# The Structure of Well Defined SiO$_2$ Supported MoO$_3$ Clusters during Sulfidation.
## An in situ EXAFS-study

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The sulfidation of a well defined MoO$_3$/SiO$_2$ catalyst has been examined by means of TPS, EXAFS, and TEM. The oxidic clusters in a 5.6 wt% MoO$_3$/SiO$_2$ catalyst are transformed into almost completely sulfided particles (MoO$_x$S$_y$) by O-S exchange at RT. A molybdenum-sulfido particle that resembles the MoS$_3$ structure is formed during sulfidation at 423 K. The MoS$_2$ phase is formed at temperatures between 523 and 573 K. The transition of MoS$_3$ into MoS$_2$ can be monitored by evolution of H$_2$S from the catalyst, with simultaneous consumption of H$_2$. The twodimensional size of the MoS$_2$ slabs can be derived from the EXAFS Mo-Mo coordination number by means of a theoretical model. The stacking height of the slabs must be elucidated by TEM.

## 1 INTRODUCTION

Many studies are dedicated to the preparation and structure of MoO$_3$ catalysts on different supports. The *sulfided* counterpart of the *oxidic* precursors of Co(Ni)/Mo(W) catalysts is one of the most abundantly investigated catalyst systems. Conversion of the oxidic catalyst into the active sulfide occurs under reaction conditions, due to the presence of sulfur containing compounds or by presulfiding. The nature of the active sites and the mechanism of the HDS reaction has received enormous attention, but the genesis of the active phase has remained relatively underfocused. Publications of Pratt et al [1] and Payen et al [2] are valuable publications in this field. The use of Temperature Programmed Sulfidation (TPS) techniques yields useful information on the sulfidation process, but it is difficult to extract information on the structure of the intermediate species during sulfidation. Therefore, other *in situ* techniques, like LRS [2,3], MES [4-7], and EXAFS [8-11] are needed. The formation of MoS$_2$ slabs can be elegantly established with (High Resolution) TEM [12-14].

A vast majority of the literature in this field is dedicated to the alumina supported catalysts, because highly dispersed alumina supported Co-Mo catalysts can easily be prepared at laboratory and industrial scale. A serious draw-back of Al$_2$O$_3$ is its tendency to form spinels with Co and Ni [15] that possess low activity in hydrotreating reactions and its poor resistance toward acid gases, like SO$_2$. SiO$_2$ does not suffer from the latter disadvantage, but it is known to form Co- and Ni-(hydro)silicates.

In this paper, a well defined MoO$_3$/SiO$_2$ catalysts will be used for a study on the sulfidation behavior. The process of sulfidation can be easily followed by TPS while monitoring both [H$_2$S] and [H$_2$]. The sulfur content of the catalyst at different sulfidation temperatures will be established with Temperature Programmed Oxidation. After determination of the sulfidation as a function of the temperature, the structure transformation (*oxide→sulfide*) will be investigated at intermediate temperatures with *in situ* techniques, such as, XANES and EXAFS, and *ex situ* TEM.

## 2. EXPERIMENTAL

### preparation of the catalyst

The catalyst used in this paper was prepared by deposition precipitation of trivalent molybdenum from homogeneous solution (HDP). Trivalent molybdenum was used in order to enhance the interaction of the aqueous precursor with the support (*aerosil 200V* from Degussa). The MoO$_3$ weight content amounts 5.6% (catalyst denoted Mo6). The structure and the preparation of the catalyst have been described elsewhere [16,17].

### characterization methods

Temperature Programmed Sulfidation (TPS) profiles are recorded in an automated microflow apparatus. Sulfidation occurs with approx. 200 mg catalyst (pelletted at 100 MPa and crushed to acquire a sieve fraction of 425-625 μm) in a 100 ml min$^{-1}$ flow of H$_2$S/H$_2$/Ar (10/40/50). After flushing the entire system, the catalyst is sulfided at RT (295 K) for 30 minutes (isothermal stage). Subsequently, the temperature program is started (5.0 K min$^{-1}$) to finish at the final temperature (usually 673 K). At the final temperature, the catalyst is exposed to the gas mixture for another 30 minutes; afterwards the sample is cooled down to RT under the same conditions. The X-ray absorption experiments were done at the SRS in Daresbury laboratory (U.K.). The energy amounts 2.0 GeV. The radiation for the X-ray absorption experiments originates from the wiggler station 9.2. The beam is monochromatized by a double Si(220) crystal monochromator. The chambers are specially designed to generate a homogeneous field and guarantee linearity of response. The solid samples are pressed at 100 MPa into a self supporting wafer with an absorbance of approximately 2.5 and fixed in the sample holder. In this *in situ* EXAFS cell, equipped with Be-windows, the catalyst can be pretreated under the desired gas atmosphere and at the desired temperature. After pretreatment the cell is flushed with helium and cooled at 77K with liquid N$_2$, the temperature used during experiments. Data are collected at each energy for 1 s and the results of usually 3 scans are averaged to reduce high- and low frequency noise. Analysis of the data is performed with the software, developed at the University of Eindhoven. The experimental references (Mo-O, Mo-S, and Mo-Mo) are obtained from the spectra of high purity Na$_2$MoO$_4$ and MoS$_2$.

## 3. RESULTS AND DISCUSSION

The TPS profile of Mo6 is presented in fig. 1. Both H$_2$S and H$_2$ consumptions are given. The results of the EXAFS analyses after sulfidation at three different temperatures are presented in Table I. These EXAFS measurements were done after TPS experiments until three different final temperatures (RT, 423 K, and 673 K).
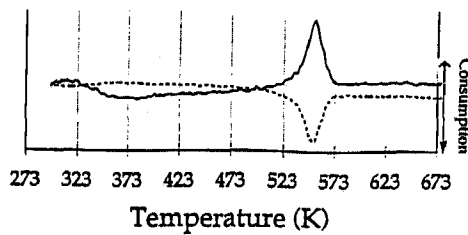
Figure 1 TPS profiles of Mo6. The solid curve is the [$H_2S$], the dotted curve is the HWD signal; $\uparrow$ indicates $H_2S$ ($H_2$) production, $\downarrow$ indicates $H_2S$ ($H_2$) consumption.

Table I Fit Parameters for the analysis of Mo6RT, Mo6423 and Mo6673.

| scatterer | $N$ | $s_N$ | $\Delta\sigma^2$ ($\cdot 10^{-4}$ $\AA^2$) | $s_{\Delta\sigma}^2$ | $R$ ($\AA$) | $s_R$ | $E_o$ | $s_E^o$ eV |
|---|---|---|---|---|---|---|---|---|
| **Mo6RT** | $N_{fit}$ = 16; $N_{allowed}$ = 31.6 | | | | | | | |
| O | 0.17 | 0.01 | -47.2 | 4.2 | 1.666 | 0.007 | -9.95 | 2.43 |
| S | 4.83 | 0.04 | 87.0 | 0.6 | 2.435 | 0.001 | 0.67 | 0.12 |
| Mo | 1.14 | 0.05 | 56.7 | 2.3 | 2.769 | 0.001 | 4.62 | 0.30 |
| Mo | 2.59 | 0.03 | 253.7 | 0.6 | 3.450 | <0.001 | 0.95 | 0.09 |
| **Mo6423** | $N_{fit}$ = 8; $N_{allowed}$ = 25.4 | | | | | | | |
| S | 8.08 | 0.01 | 99.8 | 0.1 | 2.445 | <0.001 | 1.46 | 0.05 |
| Mo | 1.72 | 0.02 | 37.6 | 0.4 | 2.755 | <0.001 | 8.76 | 0.13 |
| **Mo6673** | $N_{fit}$ = 16; $N_{allowed}$ = 38.5 | | | | | | | |
| S | 6.00 | 0.03 | 20.5 | 0.3 | 2.407 | <0.001 | 2.86 | 0.05 |
| Mo | 4.68 | 0.03 | 33.3 | 0.3 | 3.161 | <0.001 | 0.54 | 0.08 |
| S | 8.48 | 0.13 | 70.9 | 1.3 | 4.733 | 0.001 | 0.83 | 0.13 |
| Mo | 2.25 | 0.18 | -30.1 | 5.7 | 6.233 | 0.006 | -0.74 | 0.79 |

Since no $H_2$-consumption is found in the low temperature region of the TPS, it is assumed that exchange between lattice oxygen and sulfur from $H_2S$ takes place, according to eq. (1):

$$MoO_3 + x\ H_2S \rightarrow MoO_{3-x}S_x + x\ H_2O \quad (1)$$

Partial exchange of oxygen by sulfur could lead to formation of oxysulfide species, $Mo^{VI}O_{4-x}S_x^{2-}$, or $Mo^{VI}O_{3-x}S_x$, as formulated in eq. (1). These species are well known in aqueous solutions. Full exchange of oxygen for sulfur atoms would result in $MoS_3$. Some

publications are known from the literature on this amorphous compound [2,3,18]. The valence of molybdenum in $MoS_3$ is, 5+, due to an internal redox reaction between molybdenum and its sulfur ligands ($Mo^{VI} \rightarrow Mo^{V}$ and $2S^{2-} \rightarrow S_2^{2-}$). The resulting *molybdenum-sulfido* complex can be denoted as $[Mo_2^{V}S_4(S_2)_2]^{2-}$, $[Mo_2(S_2)_6]^{2-}$ or $Mo_2S_8^{2-}$[2]. At RT the sulfidation of Mo6 proceeds significantly: $N_{Mo-S}$= 4.83, whilst $N_{Mo-O}$=0.17. The $N_{Mo-S}$ reaches the value of eight after sulfidation 423 K. The Mo-Mo coordination distance after sulfidation at RT and 423 K points at the formation of $MoS_3$ (R~2.78 $\AA$).
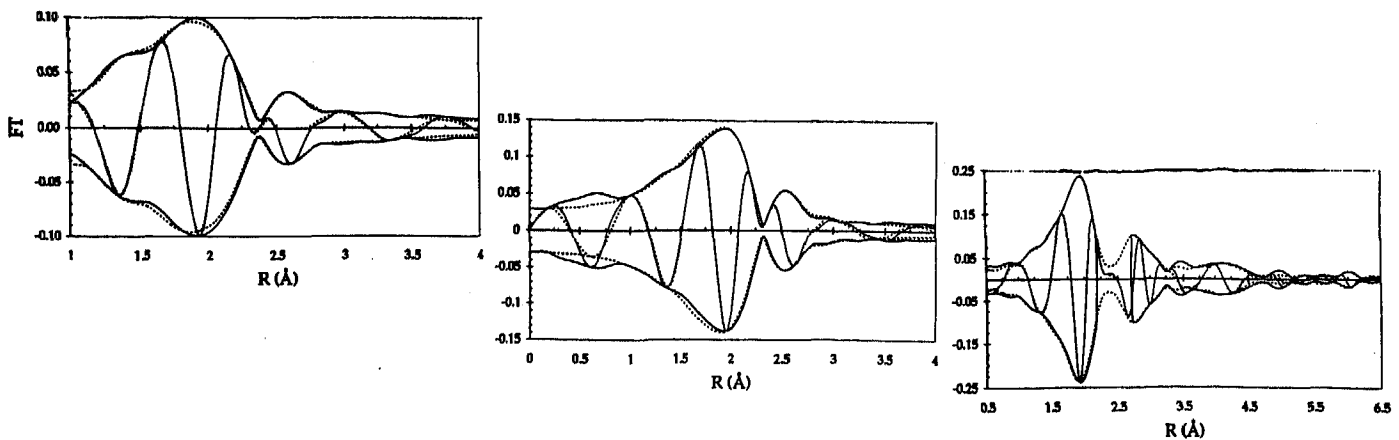






Figure 2-4. Magnitude and imaginary part of the $k^1$ weighed FT of the isolated $\chi(k)$ (solid curve) and fit (dotted curve) of (2) Mo6RT ($\Delta k$=3.70-12.84 $\AA^{-1}$), (3) Mo6423 ($\Delta k$=3.70-13.72 $\AA^{-1}$) and (4) Mo6673 ($\Delta k$=3.70-12.83 $\AA^{-1}$)

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The unstable $MoS_3$ can easily decompose into $MoS_2$ and S (or $H_2S$ in the presence of $H_2$). The expulsion of excess sulfur is manifested in the TPS profile by the $H_2S$ evolution peak, that coincides with $H_2$ consumption. From the color of the sample and the properties of $MoS_3$ it is likely that $MoS_2$ is formed during this transformation (eq. (2)).

$$MoS_3 + H_2 \rightarrow MoS_2 + H_2S \qquad (2)$$
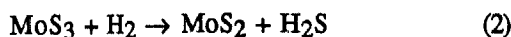
The Mo-S and the Mo-Mo coordination distances in Mo6673 correspond perfectly with the values of bulk $MoS_2$ (i.e. 2.41 and 3.16 Å). The coordination number for Mo-S after sulfidation at 673 K is close to six, as expected for the hexagonal coordination in $MoS_2$. The $k^1$-weighed FT's and the best fits on Mo6RT, Mo6423 and Mo6673 (cursive number indicating the sulfidation temperature) are shown in fig. 2-4. The valence of molybdenum changes during sulfidation. Unequivocally, molybdenum is initially present as a hexavalent ion in oxidic form, and tetravalent in its final sulfidic state. At intermediate stages, however, the valence is unknown. Pentavalent molybdenum exists in $MoS_3$.

Whilst the molybdenum-sulfur coordination probes the average first shell around the molybdenum atom and the S/Mo ratio by comparison with TPO, the $N_{Mo-Mo}$ is a direct measure of the size of the particle. In the case of Mo6673 the structure of the particle is precisely known, since it duplicates $R_{Mo-S}$ and $R_{Mo-Mo}$ of bulk $MoS_2$. Thus, assuming the $MoS_2$ structure, $N_{Mo-Mo}$ can be applied to estimate the size of the $MoS_2$-particles. Because of the simple two-dimensional structure of $MoS_2$, $N_{Mo-Mo}$ is a good measure of the slab size. If a two-dimensional layer (size $n \times n$) of hexagonally ordered molybdenum atoms is assumed, as in a $MoS_2$, four different positions can be distinguished. A simple formula for the theoretical value of N ($N_{model}$) as a function of the size of the slab can be derived (equation 3):

$$N^{model} = 6 - \frac{8}{n} + \frac{2}{n^2} \qquad (3)$$

This equation is only valid for cases, where $MoS_2$ is present. Thus, only the slab size of sample Mo6-673 can be estimated in this way. Substitution of the $N_{Mo-Mo}^{EXR}$ found after sulfidation (4.68, see table I) in equation 3 yields a value for $n$ of 5.0. A value of 5.0 corresponds to $n^2$=25 molybdenum atoms.

One aspect is neglected in this model for the calculation of the particle size of the $MoS_2$-crystallites: in a catalyst the $MoS_2$ phase is present as a stack of $MoS_2$ slabs. The distance between these slabs is 6.16 Å and cannot be properly analyzed by EXAFS. Therefore, a complementary technique is required to investigate the height of the $MoS_2$ stacks. TEM is very appropriate for this application[1,2,4,12-14]. TEM investigation of Mo6-673 reveals small slabs with an a maximum stack height of 3. Examination of Mo6-423 discloses no slabs.

## 4. Concluding Remarks

An *in situ* study on the structure of a $MoO_3$ catalyst during sulfidation can only be successful, when the initial structure of the oxidic phase is very well known. Therefore, a well defined and thoroughly characterized catalysts was used. It appears, that sulfidation roughly proceeds by $H_2S$ uptake at low temperatures (below 523 K), which transforms the catalyst into the brownish

$MoS_3$. Subsequently, the instable $MoS_3$ is reduced under the influence of $H_2$ to obtain $MoS_2$.

During sulfidation at low temperatures the clusters assume a structure comparable to that of $MoS_3$, evidenced by the characteristic, short $R_{Mo-Mo}$ of 2.75 Å. The exchange of oxygen for sulfur anions in Mo6 has simultaneously reduced the molybdenum to 5+. This implies that $S_2^{2-}$ anions are present, as in $MoS_3$.

The instability of the $MoS_3$-like structure in Mo6423 leads to expulsion of $H_2S$ at approx. 553 K under consumption of $H_2$. The eventually formed cluster has the structure of $MoS_2$, as shown by the $R_{Mo-S}$ value of 2.41 Å and the $R_{Mo-Mo}$ value of 3.16 Å. The $N_{Mo-S}$ value perfectly matches the 6-coordination in $MoS_2$. This is in agreement with the black color of the sample. The two dimensional slab size can be estimated from $N_{Mo-Mo}$ by a simple model. A slab size of approximately 25 molybdenum atoms is found. The mean stack height, derived from TEM is ca. 2-3.

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