

Effect of Pd-promoted tungsten carbide catalysts in the hydrogenolysis of cellulose.

Glauco Ferro Leal^{1,2} (PG)*, Antônio Aprigio da Silva Curvelo^{1,3} (PQ), Cristiane Barbieri Rodella² (PQ)

¹ Institute of Chemistry of São Carlos (IQSC) – University of São Paulo (USP), São Carlos-SP, Brazil. ² Brazilian Synchrotron Light Laboratory (LNLS) – Brazilian Center for Research in Energy and Materials (CNPEM), Campinas-SP, Brazil. ³ Brazilian Bioethanol Science and Technology (CTBE) – CNPEM, Campinas-SP, Brazil. *glaucoleal@iqsc.usp.br

Key-words: Heterogeneous Catalysis, Tungsten Carbide, Cellulose, Hydrogenolysis.

Introduction

Cellulose, composed by units of β -D-glucopyranose, is the major component of lignocellulosic biomass and is an alternative to oil as raw material for sustainable production of biofuels and chemicals of industrial interest.¹ The heterogeneous catalysis is a promising route to promote the transformation of cellulose into higher value-added products due to easiness in the separation of product/catalyst and control of reaction parameters. The catalytic conversion of cellulose begins with the hydrolysis of polysaccharides into glucose monomers and subsequently the monosaccharide can be transformed through different chemical reactions. The use of catalysts based on transition metals carbides is a promising alternative to catalytic hydrogenation and hydrogenolysis of cellulose.² The catalytic properties of metal carbides are directly related to structural parameters, surface, crystalline phase and type of promoter. Thus, this work consists in the synthesis and characterization of catalysts of tungsten carbide supported on activated carbon and promoted with palladium for the catalytic conversion of cellulose under H₂ pressure.

Results and Discussion

The catalysts were prepared by incipient wetness impregnation of the metallic precursors on activated carbon presenting the weight proportion of 30% of W impregnated in activated carbon and 1% of Pd dispersed in the W/C. Non-promoted samples and Pd supported on carbon were also prepared for comparison. After drying overnight at 120°C, the samples were carburized with the gas mixture of the CH₄/H₂ (10:90 v/v) from room temperature up to 850°C, 10°C min⁻¹, 40 min of isothermal treatment at the final temperature and passivation with 2%O₂/He at room temperature overnight. The X-ray diffraction analysis showed that the catalyst W_xC/C is composed by a mixed carbide phases (WC, WC_{1-x} and W₂C), whereas the catalyst 1%PdW_xC/C is predominantly composed by W₂C and Pd⁰. The BET analysis showed the surface area and total pore volume decreases in the Pd-promoted sample

(502 m² g⁻¹ and 0,49 cm³ g⁻¹) compared to W_xC/C (709 m² g⁻¹ and 0,67 cm³ g⁻¹). Figure 1 shows that the cellulose conversion was similar for the Pd-promoted and non-promoted catalysts. However the product distribution was affected by the presence of Pd in the catalyst. Using W_xC/C (Fig. 1-A), the major product obtained was acetol, while using 1%PdW_xC/C the major product was ethylene glycol (Fig. 1-B). It is worth saying that Pd/C catalyst exhibited lower conversion and the major product was acetol in the same reaction condition of carbides catalysts.

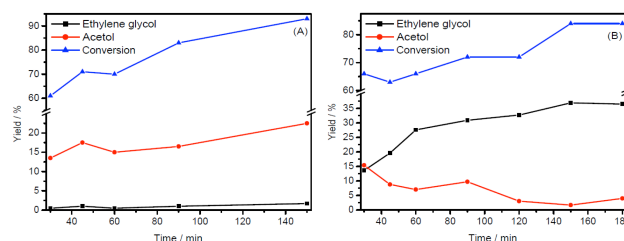


Figure 1. Distribution of products and conversion of substrate using the catalyst A) W_xC/C and B) 1%PdW_xC/C.

The catalyst 1%PdW_xC/C favors the route of ethylene glycol formation. Through hydrolysis of cellulose, retro-aldol step reactions and hydrogenation, the glucose monomer is converted into ethylene glycol.³

Conclusions

The presence of Pd is essential for stabilizing the W₂C phase during the carburizing process. Moreover, the interaction Pd/W seems to be important for the catalytic activity producing ethylene glycol from cellulose.

Acknowledgements

CNPq for the scholarship granted, and to FAPESP and CAPES for financial support. Also LNLS and CTBE for the physical and chemical analysis.

¹ Cherubini, F.; Stromman, A. H. *Biofuels, Bioprod. Bioref.* **2011**, *5*, 548.

² Ji, N.; Zhang, T.; Zheng, M.; Wang, A.; Wang, H.; Wang, X.; Chen, J. *G. Angew. Chem. Int. Ed.* **2008**, *47*, 8510.

³ Ooms, R.; Dusselier, M.; Geboers, J. A.; Beeck, B. O.; Verhaeven, R.; Gobechiya, E.; Martens, J. A.; Redl, A.; Sels, B. F. *Green Chem.* **2014**, *16*, 695.