Screening of Catalysts for Bio-oil Hydrodeoxygenation

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Introduction

A prospective route for production of bio-fuels is the conversion of biomass into bio-oil through pyrolysis followed by upgrading via hydrodeoxygenation (HDO) [1]. Through the pyrolysis, the bulk biomass is converted into a more energy-dense oil, called bio-oil. This is a viscous, polar, and acidic oil with a low heating value and high chemical instability, making it unsuitable as a fuel. These unfavourable characteristics are all associated with high contents of water (10-30 wt%) and oxygen containing organic compounds (30-40 wt% oxygen) in the oil [2]. In HDO the bio-oil is treated with hydrogen at a pressure of up to 200 bar and temperatures in the range 200-400 °C. This converts the oxygenates to a hydrocarbon product which will separate from the water and ultimately give a product equivalent to crude oil [1].

One of the major challenges in this concept is to find a catalyst for HDO which has a high activity for the deoxygenation reaction, but at the same time a sufficient lifetime [1]. A catalyst for HDO has to be bifunctional as both an activation of the oxy-compound and a donation of hydrogen is necessary for the reaction to take place [3]. Depending on the type of catalyst, these two steps can occur differently.

In the current work, three different types of catalysts for HDO have been tested: oxide catalysts, methanol synthesis catalysts, and reduced metal catalysts.

Experimental

All catalysts were prepared by the incipient wetness technique. Hereafter they were dried at 100 °C over night and calcined at 400°C for 4 h. Catalyst testing was performed in a 300ml batch reactor (Parr 4566). Analysis of the product was made on a Shimadzu GCMS/FID-QP2010UltraEi fitted with a Supelco Equity-5 column.

Results & Discussion

Figure 1 summarizes the results from the tested catalysts. A very low activity was found for the oxide and methanol synthesis type catalysts and neither of these achieved a conversion above 10%.

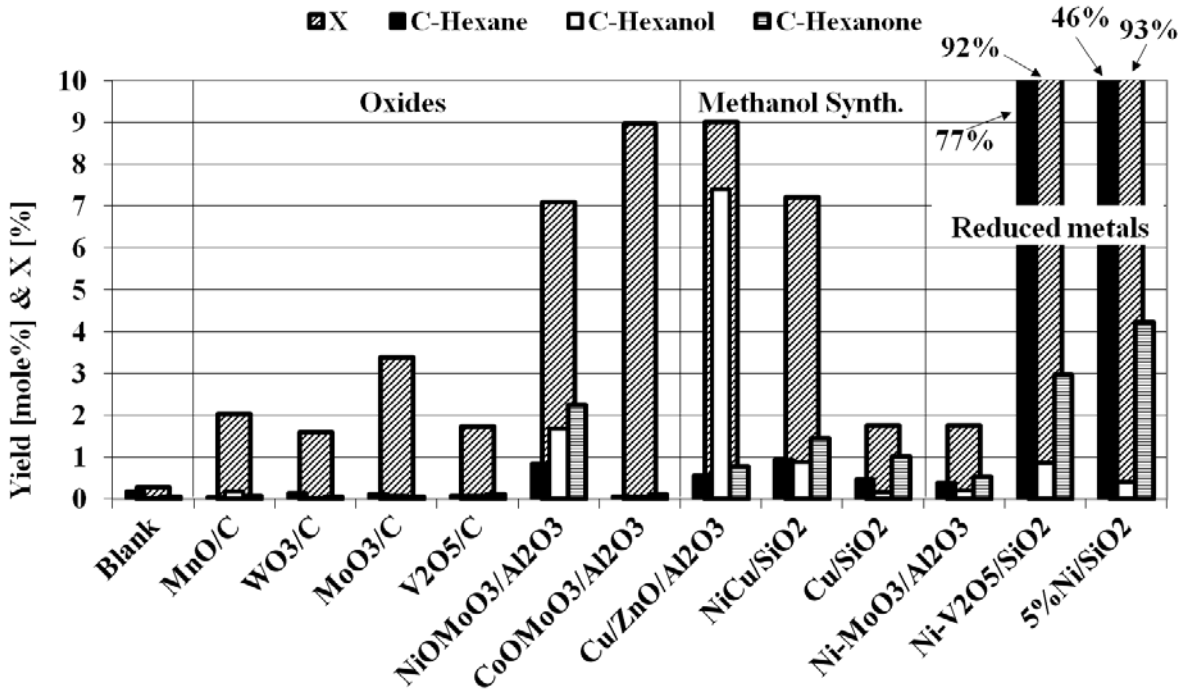

Figure 1 Yield and conversion over different types of catalysts. The experiments were conducted with 0.5 g of catalyst in 90 ml water and 10 g phenol. T=275 °C, P=100 bar, t=4 h.

Reduced metals are in Figure 1 represented by Ni, but were also tested in the combination with oxides. It was found that Ni based catalysts appeared to have a high activity relative to the other systems tested. Furthermore it was found that a system of Ni in combination with V_2O_5 had an even higher activity for HDO compared to Ni alone, as a much higher yield of cyclohexane was observed.

Conclusions

These results show that none of the here tested oxide type nor methanol synthesis type catalysts have a significant activity for HDO. Instead, Ni based catalysts appear very attractive and especially in the combination with an oxide, as V_2O_5.

References

[1] P.M. Mortensen, J.-D. Grunwaldt, P.A. Jensen, A.D. Jensen, A Review of catalytic upgrading of bio-oil to engine fuels, Appl. Catal. A, 407, 2011.

[2] Q. Zhang, J. Chang, T. Wang, Y. Xu, Review of biomass pyrolysis oil properties and upgrading research, Energy Convers. Manage., 48, 2007.

[3] V.A. Yakovlev, et al., Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel, Catal. Today, 144, 2009.