HDO over ZrO_2-supported metal catalysts using γ-valerolactone as model feed

Susanna Wallenius,[a] **Marina Lindblad,**[a,*] **Kaisa Lamminpää,**[a] **Mats Käldström**[a]

[a]*Neste Corporation, Research and Development, Porvoo, 06101, Finland*
**Corresponding author: marina.lindblad@neste.com*

Abstract: Oxygen removal reactions have a crucial role in the production of hydrocarbon-based renewable fuel components from lignocellulose-derived precursors. In this study Pt, Rh, Ru and Ni supported on ZrO_2, as well as Pt supported on WO_x- and LaO_x-modified ZrO_2 were evaluated as hydrodeoxygenation (HDO) catalysts using γ-valerolactone (GVL) as model feed and a commercial sulfided $NiMo/Al_2O_3$ hydrotreatment catalyst as reference. The bifunctional Pt/WO_x-ZrO_2 catalyst showed high selectivity for hydrocarbon formation. This was attributed to a suitable balance between its metal and acid properties promoting both hydrogenation and ring-opening reactions.

Keywords: Lignocellulose derivatives, Catalysts, Hydrodeoxygenation, Hydrocarbons.

1. Introduction

The utilization of lignocellulose-derived platform molecules for the production of renewable chemicals and traffic fuels has attracted much interest in recent years. A typical chain length of platform molecules originating from lignocellulose-derived sugars varies in the range of 2-6 carbon atoms. For the production of liquid traffic fuels via platform molecules, carbon chain length increase[1] and oxygen removal reactions are required to have hydrocarbons suitable as drop-in gasoline, diesel or aviation fuel components. This study focuses on the evaluation of hydrodeoxygenation (HDO) catalysts for oxygen removal from lignocellulose fuel precursors using γ-valerolactone (GVL) as a model feed. The lactone structure represents a reactive group commonly observed in lignocellulose derivatives.

2. Experimental

The model compound, γ-valerolactone (Sigma-Aldrich ≥99 %), was used as received without any dilution. The supported metal catalysts tested were prepared by incipient wetness impregnation of the metal precursor ($Rh(NO_3)_3$, $RuCl_3 \cdot nH_2O$, $Pt(NH_3)_4(NO_3)_2$, $Ni(NO_3)_2$) on commercial ZrO_2, WO_x-ZrO_2 or LaO_x-ZrO_2 materials. The target metal content for the noble metals was 1 wt% and for nickel 14 wt%. A commercial sulfided hydrotreatment catalyst ($NiMoS/Al_2O_3$) was used as a reference. The metal catalysts were reduced in situ at 400 °C for 5 hours prior to the HDO reaction. The reactions were conducted in a 16-fold trickle bed unit as part of a catalyst screening experiment at the high throughput experimentation company hte GmbH. The experiments were carried out in hydrogen atmosphere at 200-275 °C, 80 bar and a weight-hourly-space-velocity (WHSV) of 0.5 h^{-1}.

3. Results and discussion

GVL and hydrogen conversions at various reaction temperatures (200-275 °C) for the HDO catalysts tested are shown in Figure 1. Full GVL conversion was achieved only at 250 °C for Pt/WO_x-ZrO_2 and $NiMoS/Al_2O_3$. Rh/ZrO_2 and Ru/ZrO_2 achieved full GVL conversion at 275 °C while simultaneously giving rise to the highest hydrogen consumption observed.

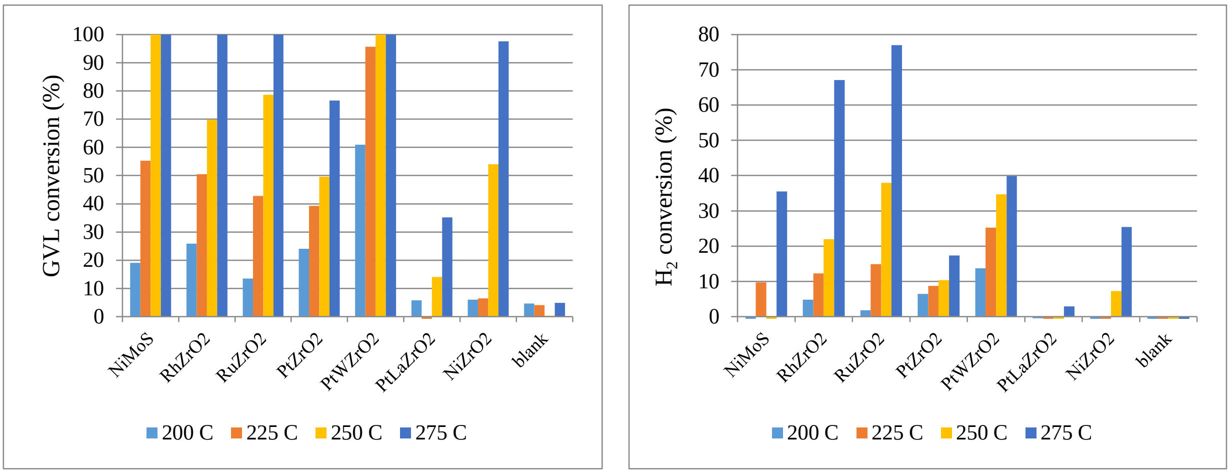

Figure 1. GVL conversion and hydrogen consumption (by GC) in HDO reactions as a function of reaction temperature.

The two main reaction routes for GVL conversion under HDO conditions, i.e. the pentanediol (PDO) and pentanoic acid (PA) routes[2], are depicted in Figure 2. As an example of the type of reaction products formed with the catalysts, the product distributions (by GC-MS) obtained in the HDO reaction at 275 °C are also shown in Figure 2. Esters and ethers were formed in acid catalyzed side reactions.

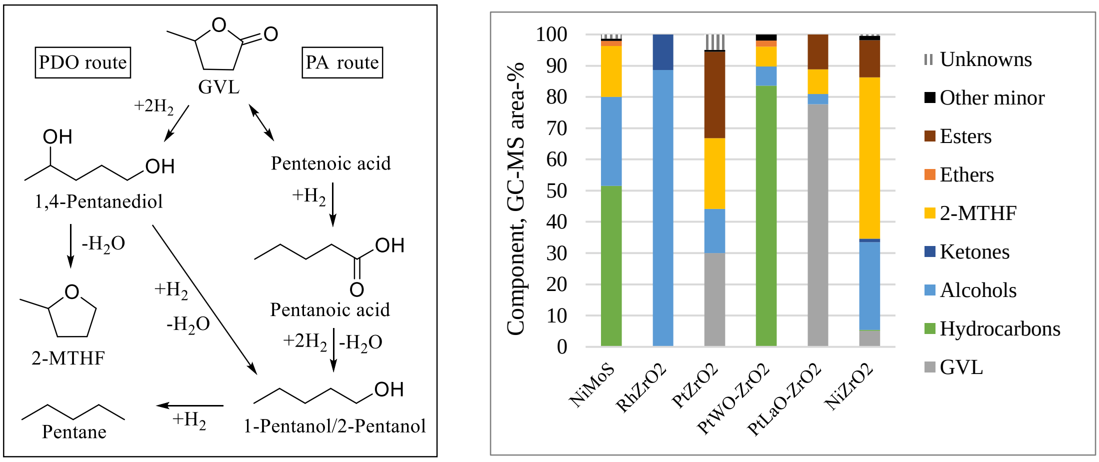

Figure 2. GVL reaction routes in HDO conditions and product distributions obtained at 275 °C.

Based on the product distributions obtained at various temperatures it was proposed that NiMoS/Al_2O_3 is active in the PDO route. Zirconia based catalysts, forming 2-MTHF and esters, were active in both PDO and PA routes. However, Pt/WO_x-ZrO_2 was mainly active in the PDO route since minor contribution from acids and esters were observed. Only Pt/WO_x-ZrO_2 and NiMoS/Al_2O_3 showed high selectivity for hydrocarbon formation. At 275 °C the main products with Ru/ZrO_2 and Rh/ZrO_2 were water and methane - the minor organic phase formed over Rh/ZrO_2 was mainly composed of alcohols.

4. Conclusions

The catalyst with the highest HDO activity and selectivity for hydrocarbons was Pt/WO_x-ZrO_2, but also NiMoS/Al_2O_3 was surprisingly active already at 250 °C. Ru/ZrO_2 and Rh/ZrO_2 - producing mainly methane - showed the highest hydrogen consumptions at 275 °C.

References

1. M. Käldström, M. Lindblad, K. Lamminpää, S. Wallenius, S. Toppinen, Ind. Eng. Chem. Res. 56 (2017) 13356-13366.
2. J.-P. Lange, R. Price, P.M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, Angew. Chem. Int. Ed. 49 (2010) 4479-4483.