

Experimental Report

Monitoring structural evolution during sulfidation and catalysis of dispersed Ni-Mo(W) phase within three-dimensional confines via in situ XAS/XES

Proposal code CH-5641

1) Abstract

Industrially applied hydrotreating catalysts consist of Ni(Co)-promoted Mo(W) sulfides, either as self-supported systems or supported on γ -alumina.^{1,2} Nevertheless, different support materials like mixed oxides or zeolites have drawn attention because of improved catalytic properties for certain applications. In this work, we encapsulated transition metal carbonyls in zeolite pores using chemical vapor deposition (CVD) according to procedure reported by Okamoto et al.³ These carbonyl precursors can be sulfided under mild conditions to form highly active sulfide species. The structures of the precursors and of the sulfide species were investigated through the experiments at ID26 from extended X-ray absorption fine structure (EXAFS) spectroscopy, high energy resolution fluorescence detection – x-ray absorption near edge structure (HERFD-XANES) spectroscopy, and valence-to-core (VtC) X-ray emission spectroscopy (XES). These well defined sulfide clusters encapsulated in the zeolite framework evolve upon contacting reactant molecules (e.g., unsaturated organics and H₂) and under reaction conditions. It is envisioned that the uniform distribution of active sites not only leads to highly active catalysts, but also facilitates establishing structure-activity relationships in these systems.

2) Short description of the actual experiment

All experiments were performed in a quartz capillary reactor (WJM-Glas, 1 mm outer diameter and 0.01-0.02 mm wall thickness) at ambient pressure. The capillary was heated from below with a hot air gas blower (FMB Oxford). The flow rate of H₂, H₂S, ethene, and He were controlled using Bronkhorst mass flow controllers. A saturator was used to saturate a stream of He with toluene for feeding toluene in the case of toluene hydrogenation experiments. The catalysts were first sulfided under H₂ and H₂S flow and then reacted with H₂ and ethene or toluene at 400 °C. The sulfidation was performed separately and then the capillary cell was isolated using Swagelok shut-off valves and placed on the sample stage for XAFS measurements. Several EXAFS measurements were taken at the Mo K-edge, followed by HERFD-XANES measurements at the Mo-K α_1 energy, and VtC XES measurements.

3) Preliminary experimental results

First results obtained at ID26 show that precursors prepared via CVD of molybdenum carbonyl are successfully converted to Mo_xS_y species during gas phase sulfidation using H₂S at 400°C. The species formed after sulfidation were the same for catalysts containing different metal loadings and they are significantly different from bulk MoS₂ measured as reference (Figure 1). The spectra of Mo_xS_y @ NaY fit the results reported in literature.³ This Mo_xS_y species is reversibly converted to a different sulfide species upon reaction with hydrogen at 400°C (Figure 2). The structure of the molybdenum sulfide species, as well as the evolution of these species upon reaction with different reactant molecules, has to be determined via in-depth analysis of the EXAFS, HERFD-XANES, and VtC XES.

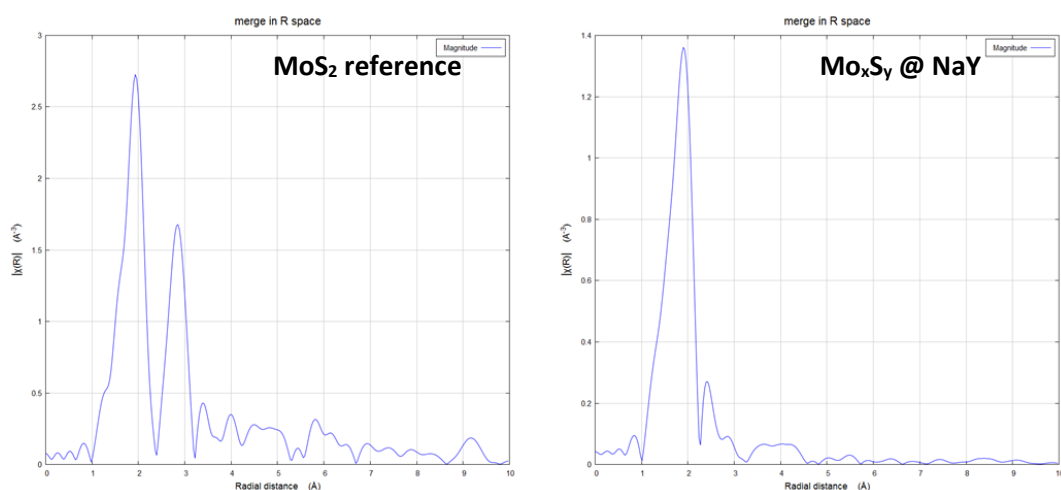


Figure 1: EXAFS analysis of $\text{Mo}_x\text{S}_y@NaY$ catalyst and MoS_2 reference.

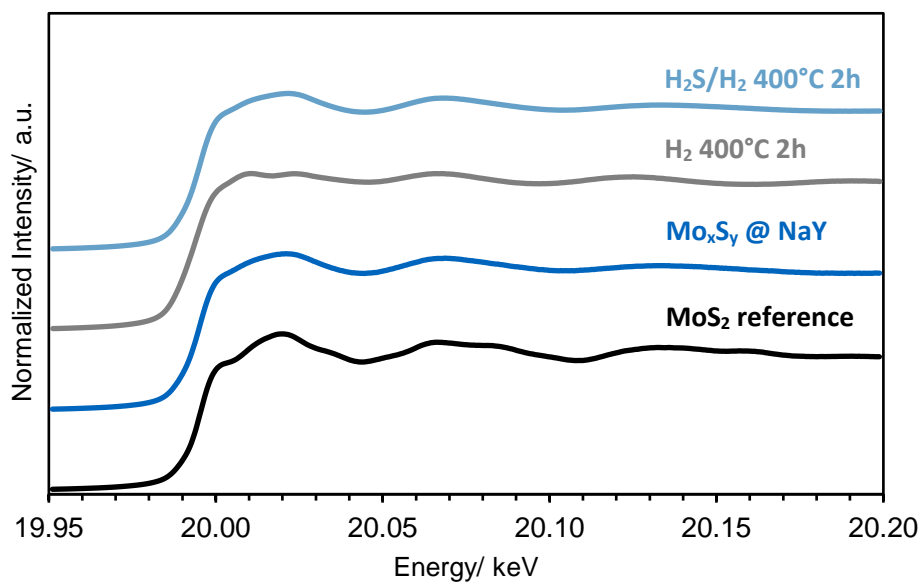


Figure 2: HERFD-XANES spectra of $\text{Mo}_x\text{S}_y@NaY$ catalyst after sulfidation, after reaction with hydrogen at 400°C and after resulfidation in comparison to a MoS_2 reference.

References

1. P. Grange, X. Vanhaeren, *Catal. Today* 36 (1997) 375-391.
2. S. Eijsbouts, S.W. Mayo, K. Fujita, *Appl. Catal., A* 322 (2007) 58-66.
3. Y. Okamoto, *Bull. Chem. Soc. Jpn.* 87 (2014) 20-58.