

Experimental Report

Determining the structure, concentration and intrinsic activity of Ni-promoted sites in Ni-Mo-W sulfide catalysts via in situ and operando studies

Proposal code CH-5303

1) Abstract

The study of Ni-promoted MoS_2 , WS_2 , and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ for hydrodefunctionalization and hydrogenation is an active research field. A family of catalysts that stands out due to its high activity and stability under the most demanding hydrotreating conditions is bulk Ni-Mo-W sulfide catalysts. The promoter effect of Ni is exerted by decoration of Ni atoms at the perimeter of Mo(W)S_2 slabs (Ni atoms replacing Mo/W atoms at the sulfide edges), which leads to the active Ni-Mo(W)-S phase. It is assumed that the concentration of Ni and its interaction with the Mo(W)S_2 phase determines the overall activity of the sulfide catalysts. During sulfidation of the oxide precursor, catalytically inactive Ni_xS_y phases are formed in parallel to the Ni-Mo(W)-S phase. Thus, the content of the active Ni-Mo(W)-S phases should be increased and accordingly the formation of Ni_xS_y species should be limited to gain a more active hydrotreating catalyst. Investigation of the transformation of the commonly used oxide precursor into the sulfide catalysts is therefore indispensable. The results obtained at BM 26 revealed that mild conditions lead to sulfidation of all three metals in a narrow temperature range (~ 50 K). This agrees with activity tests (performed at TU München) as the highest hydrotreating activity was obtained using these sulfidation parameters. Thus, transformation of the three metals from an oxide to a sulfide in a narrow temperature range leads to a better interaction of Ni with Mo(W) phases and in turn to a higher concentration of active sites.

2) Short description of the actual experiment

All experiments were performed in a quartz capillary reactor (1 mm outer diameter and 0.02 mm wall thickness (WJM-Glas)). The sample in the capillary was heated from below with a hot air gas blower (FMB Oxford) and the pressure was set to 4 bar using a back pressure regulator. The molar ratio of S (as dimethyl disulfide) to H was 10 during liquid phase sulfidation. The temperature was increased stepwise and several EXAFS scans (in fluorescence) were taken at the Ni K-edge, the Mo K-edge, and the W L_{III} -edge. With these experiments, the change in the EXAFS spectra from oxides to sulfides was monitored and can be correlated with temperature for all three metals. Thus, the sulfidation progresses with temperature and time of each metal, i.e., Ni, Mo, and W, can be compared and possible change in the coordination geometry as well as interactions among the metals can be elucidated.

3) Preliminary experimental results

First results obtained at BM 26 show that the transformation of Ni and Mo appears in the same temperature range, i.e., 225 – 250 °C. In contrast, W is sulfided between 250 °C and 275 °C (*Figure 1*). The more demanding condition for sulfidation of W is in agreement with literature.^[1] However, the differences in sulfidation temperatures are generally larger than the ones observed here.^[1-2] Thus, the applied sulfidation parameters lead to a sulfidation of the metals into the active sulfide phase in a narrow temperature range. The transformation of the oxide to the sulfide is complex and contains various O-S exchanges and reduction steps of each metal. If these steps occur at approximately the same time, i.e., the same temperature, a better interaction among the different metal phases occurs leading to a higher concentration of Ni incorporated at the Mo(W)S_2 edge and less segregation of inactive Ni_xS_y phases. This agrees with activity test at TU München because the catalyst synthesized with these sulfidation parameters shows the highest hydrodenitrogenation and hydrodesulfurization activities. At 350 °C, the highest temperature used, new features in the EXAFS arise. This may be caused by a final

reconstruction of the material. However, a more in-depth analysis of the recorded EXAFS needs to be done to better understand the ongoing process during sulfidation.

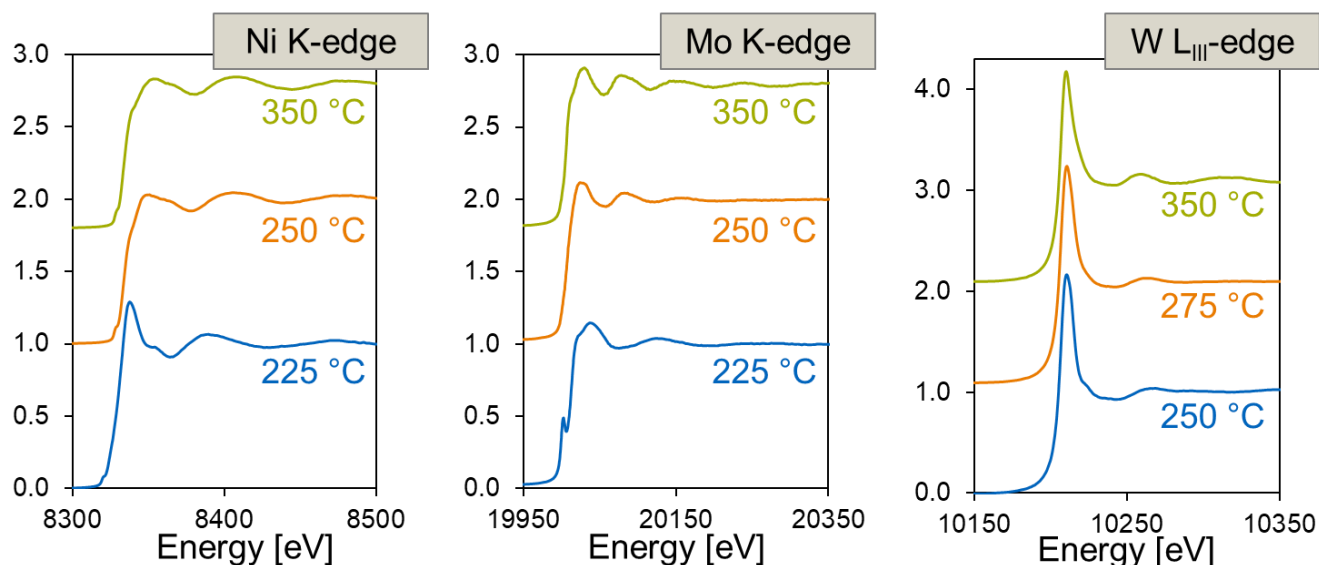


Figure 1 EXAFS of the trimetallic Ni-Mo(W) oxide precursor recorded during liquid phase sulfidation at the Ni K-edge, the Mo K-edge and the W L_{III}-edge at 225 °C, 250 °C, 275 °C and 350 °C.

Monitoring structural evolution during sulfidation and catalysis of dispersed Mo phase within three-dimensional confines

During the beam-time at BM 26, experiments were also carried out to collect preliminary data on the structural characterization of dispersed Mo phase in a H-Y zeolite during sulfidation, as a first step into a newly proposed thrust of activity, namely transition metal sulfides encaged in the (sub)nanometric confines of ordered porous materials (e.g., zeolites). However, there is currently limited knowledge about dispersion, local structure and electronic state of the sulfide phase encaged in zeolites, in its as-prepared state and under working conditions. In the first instance, we were interested in the structural changes of a MoO₃ cluster located in the cages of a zeolite, prepared according to known synthesis protocols.^[3] The experiment for this type of material was executed the same way as described in the previous section. EXAFS scans were taken at the Mo K-edge within typical temperatures used for sulfidation, i.e., 200 °C, 250 °C, 300 °C, and 350 °C.

Early results suggest that the MoO₃ clusters located in the cages of the zeolite support transform into MoS₂ structures at slightly higher temperatures (above 250°C) than in conventional bulk transition metal sulfide catalysts. A more detailed analysis will be undertaken to identify the nature of the formed sulfide phase and to correlate it with the hydrogenation activity of the sample.

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- [2] L. Coulier, V. H. J. de Beer, J. A. R. van Veen, J. W. Niemantsverdriet, *Journal of Catalysis* **2001**, *197*, 26-33.
- [3] W. Ding, S. Li, G. D Meitzner, E. Iglesia, *The Journal of Physical Chemistry B* **2001**, *105*, 506-513.