Title:

The role of the promoter in hydrotreating catalysts under catalytically relevant conditions

Scientific background:

Cobalt-promoted MoS_2 nanoparticles supported on γ-alumina are excellent catalysts for the hydrodesulfurization (HDS) of refinery feedstocks. Key drivers in improving their activity were the discovery that active sites involve Co substituted at the edges of two-dimensional MoS_2 sheets, the so-called 'Co-Mo-S' model, and that promotion can be optimized by structure directing agents. Most researchers ascribe the beneficial effect of organic chelants to the formation of stable Co complexes, delaying its sulfidation to temperatures where MoS_2 is formed [1]. While these observations generally hold true for catalyst activation in H_2/H_2S at atmospheric pressure (standard laboratory conditions), we have previously shown that the same trends do not apply to activation under industrially more relevant conditions (20 bar pressure, gas/oil mixture) [2]. As such, new insights are required to explain the role of activation conditions (pressure, sulfur source) and catalyst preparation on the structure and activity of HDT catalysts under refinery conditions. For this purpose, we developed an in-situ XAS microreactor that is suitable for studying heterogeneous catalysts in a mixed gas-liquid feed at 20 bar pressure and up to 350°C.

Experimental:

We have carried out *in situ* EXAFS and XANES measurements on the Co K and Mo K edge. To obtain high-quality spectra at both metal edges, an experimental cell was developed with interchangeable windows: 0.5 mm thick glassy carbon windows were used at the Mo K edge and 0.2 mm single crystal diamond windows were used at the Co K edge. We studied the gas-phase and liquid-phase activation of various CoMo/γ-Al_2O_3 catalyst precursors differing in preparation procedure. In gas-phase activation, catalysts were subjected to 20 bar H_2/H_2S (20 ml/min), whereas in liquid-phase activation, catalysts were subjected to 20 bar H_2 (20 ml/min) and model diesel (5% tert-nonylpolysulfide dissolved in n-hexadecane). Gas-phase activation is a measure for the sulfidation kinetics from room temperature to 350°C, whereas liquid-phase sulfidation is comparable to industrial activation of these catalysts.

Results obtained and their significance in the respective field of research :

We started by following the oxide-to-sulfide conversion by fast XANES scans (<5 mins) at both the Mo K-edge and noticed that the data quality was excellent. Noteably, even at the boiling point of the diesel feed we obtained good quality spectra. This was previously an issue in transmission mode and limited us to XANES measurements to probe the fraction of sulfided species [2]. Consequently, we optimized EXAFS scan parameters and decreased the time-per-scan to 6 minutes in step-scan mode, without significant loss of information. This is the first example of such an application at the DUBBLE beamline and, to the best of our knowledge, the first time in-situ EXAFS was performed on a heterogeneous catalyst in a gas-liquid plug-flow reactor.
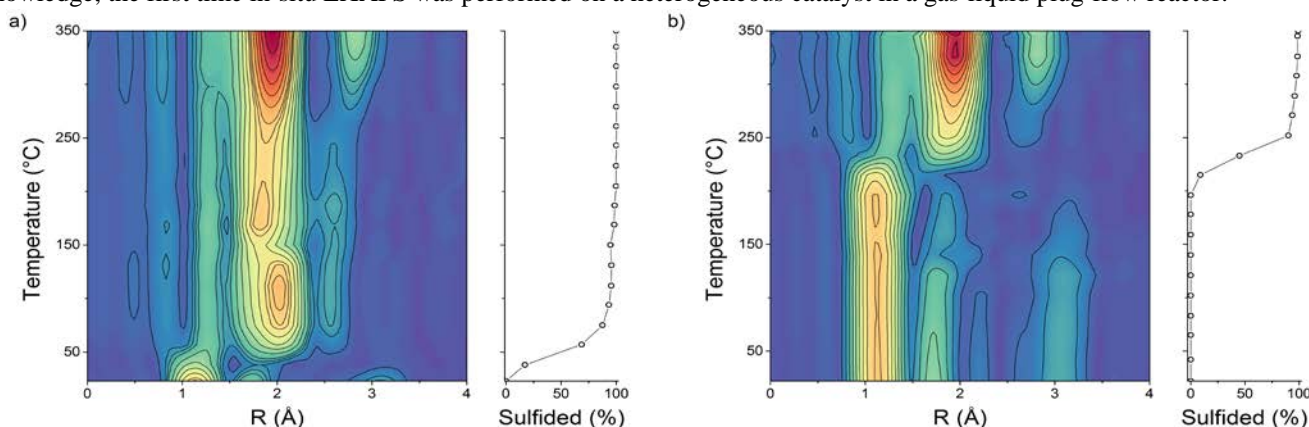

Figure 1: time-resolved Mo K-edge EXAFS of the sulfidation of CoMo-Cit/γ-Al2O3 from room temperature to 350°C at 20 bar pressure. a) gas-phase sulfidation in H_2/H_2S(10%). b) liquid-phase sulfidation in H_2 and diesel (containing 2 wt% S). The k^3-weighted magnitude of the Fourier transform of all collected spectra is plotted as a contour plot (left) and the fraction of sulfided Mo, obtained by LCF of the XANES part of the spectra, is plotted on the right.

Figure 1 shows time-resolved EXAFS scans of the gas-phase (left) and liquid-phase (right) activation of a CoMo/γ-Al$_2$O$_3$ catalyst with citric acid as additive. The additional information obtained from EXAFS, compared with XANES, is immediately apparent from Figure 1a. While a linear combination fit (LCF) of the XANES part of the spectra shows that the catalyst is essentially sulfided above 50°C, EXAFS reveals that there are three sulfided Mo species present at different temperature regimes. The first is an intermediate that is formed at 50°C and disappears at 150°C. This intermediate is six-fold coordinated to sulfur (CN_{Mo-S} = 5.6) at a relatively long bond distance (2.44 Å). The Mo is well-dispersed at this stage (CN_{Mo-Mo} = 0.6) with a short Mo-Mo bond distance (2.79 Å). At 150°C, a shift towards a shorter Mo-S bond distance is observed (2.37 Å) accompanied with a reduction in the Mo-S CN (4.2). Above 250°C, the formation of MoS$_2$ was observed for all catalysts, in agreement with our previous results. At 350°C, the catalyst was fully converted to MoS$_2$ (CN_{Mo-S} = 5.6 @ 2.41 Å; CN_{Mo-Mo} = 3.3 @ 3.17 Å).

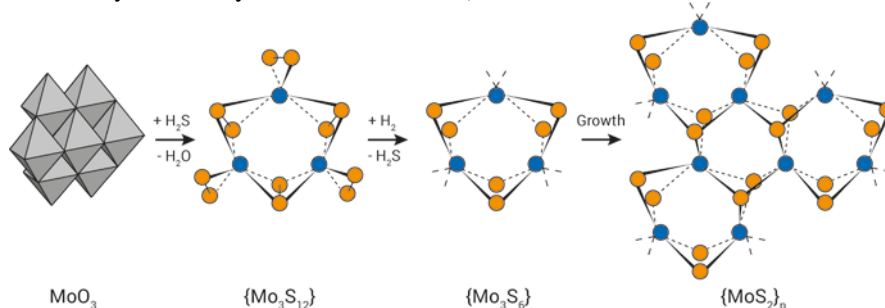MoO_3 $\{Mo_3S_{12}\}$ $\{Mo_3S_6\}$ $\{MoS_2\}_n$

Figure 2: Proposed mechanism for the sulfidation of Mo, based on our EXAFS results and on model studies of the thermal decomposition of thiomolybdates [3]. Molybdenum is represented by blue circles and sulfur is represented by orange circles.

Based on EXAFS and additional data from our lab (XPS, TEM), we propose the following mechanism for high pressure gas-phase sulfidation of CoMo catalysts (Figure 2). At low temperature, well dispersed Mo sulfides are formed with a structure similar to thiomolybdate clusters such as $(Mo_3S_{13})^{2-}$ [3]. Sulfur is most likely bonded to Mo as terminal or bridging S_2^{2-} groups as indicated by the relatively long Mo-S bond. At 150°C a second intermediate is formed by sulfur elimination (CN_{Mo-S} 6 → 4). The decreased Mo-S bond distance points to reduction of S_2^{2-} groups to bridging or terminal S^{2-}. The proposed triangular clusters formed at low temperature are highly irregular, as indicated by the low Mo-Mo CN. Above 250°C, the intermediates crystalize to MoS$_2$.

During liquid-phase sulfidation (no H$_2$S in the feed) the oxidic Mo precursor remains stable up to approximately 200°C (Figure 1b). At this point, the organosulfides dissolved in the diesel feed thermally decompose and form H$_2$S in situ. The temperature of the sulfidation is now sufficient to convert the oxide to MoS$_2$ almost directly. This same effect was also observed for Co (Figure 3). We propose that sulfided Mo clusters have increased mobility due to weaker support interaction and tend to aggregate during gas-phase sulfidation (observed by TEM, not shown here). Consequently, aggregates crystallize into stacked MoS$_2$ sheets (gas-phase), whereas direct crystallization to MoS$_2$ yields single layers (liquid-phase sulfidation). This mechanism may rationalize the finding that refinery catalysts activated in oil have a lower stacking degree than their gas-phase activated counterparts [4]. Additional experiments are carried out in our lab to confirm this hypothesis.

To summarize, we have observed structural transitions during the activation of HDT catalysts under relevant operating conditions with high precision. This information allowed us to propose a mechanism for the active phase formation that rationalizes the structural differences observed between model catalysts and refinery catalysts.
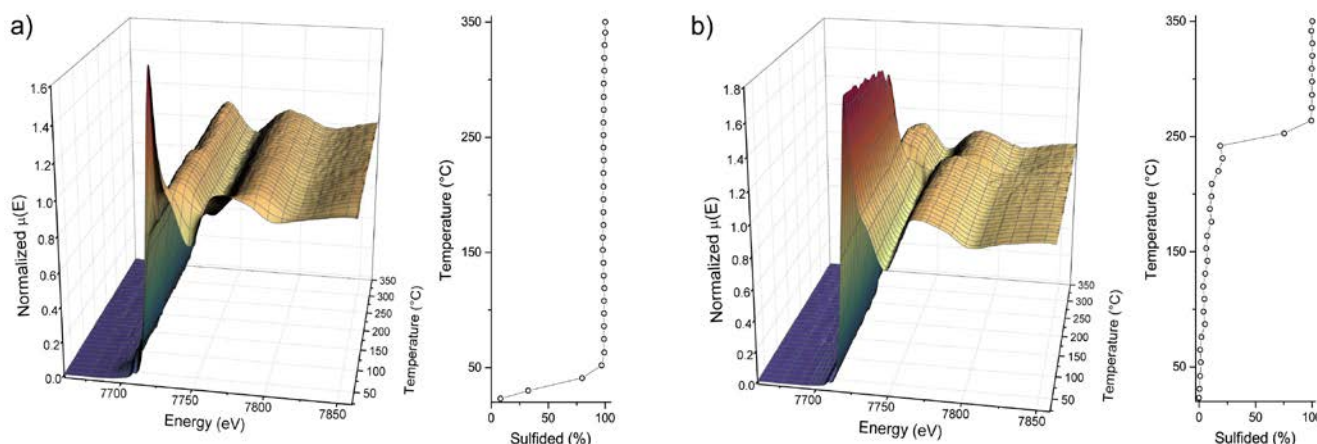

Figure 3: time-resolved Co K-edge XANES of the sulfidation of CoMo-Cit/γ-Al2O3 from room temperature to 350°C at 20 bar pressure. a) gas-phase sulfidation in H$_2$/H$_2$S(10%). b) liquid-phase sulfidation in H$_2$ and diesel (containing 2 wt% S).

Scientific prospect

The data will be published in two papers, one concerning the active phase genesis under catalytically relevant conditions, the other concerning the incorporation of the Co promoter into the MoS$_2$ phase. For the second publication, data obtained at DUBBLE (sulfidation kinetics) will be combined with data obtained at SuperXAS, SLS (RIXS, HERFD-XANES) in an attempt to elucidate the location of Co in the active phase.

References:
[1] R. Cattaneo *et al.*, J. Catal., 2001, 199, 318-327.   [2] Experiment number 26-01-997.
[3] A. Müller *et al.*, Appl. Catal., 1990, 62, L13-L17.   [4] S. Eijsbouts *et al.*, J. Catal. 2005, 229, 352-364.