PRODUCTION OF VALUABLE LIQUID PRODUCTS FROM CELLULOSE OVER RUTHENIUM-TUNGSTEN CATALYSTS ON ACTIVATED CARBON

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Cellulose is the most abundant and non edible biopolymer of the world. Therefore, the utilization of this macromolecule and its integration in a bio-refinery concept is essential. Herein we report about effective conversion of cellulose via one-pot hydrogenolysis in a batch reactor.

The hydrogenolysis of cellulose under hydrothermal conditions and use of solid catalysts yields ethylene glycol (EG) and other valuable polyols such as propylene glycol (PG), butanediol (BDO), and sorbitol. Besides our high active nickel-tungsten catalysts[1], another self-prepared catalyst containing ruthenium (Ru/W on activated carbon(AC)) can also decompose cellulose with full conversion and the polyol yield was more than 79% within 3 hours reaction time. The main products were ethylene glycol and sorbitol with the yield of 48.2% and 15.4%, respectively. The Ru/W/AC catalyst was tested for its re-usability in a recycling test which showed a very good stability in six runs. In the last (seventh) recycling run, the yield of polyols decreased to 50.8%. Also the polyol distribution differed strongly. The yield of ethylene glycol was drastically smaller (6.4%) meanwhile the yield of sorbitol increased to 28.4%. The ICP analysis confirmed leaching of tungsten in each recycling run. Interestingly, leaching of this active component responsible for the cracking of 1,4-β-glycosidic bond in the cellulose macromolecule and other C-C bonds may be the key homogenously catalyzed step in the degradation of cellulose. Similar to our observation, it was reported, that the interplay of tungstenic acid and soluble hydrogen tungsten bronze (H_xWO_3) is important in cellulose hydrogenolysis[2]. Additionally, we investigated the influence of reaction conditions (temperature, H_2 pressure, cellulose/catalyst ratio) in order to optimize the cellulose hydrogenolysis and the polyol yield.

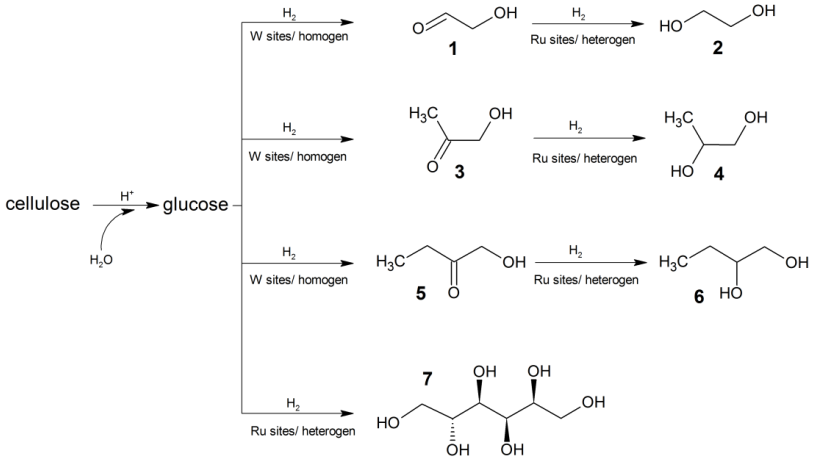

Figure 1. Reaction scheme of the hydrogenolysis of cellulose over Ru/W/AC with the main products: glycolaldehyde **1**, ethylene glycol **2**, 1-hydroxy-2-propanone **3**, propylene glycol **4**, 1-hydroxy-2-butanone **5**, 1,2-butanediol **6**, sorbitol **7**.

References

[1] K. Fabicovicova, O. Malter, M. Lucas, P. Claus, *Green Chemistry* **2014**, *16*, 3580-3588.

[2] Z. Tai, J. Zhang, A. Wang, M. Zheng, T. Zhang, *Chemical Communications* **2012**, *48*, 7052-7054.