Carbon Nanofiber Supported Nickel Catalysts for the reductive splitting of Cellulose

W. Schutyser, S. Van de Vyver, J. Geboers, M. Dusselier, P.A. Jacobs and B.F. Sels
(1) Centre for Surf. Chem.&Catal., KULeuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium
* E-mail: bert.sels@biw.kuleuven.be; wouter.schutyser@biw.kuleuven.be

The hydrolytic hydrogenation of cellulose to sugar alcohols by bifunctional catalysts is a very promising route for cellulose valorization.[1] This presentation shows that carbon nanofibers (CNFs) possess interesting features that make them suitable candidates for application as catalyst supports in these biomass-related reactions.[2] The hydrolytic hydrogenation of cellulose over reshaped Ni particles, attached at the tip of CNFs, is therefore illustrated.[3] In fact, despite the large Ni particle size, the catalyst shows a very high activity, and is able to produce fairly high hexitol yields from cellulose in a one pot slurry reactor. Influence of reaction conditions (T, P, ...) will be highlighted, but also the impact of the cellulose reactivity (in terms of its structural information from FT-IR, solid state ^{13}C MAS NMR and XRD) will be demonstrated.
The catalyst actually possesses two catalytic functions, namely acid groups to catalyze the hydrolysis of cellulose to glucose and metal sites to hydrogenate glucose to hexitols. Tuning of the bifunctional property of the catalyst is a prerequisite for high hexitol selectively [4]. Various strategies to introduce acidity in fishbone-type CNFs were therefore attempted, and different Ni loadings were introduced on the oxidized fibers. A detailed study will be shown that explains the influences of the nature of oxidation agent (HNO_3 vs. 1:1 mixtures of HNO_3/H_2SO_4), Ni activation (different reduction temperatures) and Ni loadings. Through variation of these synthesis parameters, the number of active Ni sites, the dispersion of the Ni particles and the number of oxygen-containing surface groups could be tuned, and the most selective catalyst was thus attained having a ratio of the acid density to the number of Ni surface atoms somewhere between 0.7 and 1.1. A lower ratio indicates an insufficient hydrolysis capacity to convert cellulose or an excessive amount of Ni surface atoms, rendering the sugar alcohols more susceptible to C-C bond hydrogenolysis and lowering the selectivity. For increasingly higher values of this ratio, glucose is likely subjected to another acid-catalyzed degradation reaction, rather than being hydrogenated to hexitols. The optimized Ni/CNF catalyst ultimately reached a 76% yield of hexitols at 93% conversion of cellulose.

References

[1] S. Van de Vyver, S. *et al*. *ChemCatChem*, **3,** 82 (2011); J. A. Geboers *et a*l., *Catal. Sci. Technol*. **1**, 714 (2011); J. A. Geboers *et al*. *Chem. Commun.*, **47**, 5590 (2011); J.A. Geboers *et al*. *Green Chem*., **13**, 2167, (2011).
[2] J. K. Chinthaginjala *et al*., *Ind. Eng. Chem. Res.* **46**, 3968 (2007); J. H. Bitter *et al*., *J. Mater. Chem.* **20**, 7312 (2010)
[3] S. Van de Vyver *et al*., *ChemSusChem* **3**, 698 (2011)
[4] S. Van de Vyver *et al.*, *ChemSusChem* (2012), DOI: 10.1002/cssc.201100782