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Influence of Promotor, H₂O and H₂S on the Hydrodeoxygenation of Biomass Pyrolysis Vapor over MoS₂ Catalysts

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Introduction

Catalytic hydropyrolysis 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 MoS₂ based catalysts is presented with emphasis on the influence of water and H₂S.

Materials and Methods

MoS₂/MgAl₂O₄ and Co(Ni)-MoS₂/MgAl₂O₄ 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% H₂S/H₂ 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 H₂ and 545-2200 ppm H₂S ($m_{\text{cat}} = 0.5\text{-}4$ g, $\text{feed}_{\text{EG}} = 0.14$ mL/min, EG WHSV = 2.3-19 h⁻¹, 40 barg, balance N₂). 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 H₂O/H₂S 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 H₂O/H₂S ratios at 400-450°C. Catalysts and support material have also been analyzed using other techniques such as ICP-OES, NH₃-TPD, XRD, BET and Raman spectroscopy.

Results and Discussion

Co(Ni)-MoS₂/MgAl₂O₄ catalysts were active and moderately selective for EG HDO. 100% conversion was obtained for 50 h on stream at 400°C with 545 ppm H₂S and EG WHSV = 2.3 h⁻¹. At these conditions, a moderate HDO product yield (ethane and ethylene) of 40-45% was observed together with an undesired cracking (C₁: CO, CO₂, CH₄) 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 MoS₂ edges. S-O exchanges may be mitigated with a higher H₂S concentration. In fact, a higher H₂S concentration reactivated and stabilized the catalyst and improved the HDO/cracking selectivity in experiments with EG WHSV = 19 h⁻¹, see Figure 1 (A+B). DFT has however indicated that a too high concentration of H₂S

inhibits S-vacancy formation at the MoS₂ S-edge thereby potentially limiting HDO. In-situ Quick-EXAFS has thus been applied to study the effect of varying H₂O/H₂S ratios on catalyst composition. The magnitude of the Fourier Transformed in-situ EXAFS spectra (Figure 1C) shows the transition from oxide (MoO_x) to sulfide (MoS₂) 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 MoS₂ crystallites with the support.

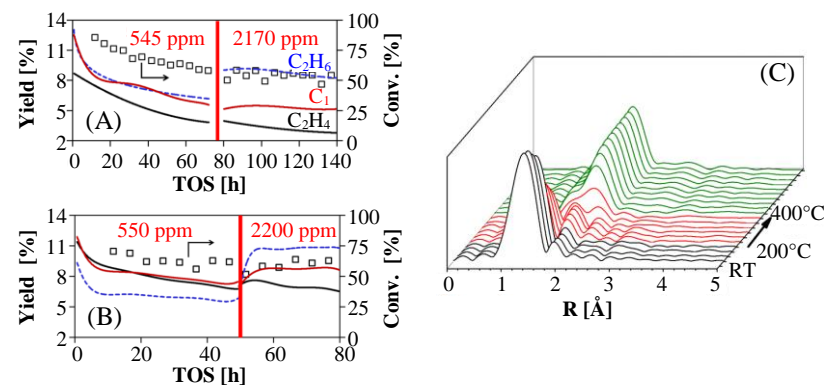


Figure 1 TOS profiles for EG conversion and gas product yields for Ni-MoS₂/MgAl₂O₄ (A) and Co-MoS₂/MgAl₂O₄ (B) at 400°C, EG WHSV = 19 h⁻¹, 28 bar H₂, 545-2200 ppm H₂S (noted with red text) and total pressure 40 barg. Magnitude of the Fourier Transformed in-situ EXAFS spectra (Mo-K-edge) for in-situ sulfidation (C) of MoS₂/MgAl₂O₄ going from oxide (MoO_x, black), through transition phases (red) to a sulfide (MoS₂, green).

DFT calculations have shown that promotion with Ni compared to Co results in more adsorbed H atoms at the S-edge of MoS₂. This higher hydrogen availability could explain the higher yield of ethane compared to ethylene observed for Ni-MoS₂/MgAl₂O₄ (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 H₂O/H₂S on catalytic HDO over MoS₂ catalysts. Understanding the mechanisms behind this influence is a key step in optimizing the catalytic hydropyrolysis process.

References

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