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

Citation for published version (APA):

DOI:
10.1002/cctc.201901390

Document status and date:
Published: 18/10/2019

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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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 supported NPs in heterogeneous catalysts 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.[15] 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 (MoS₃) species are highly dispersed. The MoS₃ 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.

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 nm⁻¹. This indicates interaction between the primary scattering entities.

110–210°C: Formation of larger and elongated scattering...
features as evidenced by an increased scattering intensity at $q < 1.0 \text{ nm}^{-1}$; 210–350°C, growth of elongated scattering features as evidenced by a change in $I(q) \propto q^{-1}$ 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 ($I(q) \propto q^0$ 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 immobilized 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 ($I(q) \propto q^{-1}$). 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 $q < 1.0 \text{ nm}^{-1}$ 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 MoS$_2$ crystallization is evidenced by EXAFS. This leads us to conclude that the high MoS$_2$ stacking degree as observed by HR-TEM must originate from aggregation of MoS$_x$ intermediates at low temperature (<150°C) as observed by SAXS. This is corroborated by activating the same catalyst in 20 bar H$_2$ 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 H$_2$S from the sulfiding agent (tart-nonyl polysulfide) at 200°C. A growing Mo–Mo contribution at 2.8 Å appeared above 250°C, indicating MoS$_2$ particle growth. The intermediate MoS$_x$ 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 ($I(q) \propto q^{-4}$) 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 MoS$_2$ 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 MoS$_x$-type structures described either by the chain model or by linked triangular clusters. We consider the model based on triangular [Mo$_3$] clusters more appropriate to describe our observations, because the chain model describes MoS$_2$ as a chain of Mo$(S^{2-})_3S^{2-}$ subunits. This ratio of Mo to bridged S$_2^{2-}$ and S$^{2-}$ ligands is clearly not in line with the transition from S$_2^{2-}$ to S$^{2-}$ ligands reported here.

Figure 4 shows the proposed formation pathway of MoS$_2$. The first MoS$_2$ structure (50–150°C) is composed of [Mo$_3$] subunits with composition Mo$_x$(S$_3$)$_y$. Subsequently, the second intermediate MoS$_3$ (150–250°C) is formed, which is connected by one or two S$^{2-}$ ligands, accounting for a Mo–S CN of 4. The [Mo$_3$] subunits must be highly disordered based on their low Mo 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 MoS$_2$ as is evident from HRTEM images (see supporting information).

Formation of MoS$_2$ NPs occurs primarily via coalescence of small MoS$_2$ nuclei in close proximity for the following reasons: i) complete rearrangement of amorphous MoS$_x$ into the MoS$_2$ structure is fast (~5 min). This implies formation of many MoS$_2$ nuclei as corroborated by the low Mo–Mo CN; ii) no notable changes in molybdenum dispersion are observed above 250°C; iii) the MoS$_2$ entities aggregate and self-assemble into layered structures resembling MoS$_2$. Thus, ‘stacked’ structures are...
Conflict of Interest

The authors declare no conflict of interest.

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