Activation of co–mo–S hydrodesulfurization catalysts under refinery conditions

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Activation of Co–Mo–S Hydrodesulfurization Catalysts Under Refinery Conditions-A Combined SAXS/XAS Study


The activation of heterogeneous catalysts is challenging to follow experimentally and poorly understood in many cases. We combine in situ and time-resolved X-ray absorption spectroscopy and small-angle X-ray scattering to study the activation of Co–Mo–S hydrotreating catalysts under conditions close to a refinery start-up, i.e., 20 bar H₂ pressure and gaseous H₂S or liquid sulfiding agents. Formation of MoS₂ nanoparticles involves three stages, namely aggregation (50–150 °C) and self-assembly (150–250 °C) of two distinct amorphous MoS₂ intermediates, followed by a transition into layered structures that closely relate to the MoS₂ structure. In stage III, these nuclei coalesce into the final MoS₂ nanoparticles. Their growth distribution and stacking degree can be tailored by controlling the aggregation step, paving the way for the synthesis of better hydrotreating catalysts. Our experimental approach enables studying a broad range of supported amorphous nanomaterials at various length scales and operating conditions relevant to important catalytic processes.

The formation of inorganic nanoparticles (NPs) is a complex process that is challenging to follow experimentally.[1] Solution precipitation of NPs from molecular precursors can usually be described by the classical nucleation paradigm,[2] although more complex formation pathways have recently been proposed that involve successive transformation of precursors and intermediates into NPs.[3] The formation of supported NPs in heterogeneous catalysts is arguably even more challenging to unravel because starting and final structures are not well defined and interaction with the support cannot be ignored.[4] As such, most studies have focused on NP formation from supported molecular precursors, which can be considered a model for more complex heterogeneous catalysts.[5]

Heterogeneous catalysts are typically composed of metallic or sulfidic NPs supported on a high surface area support, which are prepared by reduction or sulfidation of an oxidic precursor.[6] An example are hydrodesulfurization (HDS) catalysts, which are essential in the production of clean transportation fuels.[7] The catalytically active phase is composed of cobalt or nickel promoted MoS₂ NPs supported on γ-alumina.[8] Dispersion is a key parameter in these catalysts, because the two-dimensional 2H-MoS₂ nanosheets can stack and only the (promoted) edge structures are believed to be involved in catalysis.[9] Industrial HDS catalysts are prepared through activation of an oxidic precursor with high molybdenum loading (~1 monolayer) by sulfidation under reducing (H₂) and sulfur-rich conditions.[10] In previous work we have shown that the activation method can drastically change the stacking degree of the MoS₂ phase; activation in gaseous H₂/H₂S results in multilayers of MoS₂ (2–4 particles per stack), whereas activation with a model gas-oil feed, which represents the industrial activation method, yields mainly MoS₂ monolayers.[11] These findings are in good agreement with investigations on commercial catalysts obtained from a refinery hydrotreater.[12]

This difference is difficult to explain based on the current literature, because no consensus has been reached on the sulfidation pathway of HDS catalysts and only few studies have focused on the formation of stacks in supported HDS catalysts.[13] Recently, Lesage et al. studied gas and liquid sulfidation of CoMo HDS catalysts in a real feedstock by in situ QEXAFS and proposed that MoS₂ dispersion was affected by the rapid nucleation of (oxy)sulfide intermediates. However, this work did not include direct observation of nanoparticle formation on the nanoscale and their chemometric approach assumed that statistically significant spectroscopic contributions correlate with chemical intermediates.[14]

In this work, we use X-ray absorption spectroscopy (XAS) and small-angle X-ray scattering (SAXS) to obtain structural information during the active phase formation of disordered Co–Mo–S catalysts at the molecular and nanoscopic level. We take advantage of recent work showing that citric acid (CA) can enhance reducibility of metal oxides in the catalyst precursor.[10] Well-defined phase transformations are observed during activation in 20 bar H₂/H₂S that are otherwise challenging to detect under atmospheric conditions or with samples that exhibit strong metal-support interaction (i.e., calcined precursors). The
intermediates detected with XAS are linked to nanoscopic structural changes observed by SAXS, giving insight into nanoparticle growth and stacking. A mechanism is proposed that explains differences observed in the stacking of industrial activated catalysts as compared to those prepared in lab-scale studies.

Figure 1 shows the Mo K-edge EXAFS in a contour plot and fit results corresponding to the activation of a CoMo/Al₂O₃ catalyst by heating to 350 °C in 20 bar H₂/H₂S. Consistent with our previous ex situ work,¹¹ sulfidation of molybdenum occurred directly after starting activation. Two additional marked structural transitions could be observed at ~140 °C and ~260 °C, so that MoS₂ formation can be described as a three-stage process (I–III). In stage I, molybdenum oxides rapidly convert into sulfided species. Sulfidation is essentially completed at 75 °C as indicated by linear combination fitting of XANES, and by the disappearance of a Mo–O contribution at ~1.5 Å (not phase corrected) along with a simultaneous rise of a Mo–S scattering contribution at ~2.0 Å in the EXAFS. The first shell Mo–S coordination number (CN) increased to nearly 6 at 150 °C. The long Mo–S bond distance (2.43 Å) indicates that sulfur is present as disulfide ligands (S₂²⁻). The second shell Mo–Mo distance is 2.81 Å with a Mo–Mo CN close to 1, indicating that the molybdenum sulfide (MoS₂) species are highly dispersed. The MoS₂ species are unstable near 150 °C, as evidenced by a sharp increase of the Mo–S disorder parameter σ² that cannot be explained by thermal effects.

The start of stage II is expressed by a reduction in the Mo–S CN and bond length (2.37 Å). Furthermore, the transition to a more stable MoS₂ structure in this temperature range is supported by a decrease of the Mo–S disorder parameter. The shorter Mo–S distance indicates that sulfur is now mainly present as sulfide ligands (S²⁻). This is most likely facilitated by hydrogenation according to $S²⁻ + H₂ → S²⁻ + H₂S$. Subtle differences in the Mo–Mo coordination number and bond distance are observed between unpromoted and promoted samples (see supporting information), indicating that cobalt interacts with the MoS₂ species. The structure dominating in stage II is stable between 150 °C and 250 °C. Above 250 °C another rapid structural transition is observed, defined by a shift of the Mo–Mo contribution to 3.17 Å, which is characteristic of MoS₂. Furthermore, the disorder parameter of the Mo–S and Mo–Mo scattering paths counterintuitively decreased with increasing temperature, indicating structural rearrangement into a more ordered phase, i.e. MoS₂ crystallization. The Mo–S and Mo–Mo CNs increased steadily during stage III, pointing to the growth of MoS₂ NPs.

Figure 3a shows that sulfidation of molybdenum during liquid phase activation differs substantially from that observed during gas phase activation. Conversion of molybdenum oxide to sulfide formation and dispersion of MoS₂ NPs was followed at the nanometre scale with SAXS. Figure 2a shows an overview of the scattering patterns from 25 °C to 350 °C during gas phase activation of the CoMo/Al₂O₃ catalyst. Scattering of the alumina support and glassy carbon reactor windows was small compared to the scattering contribution of molybdenum particles, which have substantially higher electronic density, so that only the scattering due to the molybdenum sulfide particles subtracted by the alumina support are shown here. Three temperature regimes can be distinguished that describe the system at the nanoscopic level during the sulfidation reaction.

50–110°C: Development and disappearance of a structure factor representing structural order in the system, as manifested by a sharp drop in scattering intensity at $q < 1.0 \text{ nm}^{-1}$. This indicates interaction between the primary scattering entities.

110–210°C: Formation of larger and elongated scattering

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**Figure 1.** Activation of CoMo–CA in 20 bar H₂/H₂S(10%). a) contour plot of the Fourier Transform (k²-weighted) of the EXAFS (k-range = 4–13 Å⁻¹) between 25 °C and 350 °C. Phase transitions are indicated by white dashed lines; b) Degree of molybdenum sulfidation as determined by LCF of XANES spectra; c) EXAFS fit parameters between 25 °C and 350 °C and indication of the three stages (I–III) during activation. The fit parameters are the coordination number CN, the bond distance R and the disorder parameter σ².
features as evidenced by an increased scattering intensity at 
$q < 1.0 \text{ nm}^{-1}$; 210–350°C, growth of elongated scattering fea-
tures as evidenced by a change in $|q| \propto q^{-1}$ for $q < 1.0 \text{ nm}^{-1}$
and a shift to lower $q$ values. A mathematical model (see
Supporting information) was developed to interpret evolution
of the molybdenum species in the system. By fitting this model
to the scattering patterns, relevant information about the size
and interaction between the scattering entities was extracted
throughout the activation process.

Scattering curves below 110°C (Figure 2) could be best
fitted using a spherical form factor ($|q| \propto q^0$ dependency). The
average size is 2.3 nm at the start of the reaction and remained
constant during sulfidation. The initial species were non-
interacting ($S(q) = 1$), indicating high dispersion. The decreased
intensity at $q < 1.0 \text{ nm}^{-1}$ was modeled with the interparticle
structure factor $S(q)$, which includes the hard sphere volume
fraction ($\eta$) as shown in Figure 2b. The decreased scattering
intensity at $q < 1.0 \text{ nm}^{-1}$ around 75°C is attributed to an
increase in particle–particle interference as expressed by $\eta$. We
propose that sulfided entities form domains with a locally
increased number of scatterers, which is a first stage of
aggregation. This implies that molybdenum oxides are immobi-
lized on the support, whereas sulfided intermediates (MoS$_x$) are
not.

Formation of elongated scattering entities takes place from
110°C to 210°C, which was modeled with a cylindrical form
factor ($|lq| \propto q^{-1}$). We note that this expression was used as
the best approximation and does not imply that species are
rigid. During this stage, the weight fraction and diameter of
globular scattering entities decreases and simultaneously the
weight fraction of elongated scattering entities increases with a
diameter comparable to the globular ones. This indicates
aggregation of the primary scattering entities in one direction.
The comparable diameter of elongated and globular entities suggests that the elongated aggregates are still composed of smaller (globular) scattering entities separated by ≤1.5 nm, so that these entities could not be discriminated within the spatial resolution of the experiment.

The intensity of scattering curves between 210°C and 350°C increases at q < 1.0 nm⁻¹ and shifts to lower q (Figure 2c), indicating growth. The average particle size increases from 2.0 nm to 2.7 nm between 200°C and 270°C and then remains constant. As such, at the nanoscopic level no structural rearrangements are observed in the temperature range in which MoS₂ crystalization is evidenced by EXAFS. This leads us to conclude that the high MoS₂ stacking degree as observed by HR-TEM must originate from aggregation of MoSₓ intermediates at low temperature (<150°C) as observed by SAXS. This is corroborated by activating the same catalyst in 20 bar H₂ and a model gas-oil feed (simulated industrial activation), which resulted in a substantially lower stacking degree as shown below starts around 200°C as manifested by the disappearance of the Mo–O contribution at 1.2–1.6 Å and appearance of a new contribution at 2.0 Å attributed to Mo–S backscattering. This is initiated by the in situ generation of H₂S from the sulfiding agent (tert-nonyl polysulfide) at 200°C[11]. A growing Mo–Mo contribution at 2.8 Å appeared above 250°C, indicating MoS₂ particle growth. The intermediate MoSₓ phases that were observed during gas phase activation could not be identified in liquid phase activation. Thus, the intermediates either do not form under these conditions or their lifetime must be shorter than the time resolution of the experiment (5 min).

An overview of the complementary SAXS patterns is shown in Figure 3b. The scattering patterns remain nearly constant below 200°C. Above this temperature, the intensity increases at low q values (< 1.0 nm⁻¹), pointing to the formation of larger scattering entities. The scattering intensity can be described by the asymptotic behavior predicted by the Porod power law (I(q) ∝ q⁻⁴) and is best modeled with two polydispersed spherical objects of different size. The average size of the main scattering entities remains constant during the sulfidation process at 2.0 ± 0.4 nm, in agreement with the observations during gas phase sulfidation.

The combined study of Co–Mo–S catalysts with in situ XAS and SAXS has revealed that MoS₂ formation involves two amorphous intermediates characterized by disulfide (50–150°C) or sulfide (150–250°C) ligands with a short Mo–Mo bond distance (2.8 Å). These structural parameters are in line with those typically reported for amorphous MoSₓ-type structures[13] described either by the chain model or by linked triangular clusters[14]. We consider the model based on triangular [Mo₃] clusters more appropriate to describe our observations, because the chain model describes MoSₓ as a chain of Mo(VI)₃SʳCN of 5–6. This structure shows similarities with that of the [Mo₅Sₓ CN]²⁻ anion.[15] The molybdenum atoms in the second MoSₓ structure (150–250°C) are connected by one or two S²⁻ ligands, accounting for a Mo–S CN of 4. The [Mo₃] subunits must be highly disordered based on their low Mo–S CN and large disorder parameter, and likely cannot be described by a single structure. These sulfur-deficient structures self-assemble into larger elongated structures, as indicated by our SAXS results, and can arrange into a precursor phase that closely resembles the layered structure of MoS₂, as evident from HRTEM images (see supporting information).

Formation of MoSₓ NPs occurs primarily via coalescence of small MoSₓ nuclei in close proximity for the following reasons: i) complete rearrangement of amorphous MoSₓ into the MoS₂ structure is fast (~5 min). This implies formation of many MoSₓ nuclei as corroborated by the low Mo–Mo CN; ii) no notable changes in molybdenum dispersion are observed above 250°C; iii) the MoSₓ entities aggregate and self-assemble into layered structures resembling MoS₂. Thus, ‘stacked’ structures are

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**Figure 4.** Representation of MoS₂ formation for HDS catalysts prepared by gas phase activation (solid arrows) or liquid phase activation (dashed arrow). Stage I: formation of MoSₓ domains: inset shows that particles are mobile. Stage II: aggregation into elongated structures composed of primary MoSₓ entities; inset shows particle growth above 200°C. Stage III: crystallization of aggregates into MoS₂; inset shows that particles grow primarily by coalescence of smaller ones. Bottom: proposed structures of the [Mo₃] subunits that constitute the building blocks of the MoSₓ intermediate phases and of MoS₂.
The combination of X-ray absorption and scattering methods applied in this study gives insight into molecular and nanoscale processes that take place during hydrotreating catalyst activation. This approach is applicable to other gas-liquid-solid catalytic processes as well and can contribute to a better understanding of the phenomena that take place under industrial operating conditions.

**Experimental Section**

Mo/Al₂O₃ and CoMo/Al₂O₃ catalysts were prepared by incipient wetness impregnation as described in the Supporting Information. Briefly, γ-Al₂O₃ was impregnated with solution of ammonium heptamolybdate, cobalt nitrate and citric acid and subsequently dried at 110 °C to achieve 10 wt% Mo-loading and Co/Mo = 0.4 molar ratio.

Combined SAXS/XAS experiments were carried out in a homemade cell at the BM26 A (DUBBLE) beamline of the ESRF as described in the Supporting Information. The catalyst was activated in 20 mL min⁻¹ H₂/He (10%), called gas-phase activation, or 20 mL min⁻¹ H₂/He/H₂S (10%), called liquid-phase activation. The ramp rate was 3 °C/min⁻¹ with a final temperature of 350 °C. The experiments were performed at the Mo K-edge (20.0 keV) using a monochromated X-ray beam with an energy slightly below the absorption edge (19.9 keV) for the SAXS measurements and scanning up to 20.3 keV for the XANES measurements. Scattering intensities were collected with a 2D MAR detector positioned at 1.97 m from the sample to allow for a usable q-range of 0.3–4.0 nm⁻¹ (corresponding to a spatial resolution of 1.5–20 nm) and transmission was measured with a photodiode positioned in the beamstop of the SAXS detector.

XANES spectra were normalized and fitted by linear combination fitting, using the oxidic and fully sulfided (after 2 h at 350 °C) referred to as liquid-phase activation. The ramp rate was 3 °C/min⁻¹ with a final temperature of 350 °C. The experiments were performed at the Mo K-edge (20.0 keV) using a monochromated X-ray beam with an energy slightly below the absorption edge (19.9 keV) for the SAXS measurements and scanning up to 20.3 keV for the XANES measurements. Scattering intensities were collected with a 2D MAR detector positioned at 1.97 m from the sample to allow for a usable q-range of 0.3 < q < 4.0 nm⁻¹ (corresponding to a spatial resolution of 1.5–20 nm) and transmission was measured with a photodiode positioned in the beamstop of the SAXS detector.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Heterogeneous catalyst · Nanoparticle formation · Hydrodesulfurization · SAXS · EXAFS