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The Structure of Well Defined SiO₂ Supported MoO₃ Clusters during Sulfidation. *An in situ EXAFS-study*

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The sulfidation of a well defined MoO₃/SiO₂ catalyst has been examined by means of TPS, EXAFS, and TEM. The oxidic clusters in a 5.6 wt% MoO₃/SiO₂ catalyst are transformed into almost completely sulfided particles (MoO_xS_y) by O-S exchange at RT. A molybdenum-sulfido particle that resembles the MoS₃ structure is formed during sulfidation at 423 K. The MoS₂ phase is formed at temperatures between 523 and 573 K. The transition of MoS₃ into MoS₂ can be monitored by evolution of H₂S from the catalyst, with simultaneous consumption of H₂. The twodimensional size of the MoS₂ 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 MoO₃ 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)}, MES⁴⁻⁷⁾, and EXAFS⁸⁻¹¹⁾ are needed. The formation of MoS₂ slabs can be elegantly established with (High Resolution) TEM¹²⁻¹⁴⁾.

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 Al₂O₃ is its tendency to form spinels with Co and Ni¹⁵⁾ that possess low activity in hydrotreating reactions and its poor resistance toward acid gases, like SO₂. SiO₂ does not suffer from the latter disadvantage, but it is known to form Co- and Ni-(hydro)silicates.

In this paper, a well defined MoO₃/SiO₂ catalysts will be used for a study on the sulfidation behavior. The process of sulfidation can be easily followed by TPS while monitoring both [H₂S] and [H₂]. 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 MoO₃ 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 μ m) in a 100 ml min⁻¹ flow of H₂S/H₂/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 N₂, 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 Na₂MoO₄ and MoS₂.

3. RESULTS AND DISCUSSION

The TPS profile of Mo6 is presented in fig. 1. Both H₂S and H₂ 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	$\Delta\sigma^2$ ($\cdot 10^{-4} \text{ \AA}^2$)	$s\Delta\sigma^2$	R ($\text{\AA}$)	s_R	E_o eV	sE^o
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):

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 $[Mo_2^VS_4(S_2)_2]^{2-}$, $[Mo_2(S_2)_6]^{2-}$ or $Mo_2S_8^{2-}$. 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 ($R \sim 2.78 \text{ \AA}$).

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 ($\Delta k = 3.70\text{--}12.84 \text{ \AA}^{-1}$), (3) Mo6423 ($\Delta k = 3.70\text{--}13.72 \text{ \AA}^{-1}$) and (4) Mo6673 ($\Delta k = 3.70\text{--}12.83 \text{ \AA}^{-1}$)

The unstable MoS₃ can easily decompose into MoS₂ and S (or H₂S in the presence of H₂). The expulsion of excess sulfur is manifested in the TPS profile by the H₂S evolution peak, that coincides with H₂ consumption. From the color of the sample and the properties of MoS₃ it is likely that MoS₂ is formed during this transformation (eq. (2)).

The Mo-S and the Mo-Mo coordination distances in Mo6673 correspond perfectly with the values of bulk MoS₂ (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 MoS₂. 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 MoS₃.

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 MoS₂. Thus, assuming the MoS₂ structure, N_{Mo-Mo} can be applied to estimate the size of the MoS₂-particles. Because of the simple two-dimensional structure of MoS₂, N_{Mo-Mo} is a good measure of the slab size. If a two-dimensional layer (size *n* × *n*) of hexagonally ordered molybdenum atoms is assumed, as in a MoS₂, 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):

$$N_{\text{model}} = 6 - \frac{8}{n} + \frac{2}{n^2} \quad (3)$$

This equation is only valid for cases, where MoS₂ is present. Thus, only the slab size of sample Mo6-673 can be estimated in this way. Substitution of the N_{Mo-Mo}^{exp} 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 MoS₂-crystallites: in a catalyst the MoS₂ phase is present as a stack of MoS₂ 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 MoS₂ 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 MoO₃ 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 H₂S uptake at low temperatures (below 523 K), which transforms the catalyst into the brownish

MoS₃. Subsequently, the instable MoS₃ is reduced under the influence of H₂ to obtain MoS₂.

During sulfidation at low temperatures the clusters assume a structure comparable to that of MoS₃, 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 S₂²⁻ anions are present, as in MoS₃.

The instability of the MoS₃-like structure in Mo6423 leads to expulsion of H₂S at approx. 553 K under consumption of H₂. The eventually formed cluster has the structure of MoS₂, 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 MoS₂. 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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