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# Influence of Promotor, H<sub>2</sub>O and H<sub>2</sub>S on the Hydrodeoxygenation of Biomass Pyrolysis Vapor over MoS<sub>2</sub> Catalysts

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## Introduction

Catalytic hydroxypropylation combines fast pyrolysis with catalytic upgrading by hydrodeoxygenation (HDO) in a single step for the production of fuel oil from biomass in which reactive pyrolysis vapors are upgraded before condensation. Catalyst activity and lifetime is challenged by carbon deposition and by the presence of alkali, nitrogen, sulfur and water. In this contribution, a combined experimental, characterization (in-situ Quick-EXAFS) and theoretical (DFT) study of catalytic HDO of biomass pyrolysis model compounds over MoS<sub>2</sub> based catalysts is presented with emphasis on the influence of water and H<sub>2</sub>S.

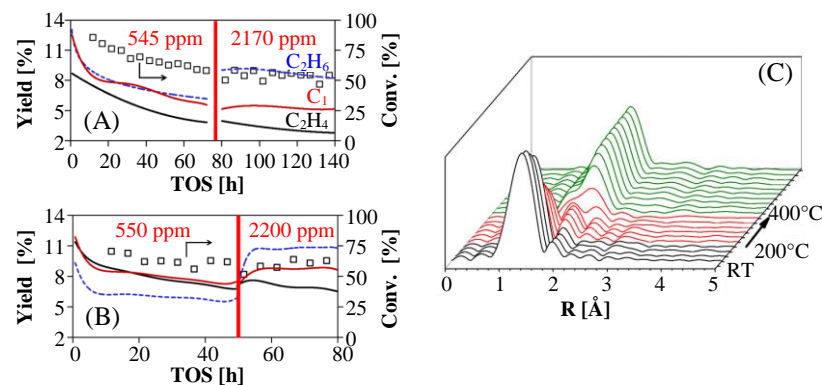
## Materials and Methods

MoS<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> and Co(Ni)-MoS<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts with 3.3 wt% Mo and Co(Ni):Mo molar ratio = 0.3 have been prepared by incipient wetness impregnation and sulfidation with 10-12% H<sub>2</sub>S/H<sub>2</sub> at 360-400°C. Ethylene glycol (EG) is a simple model polyol representing the cellulosic fraction of biomass. Catalytic HDO tests were conducted in a fixed bed reactor at 350-450°C, 28 bar H<sub>2</sub> and 545-2200 ppm H<sub>2</sub>S (m<sub>cat</sub> = 0.5-4 g, feed<sub>EG</sub> = 0.14 mL/min, EG WHSV = 2.3-19 h<sup>-1</sup>, 40 barg, balance N<sub>2</sub>). Products were separated into gas (online analysis by GC/TCD) and liquid (offline analysis by GC-MS/FID). DFT calculations were used to predict the influence of varying H<sub>2</sub>O/H<sub>2</sub>S ratios on the stability of the sulfide/oxide phases and reaction pathways. The Quantum Espresso code was applied in combination with the BEEF-vdW exchange correlation functional. In-situ Quick-EXAFS was conducted at the SLS SuperXAS beamline [1] at the Co-, Ni- and Mo-K-edge of prepared catalysts during sulfidation and subsequent exposure to varying H<sub>2</sub>O/H<sub>2</sub>S ratios at 400-450°C. Catalysts and support material have also been analyzed using other techniques such as ICP-OES, NH<sub>3</sub>-TPD, XRD, BET and Raman spectroscopy.

## Results and Discussion

Co(Ni)-MoS<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts were active and moderately selective for EG HDO. 100% conversion was obtained for 50 h on stream at 400°C with 545 ppm H<sub>2</sub>S and EG WHSV = 2.3 h<sup>-1</sup>. At these conditions, a moderate HDO product yield (ethane and ethylene) of 40-45% was observed together with an undesired cracking (C<sub>1</sub>: CO, CO<sub>2</sub>, CH<sub>4</sub>) yield of 30-35%. Catalyst deactivation is believed to be caused by carbon deposition (3.5-9.5 wt% on spent catalysts) and exchange of S by O at the active MoS<sub>2</sub> edges. S-O exchanges may be mitigated with a higher H<sub>2</sub>S concentration. In fact, a higher H<sub>2</sub>S concentration reactivated and stabilized the catalyst and improved the HDO/cracking selectivity in experiments with EG WHSV = 19 h<sup>-1</sup>, see Figure 1 (A+B). DFT has however indicated that a too high concentration of H<sub>2</sub>S

inhibits S-vacancy formation at the MoS<sub>2</sub> S-edge thereby potentially limiting HDO. In-situ Quick-EXAFS has thus been applied to study the effect of varying H<sub>2</sub>O/H<sub>2</sub>S ratios on catalyst composition. The magnitude of the Fourier Transformed in-situ EXAFS spectra (Figure 1C) shows the transition from oxide (MoO<sub>x</sub>) to sulfide (MoS<sub>2</sub>) during catalyst sulfidation. The EXAFS fit for the resulting sulfide phase shows contributions from Mo-S (2.40Å) CN = 4.2±0.3 and Mo-Mo (3.15Å) CN = 0.37±0.07. The presence of a small Mo-O contribution (Mo-O (1.61Å) CN = 0.24±0.07) indicates incomplete sulfidation which is possibly caused by interaction of highly dispersed MoS<sub>2</sub> crystallites with the support.



**Figure 1** TOS profiles for EG conversion and gas product yields for Ni-MoS<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> (A) and Co-MoS<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> (B) at 400°C, EG WHSV = 19 h<sup>-1</sup>, 28 bar H<sub>2</sub>, 545-2200 ppm H<sub>2</sub>S (noted with red text) and total pressure 40 barg. Magnitude of the Fourier Transformed in-situ EXAFS spectra (Mo-K-edge) for in-situ sulfidation (C) of MoS<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> going from oxide (MoO<sub>x</sub>, black), through transition phases (red) to a sulfide (MoS<sub>2</sub>, green).

DFT calculations have shown that promotion with Ni compared to Co results in more adsorbed H atoms at the S-edge of MoS<sub>2</sub>. This higher hydrogen availability could explain the higher yield of ethane compared to ethylene observed for Ni-MoS<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> (Figure 1A). DFT calculations for EG HDO reaction pathways are being conducted.

## Significance

To our knowledge, this is the first catalytic HDO study which combines the experimental and theoretical investigation with advanced in-situ XAS characterization to unravel the influence of promotion and H<sub>2</sub>O/H<sub>2</sub>S on catalytic HDO over MoS<sub>2</sub> catalysts. Understanding the mechanisms behind this influence is a key step in optimizing the catalytic hydroxypropylation process.

## References

1. Müller, O., Nachttegaal, M., Just, J., Lützenkirchen-Hecht, D., Frahm, R., J. *Synchrotron Rad.* 23, 260 (2016).