–4] the basic concept of our catalyst design relies on the entanglement of threadlike carbon nanofibers around the water-insoluble cellulose matrix. In this manner, an efficient accessibility of the Ni catalyst particles attached at the tip of the nanofibers allows for immediate hydrogenation of released glucose units. Although it has been suggested that the hydrolysis of cellulose proceeds through Brønsted acidity formed in water at high temperature, we cannot exclude the action of the intrinsic acid sites on the catalyst support material to obtain a consistent picture. In our study, γ -Al₂O₃ is needed as a support to disperse Ni for the growth of carbon nanofibers. Aside from its dispersion ability, the present results clearly point to a decisive influence of γ -Al₂O₃ on the hydrolysis properties of the bifunctional catalyst. To demonstrate this support effect, we have substituted γ -Al₂O₃ for MgAl₂O₄ in the CVD process of methane. While the structural properties of the catalyst appeared unaffected, carbon nanofibers grown on Ni/MgAl₂O₄ were clearly less selective for the production of sugar alcohols (entries 5 and 12).

Despite the well-documented role of Ni as a hydrogenolysis catalyst,^[8] sorbitol appears to be surprisingly stable towards C–C and C–O bond breaking in the presence of Ni/CNF. When relating the catalytic results in Table 1 to the above characterization information, we tentatively associate the high selectivity of the Ni/CNF catalyst to the structure-sensitive nature of the metal-catalyzed reactions. Progress in understanding the growth mechanism of carbon nanofibers has demonstrated the reaction-induced reshaping of Ni nanocrystals,^[11] unveiling a larger proportion of the thermodynamically more stable Ni(111) surfaces. This crystallographic reconstruction of the Ni nanoclus-

Table 1. Cellulose conversion on Ni catalysts.^[a]

Entry	Catalyst	p ^[b] [MPa]	Conversion [%]	Yield [%]					
				sorbitol	mannitol	erythritol	glycerol	1,2-propanediol	ethylene glycol
1	None ^[c]	4	48.1	0.0	0.0	0.0	0.0	0.0	0.0
2	3.0% Ni/Al ₂ O ₃	4	78.0	4.7	1.2	1.5	0.0	1.3	12.3
3	3.0% Ni/AC	4	80.6	9.5	2.6	4.6	0.0	6.9	8.7
4	3.0% Ni/CNF	2	88.9	12.3	3.4	4.2	0.6	8.0	7.7
5	3.0% Ni/CNF	4	79.2	18.3	4.1	5.8	0.8	8.0	6.8
6	3.0% Ni/CNF	6	93.9	22.7	4.9	7.8	1.8	7.1	6.5
7	3.0% Ni/CNF ^[d]	6	87.1	29.8	5.0	9.5	2.2	4.3	4.6
8	3.8% Ni/CNF	4	89.9	15.1	3.9	5.6	1.6	9.7	7.4
9	6.1% Ni/CNF	4	85.0	6.9	2.0	1.0	0.0	2.8	5.3
10	3.0% Ni/CNF ^[e]	6	92.2	50.3	6.2	12.8	1.0	1.2	2.5
11	3.0% Ni/CNF ^[f]	6	88.4	47.9	7.2	5.6	0.5	4.3	5.9
12	3.0% Ni/CNF ^[g]	4	80.1	8.5	2.0	3.6	3.2	1.2	1.5
13	3.0% Ni/CNF ^[h]	6	94.0	47.0	6.9	10.7	0.1	1.5	6.4

[a] Reaction conditions: cellulose 1 g, Ni catalyst 0.5 g, water 50 mL, 503 K, 4 h. [b] Initial H₂ pressure at room temperature. [c] HPLC analysis showed the presence of oligosaccharides. [d] 3.0% Ni/CNF catalyst at 483 K for 24 h. [e] Ball-milled cellulose feed at 463 K for 24 h. [f] Ball-milled cellulose 5 g, Ni catalyst 2.5 g, water 50 mL, 463 K, 24 h. [g] 3.0% Ni/CNF catalyst formed from Ni/MgAl₂O₄. [h] 3.0% Ni/CNF in the third run (same reaction conditions as in [e]).

ters was confirmed by powder X-ray diffraction analysis (Supporting Information, Figure S2). It seems that the faceted Ni pear-shape implies distinguished catalytic behavior compared to reference polycrystalline Ni catalysts;^[12] consider, for example, the orders-of-magnitude lower sorbitol yields reported on conventional Ni/Al₂O₃ and Ni/AC catalysts. It should be stressed that simple impregnation of carbon nanotubes with Ni, which consists of small Ni particles at the outer surface of the tubes instead of larger reshaped Ni particles attached at the tips, affords poor yields of less than 1% sorbitol (an observation recently recognized by Deng and co-workers).^[5] Although details of the direct correlation between surface structure and product distribution are still under intense study, we suggest that the bond-breaking selectivity is controlled by controlling the shape of the Ni particles during the carbon nanofiber growth process.

An intriguing way to improve the yield of sugar alcohols relies on mild pretreatment of cellulose using mechanical ball-milling, which is expected to increase the amorphous fraction (for SEM images, XRD patterns, CP/MAS ¹³C NMR, and IR spectra of the feedstock before and after pretreatment, see the Supporting Information).^[13] When ball-milled cellulose was exploited as substrate, an overall unprecedented yield of 70% sugar alcohols was achieved with Ni/CNF (entry 10). The rationale behind this improved result is found in the mechanical disruption of microcrystalline cellulose by breaking hydrogen bonds, which translates into a better accessibility of the β-glycosidic linkages, higher reaction rates, and hence to higher yields of polyols at lower temperatures (463 vs. 503 K). Moreover, similar catalytic results are observed when starting from a five times more concentrated cellulose feed (viz. 10 wt%, entry 11). With this knowledge, we anticipate that the Ni/CNF catalysts might also be well-suited in biorefineries for the bifunctional conversion of cello-oligomers, formed for example during the selective depolymerization of cellulose or wood, using acidic resins in ionic liquids.^[14]

A final issue concerns the stability of the Ni/CNF catalyst, which was studied by ICP–AES analysis of the reactor effluent. After 24 h reaction at 483 K, negligible Ni leaching of 3.8 ppm was measured. The reactions with ball-milled cellulose were repeated up to three times to evaluate the catalyst recyclability and deactivation behavior. After each run, the used Ni/CNF catalyst was separated by centrifugation of the reaction mixture and washed with distilled water. Similar conversions of cellulose were achieved in the third run, with a slight reduction in the sorbitol yield of 3.3% (entry 13), which might be due to the physical loss of some catalyst during the recycle steps.

In conclusion, we have demonstrated that carbon nanofibers grown on γ-Al₂O₃-supported Ni allow the high-yield production of sugar alcohols from cellulose. One general concern in the catalyst design for bifunctional cellulose conversion is the accessibility of the active metal sites in porous solids. In the current study this is not an issue because the Ni particles are attached at the tip of the carbon nanofibers. When compared to reported Ni-based catalysts, the unexpected hexitol yield of these Ni particles is assumed to be based on a synthesis-induced reshaping of their crystal structure, allowing the suppression of undesired C–C and C–O bond breaking.

Experimental Section

Nickel–carbon nanofiber catalysts were prepared by chemical vapor deposition (CVD) of methane over Ni/γ-Al₂O₃. Detailed synthesis procedures as well as various characterization methods are provided as Supporting Information. In a typical reaction, cellulose (Sigma–Aldrich; microcrystalline Avicel PH-101, 1 g), Ni/CNF (0.5 g), and water (50 mL) were loaded in a stainless steel autoclave (Parr Instruments Co., 100 mL). The reaction mixture was stirred at a rate of 700 rpm, pressurized with H₂ to 4 MPa at room temperature, and subsequently heated at 503 K for 4 h. After the reaction, the product mixture was centrifuged, filtered, and analyzed by HPLC [Agilent 1200 Series, RI detector, Varian Metacarb 67 C column (300×6.5 mm), mobile phase: water]. The product yield was calculated as follows: yield (%) = (weight of polyol)/(weight of cellulose charged in reactor). The conversion of cellulose was determined by total organic carbon (TOC) analysis of the liquid phase, as reported earlier.^[4b]

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