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

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A. CATALYST PREPARATION
For the growth of carbon nanofibers, 20 wt% Ni/\gamma-Al_2O_3 was prepared by impregnating \gamma-Al_2O_3 (Condea Chemie; Puralox, 155 m^2/g) with an aqueous solution of Ni(NO_3)_2.6H_2O (Alfa Aesar), subsequent drying at 353 K, calcination in static air at 873 K (heating rate 5 K/min) for 5 h, and then reduction under H_2 at 873 K for 1 h. Samples of 0.5 g catalyst precursor were placed in a quartz reactor and the carbon nanofibers were grown at 873 K under CH_4 flow (80 ml/min) for 3.5 h. The resulting catalyst is denoted as 3.0% Ni/CNF, where 3.0% represents the nominal weight value of Ni loaded on the carbon nanofibers. The reference catalysts, viz. Ni/\gamma-Al_2O_3 and Ni/AC, were prepared by impregnation of \gamma-Al_2O_3 (Condea Chemie; Puralox, 155 m^2/g) and activated carbon (Sigma-Aldrich; Darco) with an aqueous solution of Ni(NO_3)_2.6H_2O.

B. CHARACTERIZATION OF THE CARBON NANOFIBERS
The carbon nanofibers grown over Ni supported on \gamma-Al_2O_3 were examined with a high resolution scanning electron microscope (SEM; Philips XL-30 FEG), equipped with an Energy Dispersed Spectroscopy (EDS) detector system (Figure S1a-b). Transmission electron microscope (TEM) images were recorded on a Philips CM30-FEG electron microscope, coupled to a post-column GIF200 system for Electron Energy Loss Spectroscopy (EELS) Measurements (Figure S1d,f). Figure S1c represents a bar chart of the carbon nanofiber diameter distribution as measured from TEM micrographs. Figure S1e shows a reconstructed element-selective image of nickel and carbon.
Figure S1. SEM images (a-b), diameter distribution (c), TEM images and TEM/EELS analysis (d-f) of the 3.0% Ni/CNF catalyst.

Powder X-ray diffraction (PXRD) patterns of the Ni/CNF catalyst were recorded at room temperature with a STOE STADI P Combi diffractometer. The diffracted intensity of CuKα radiation (wavelength of 0.154 nm) was measured in a 2θ range between 0° and 60°. Figure S2 below displays the diffractogram of the as-prepared 3.0% Ni/CNF catalyst. The identified diffraction peaks are indicated with an arrow. Clearly, for Ni nanoclusters located at the end of the carbon nanofibers, the intensity of the more exposed Ni(111) surface exceeds the reflections of the other crystal planes.

Figure S2. Powder X-ray diffraction pattern of the 3.0% Ni/CNF catalyst.
Nitrogen physisorption data were recorded with a Micromeritics Tristar 3000 apparatus at 77 K. Prior to physisorption measurements, the catalyst samples were evacuated at 473 K for 12 h. The N\textsubscript{2} adsorption isotherm of 3.0% Ni/CNF in Figure S3 can be classified as a type IV isotherm with a type B hysteresis loop (S. J. Gregg, K. S. W. Sing, *Adsorption; Surface Area, and Porosity*, Academic Press, New York, 1982). The agglomerated carbon nanofibers show a mesoporous structure, their Brunauer-Emmet-Teller (BET) specific surface area is measured to be 76 m\textsuperscript{2}g\textsuperscript{-1} and their total pore volume 0.16 cm\textsuperscript{3}g\textsuperscript{-1}.

![N2 adsorption-desorption isotherm of 3.0% Ni/CNF.](image)

**Figure S3.** N\textsubscript{2} adsorption-desorption isotherm of 3.0% Ni/CNF.

Raman measurements were performed by putting the samples on top of a cleaned glass cover slip on an Olympus IX71 microscope. As excitation source a 633 nm wavelength laser was used. A narrow bandpass filter centered at 633 nm was used to spectrally clean the laser source. The laser light was reflected in the microscope on a 633 nm dichroic mirror towards a 100x 1.3 NA Olympus objective (immersion oil objective UplanFL N) that focused the laser on the sample and collected the Raman signal. A 655 nm longpass filter was used to block the 633 nm laser light in the detection path. The Raman spectrum was recorded by using a Chromex Inc. Model 250 IS polychromator (600 lines per mm blazed at 500 nm) and a liquid N\textsubscript{2} cooled CCD camera from Princeton Instruments Inc. (Model LN/CCD-512-TKB/1/VISAR). Raman spectra of the samples are shown in Figure S4. All the spectra have two typical peaks centered around 1330 cm\textsuperscript{-1} (D-mode) and 1590 cm\textsuperscript{-1} (G-mode). The integral intensity ratio $I_D/I_G$ for the 3.0% Ni/CNF is 1.8, which corresponds to an in-plane graphitic
crystallite size $L_a$ of 21.4 nm (see also figure S1f for the correlation of the crystallite size $L_a$ and the fiber diameter; M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio, R. Saito, Phys. Chem. Chem. Phys. 2007, 9, 1276–1291).

**Figure S4.** Raman characterization of the carbon nanofiber supported nickel catalysts: 3.0% Ni/CNF (a), 6.1% Ni/CNF (b) and 3.8% Ni/CNF (c).

Ni dispersions were determined using CO chemisorption. The Ni/CNF sample was loaded into a tubular reactor and pretreated in a stream of 20 mL/min of H$_2$ (Air Liquide, 99.9997%) at 573 K (heating rate 5 K/min) for 1 h, and subsequently cooled to RT under a He (Air Liquide, 99.9997%) flow of 20 mL/min. For the titration of the Ni surface, the He flow was reduced to 10 mL/min and pulses of 5 μL of 100% CO were given with an interval of 2 min. The CO concentration in the outlet stream was followed with a Pfeiffer Omnistar quadrupole mass spectrometer. In the calculation of the dispersion, adsorption of 1 CO molecule per accessible Ni atom was assumed. The CO chemisorption analysis of 3.0% Ni/CNF yields a Ni dispersion of 0.17% (Figure S5).

**Figure S5.** CO chemisorption analysis of the 3.0% Ni/CNF catalyst.
C. PRETREATMENT AND CHARACTERIZATION OF CELLULOSE

Cellulose (Avicel PH-101, microcrystalline) was characterized (1) as received from Sigma-Aldrich and (2) after ball-milling pretreatment. Ball-milling with 25 g of cellulose was carried out using ZrO₂ balls (mass of 7.5 g and diameter of 1.8 cm). SEM images of samples before and after 24 h ball-milling are given in Figure S6.

![Figure S6. SEM characterization of cellulose before (a-b) and after ball-milling (c).](image)

Figure S6. SEM characterization of cellulose before (a-b) and after ball-milling (c).

Figure S7 shows XRD patterns taken of cellulose samples unmilled and ball-milled for 24 h. In the untreated cellulose, the major peak at \(2\theta = 22.5^\circ\) can be assigned to the crystalline plane 002. A comparison of the patterns clearly reveals a significant decrease in crystallinity of the cellulose feedstock after ball-milling pretreatment.

![Figure S7. Powder X-ray diffraction patterns of microcrystalline Avicel cellulose (a) and cellulose after the ball-milling pretreatment (b).](image)

Figure S7. Powder X-ray diffraction patterns of microcrystalline Avicel cellulose (a) and cellulose after the ball-milling pretreatment (b).

The \(^{13}\text{C}\) CP MAS NMR spectra of cellulose with and without ball-milling were recorded on a Bruker Avance DSX400 spectrometer (9.4 T). 4400 scans were accumulated with a recycle delay of 10 s. The contact time was 4 ms. The samples were packed in 4 mm rotors, and the spinning frequency of the rotor was 5000 Hz.
Tetramethylsilane was used as shift reference. The decreasing peak ratios of $C_4(86-92 \text{ ppm})/C_4(79-86 \text{ ppm})$ and $C_6(63-67 \text{ ppm})/C_6(56-63 \text{ ppm})$ in Figure S8 are in good agreement with the reported literature observations (H. Zhao, J. H. Kwak, Y. Wang, J. A. Franz, J. M. White, J. E. Holladay, *Energy Fuels*, 2006, 20, 807–811). This, in interplay with the above XRD data, strongly suggests that more disordered cellulose is produced after the mechanical ball-milling treatment. Furthermore, line widths are larger in the amorphous sample which is due to the large distribution of molecular orientations.

**Figure S8.** $^{13}$C NMR spectra of cellulose before (a) and after ball-milling (b).

IR spectra were recorded under vacuum from KBr pellets on a Bruker IFS 66v/S instrument. The spectra in Figure S9 also show the changes in the cellulose structure after ball-milling. The less pronounced band at 1430 cm$^{-1}$ is another strong indication of a less ordered cellulose sample, since it is assigned to the CH$_2$ scissoring motion in the cellulose I crystal. The ball-milling allows the regular arrangement of the CH$_2$OH group on C$_6$ to relax into a more random one, resulting in a broader band at 1430 cm$^{-1}$.

**Figure S9.** IR spectra of cellulose before (a) and after ball-milling (b).
D. CATALYTIC CONVERSION OF CELLULOSE

In a typical reaction, cellulose (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 heated at 503 K for 24 h. After reaction, the product mixture was centrifuged, filtered over a 0.45 µm PTFE filter and the filtrate was analyzed by HPLC (Agilent 1200 Series, Varian Metacarb 67C column (300 x 6.5 mm), mobile phase: water), equipped with an RI detector (Figure S10). Time profiles of cellulose conversion and yields to sorbitol, mannitol and erythritol are given in Figure S11. Table S1 lists the main data on the catalytic conversion of cellulose using literature Ni-based catalysts.

![Figure S10](image1)

**Figure S10.** HPLC spectra of cellulose conversion over 3.0% Ni/CNF. (1) cello-oligomers, (2) erythritol, (3) ethylene glycol + 1,2-propanediol, (4) glycerol + mannitol, (5) sorbitol. The ratio of polyols in (3) and (4) was determined after derivatisation on a HP 5890 GC equipped with a 50 m CP-Sil-5CB column and FID-detector.

![Figure S11](image2)

**Figure S11.** Time profile of the Ni/CNF catalyzed conversion of cellulose (X) and yield to polyols (Y). Conditions: microcrystalline Avicel cellulose 1 g, 3.0% Ni/CNF 0.5 g, water 50 ml, initial H₂ pressure 6 MPa, 483 K, 24 h. (●: conversion, ▲: yield sorbitol, ×: yield erythritol, ■: yield mannitol)
Table S1. Recent developments on the catalytic conversion of cellulose into polyols over Ni-based catalysts in various conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Reaction conditions$^{[a]}$</th>
<th>Cellulose (wt%)</th>
<th>Conversion (%)</th>
<th>Yield (%)$^{[b]}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S</td>
<td>M</td>
</tr>
<tr>
<td>1.</td>
<td>60% Ni/SiO$_2$-Al$_2$O$_3$</td>
<td>463 K, 5 MPa H$_2$</td>
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<td>n.r.$^{[c]}$</td>
<td>2</td>
<td>n.r.$^{[c]}$</td>
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<tr>
<td>2.</td>
<td>2% Ni-30% W$_2$C/AC</td>
<td>518 K, 6 MPa H$_2$</td>
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<td>100</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>3.</td>
<td>3% Ni/AC</td>
<td>518 K, 6 MPa H$_2$</td>
<td>1</td>
<td>69</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4.</td>
<td>1% Ni/CNT$^{[e]}$</td>
<td>458 K, 5 MPa H$_2$</td>
<td>0.8</td>
<td>n.r.$^{[c]}$</td>
<td>&lt;1</td>
<td>n.r.$^{[c]}$</td>
</tr>
<tr>
<td>5.</td>
<td>5% Ni-25% W/SBA-15</td>
<td>518 K, 6 MPa H$_2$</td>
<td>1</td>
<td>100</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

[a] Initial H$_2$ pressure measured at room temperature. [b] S = sorbitol; M = mannitol; Ery = erythritol; EG = ethylene glycol. [c] n.r. not reported. [d] Combined sugar alcohol yield. [e] Cellulose pretreated in 85% H$_3$PO$_4$ at 50 °C for 40 min (33% crystallinity).