The observation of nanometer-sized entities in sulphided Mo-based catalysts on various supports

P.J. Kooyman [a], E.J.M. Hensen [b,*], A.M. de Jong [b], J.W. Niemantsverdriet [b] and J.A.R. van Veen [c]

[a] *National Centre for High Resolution Electron Microscopy, Rotterdamseweg 137, 2628 AL Delft, The Netherlands*
[b] *Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*
[c] *Shell Research and Technology Centre Amsterdam, PO Box 38000, 1030 BN Amsterdam, The Netherlands*

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The progressive sulphidation of molybdenum-based hydrotreating model catalysts is studied using HRTEM and XPS. The catalysts are sulphided quasi *in situ* and prepared for TEM measurements in a glovebox. Subsequently, a specially developed vacuum-transfer specimen holder is used for transfer to the TEM. Using this procedure, a previously unknown feature is observed in the catalysts. Apart from the well-known slab-like structure of bulk molybdenum disulphide, nanometer-sized spherical entities of molybdenum sulphide or oxysulphide are observed. For a series of model CoMo/silica catalysts, these "spots" predominantly occur after mild sulphidation procedures. At higher sulphidation temperatures, these spots exist next to the slabs of MoS_2-like material. Comparison with practical molybdenum-based hydrotreating catalysts shows that these, too, can contain spots next to or instead of slabs, depending on precursor preparation and sulphidation procedures.

KEY WORDS: molybdenum sulphide; hydrotreating catalysis; characterisation; TEM; XPS; nanometer-sized entities

1. Introduction

Catalysts based on molybdenum sulphide are widely used in the petrochemical industry. Due to their importance in processes such as hydrodesulphurisation (HDS) of oil, a lot of research effort is spent in order to try to understand what the active sites are and how the efficiency of these catalysts can be improved.

The active phase in Mo-based hydrotreating catalysts is generally considered to consist of MoS_2 slabs with the promoter (Co, Ni) atoms decorating their edges. These slabs can easily be observed using transmission electron microscopy (TEM), and usually no other sulphidic phases are present (with the exception of bulk Co or Ni sulphides in sub-optimal catalysts).

The structure of the active phase for sulphided tungsten-based catalysts is expected to be similar to that of their molybdenum counterparts, indicating that slabs of Ni-decorated WS_2 are expected to be the main feature in TEM images of these catalysts. However, in a recent quasi *in situ* HRTEM study of sulphided NiW/Al_2O_3 catalysts, besides the expected slabs, also nanometer- and sub-nanometer-sized particles were observed, which were identified as (at least partially) sulphided W-containing species [1]. The performance of such partially sulphided catalysts in, *e.g.*, liquid-phase DBT HDS was found to be surprisingly high.

* Current address: Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

The probability of detecting such (sub-)nanometer particles ("spots") in TEM images of practical supported (Co, Ni)Mo catalysts is low for several reasons. Firstly, in most studies the samples are exposed to ambient air between sulphidation and TEM analysis. The large slabs are already less stable under the electron beam in the TEM when they have been exposed to air, and the spots are much more sensitive to exposure to air [2]. Secondly, Mo-based catalysts are easier to sulphide than W-based catalysts, presumably making it difficult to arrest the sulphiding process at a stage in which an intermediate Mo (oxy)sulphidic phase is dominant. Thirdly, many TEM studies on practical molybdenum-sulphide-based catalysts use relatively thick microtomed specimens. The thickness of such specimens limits the visibility of (sub-)nanometer particles.

Eijsbouts *et al.* [3,4] presumed that very small MoS_2 particles, $\sim$0.5 nm diameter, exist in mildly sulphided supported (Co,Ni)Mo catalysts, although they were found to be invisible in their TEM work. However, their TEM work was performed *ex situ* on microtomed samples. The present experimental conditions (quasi *in situ*, ground sample) would give a higher possibility of observing such small MoS_2 particles, if in fact they are present in the samples. In calcined (non-sulphided) catalysts prepared for TEM by grinding small (oxidic) particles, from about 0.5 nm in diameter, are sometimes observed [2,5,6], indicating that such small particles can indeed be detected using TEM/HREM, in line with our observations on W-based catalysts [1] mentioned above.

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2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of $CoMo/SiO_2$ model catalysts

"Stöber" silica spheres [7] are prepared by controlled hydrolysis and condensation of tetraethylorthosilicate (TEOS) in mixtures of water/ammonia and ethanol. This spherical silica model support (pore volume 1 ml/g, surface area 30 m^2/g) has been used to prepare sulphided CoMo catalysts. The support was dried at 385 K for 24 h before impregnation. The catalyst precursor was prepared by impregnation with an aqueous solution of Co and Mo complexed with nitrilotriacetic acid (NTA) [8]. The loading of this model catalyst precursor is 1.4 wt% Mo, which gives a surface concentration of Mo equivalent to the loading of 12 wt% Mo on a 250 m^2/g silica support. Co content is 0.3 wt%.

The model catalysts were sulphided quasi *in situ*, using a mixture of 10% H_2S in H_2 at a flow rate of 60 ml/min while heating the catalyst to the desired sulphidation temperature at a rate of 2 K/min. The temperature was then kept at the sulphidation temperature for half an hour. Subsequently, the samples were cooled to room temperature in flowing He, transferred to a glovebox and prepared for TEM or XPS without exposure to air.

2.1.2. Preparation of $NiMo/Al_2O_3$

A sieve fraction (125–250 μm) of alumina (Ketjen CK300, pore volume 0.66 ml/g, surface area 263 m^2/g) was used as support material. The support was calcined at 575 K for 2 h and dried overnight at 385 K before impregnation. The catalyst was prepared by co-impregnation using ammonium heptamolybdate (Merck, >97%) and nickel nitrate (Merck, p.a.) solution in ammonia. After impregnation, the catalyst was dried in air for 16 h at 385 K and calcined in static air for 2 h at 725 K after heating to this temperature in 1 h. Catalyst loading as determined using AAS is 1.4 wt% Ni and 9.6 wt% Mo.

The catalyst was sulphided in a mixture of H_2S/H_2 (Scott, 10% H_2S). The gas flow was kept at 60 ml/min, while heating the catalyst at a rate of 6 K/min to 675 K. The temperature was then kept at 675 K for 2 h. Subsequently, the sample was cooled to room temperature in flowing He. The catalyst was transferred to a glovebox and prepared for TEM without exposure to ambient air.

2.1.3. Preparation of Mo/SiO_2

A sieve fraction of 125–250 μm of silica (Shell, pore volume 1.25 ml/g, surface area 210 m^2/g) was used for catalyst preparation. The support was calcined at 575 K for 2 h and dried overnight at 385 K before pore volume impregnation with ammonium heptamolybdate (Merck, >97%) solution in ammonia. The catalyst was dried for 1 h at room temperature, subsequently at 385 K overnight, and finally calcined in static air for 2 h at 725 K after heating in 1 h to this temperature. Catalyst loading as determined using AAS is 7.5 wt%.

The catalyst was sulphided using the procedure described above for the NiMo/alumina catalyst.

2.2. (High resolution) transmission electron microscopy

High resolution transmission electron microscopy was performed using a Philips CM30ST equipped with a field emission gun operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a Cu 400 mesh grid under exclusion of air in a protective atmosphere glovebox (Ar, maximum partial pressures for oxygen and water of 1 ppm) by dripping a few drops of a suspension of the ground catalyst in *n*-hexane onto the grid followed by drying at ambient temperature. Samples were transferred to the microscope in a special vacuum-transfer sample holder under exclusion of air [9]. Qualitative EDX elemental analysis was performed using a LINK EDX system.

2.3. X-ray photoelectron spectroscopy (XPS)

The state of sulphidation of the CoMo/Stöber silica sphere model catalysts was studied using XPS. XPS spectra were obtained with a VG Escalab 200 spectrometer equipped with an Al Kα source and a hemispherical analyser connected to a five-channel detector. Measurements were performed at 20 eV pass energy. Energy correction was performed by using the C 1 s peak at 284.7 eV as a reference.

3. Results and discussion

All samples presented in this paper show the presence of nanometer-sized entities. These nanometer-sized entities are present either instead of or next to the well-known slabs of MoS_2-like material. Areas where these entities are the only visible features next to the support material contain both the relevant metals (Mo, Mo and Ni, or Mo and Co) and sulphur, according to EDX elemental analysis. However, TEM and EDX analysis alone, although they give detailed local information, cannot determine the degree of sulphidation of these systems. On the other hand, XPS analysis can give detailed (albeit averaged) information on the degree of sulphidation of these systems. Thus, by combining TEM and XPS data, we can draw more precise conclusions concerning the degree of sulphidation of the spots.

The observed nanometer-sized entities are very similar to the spots described for tungsten-based hydrotreating catalysts [1]. For tungsten-based sulphidic catalysts, the nanometer-sized entities have been shown to be partially sulphided species with significant catalytic activity. For the molybdenum-based spots reported here, the catalytic activity will be investigated in a future research project.

3.1. Practical catalysts

An example of these nanometer-sized entities as they have been observed for a sulphided NiMo/alumina catalyst

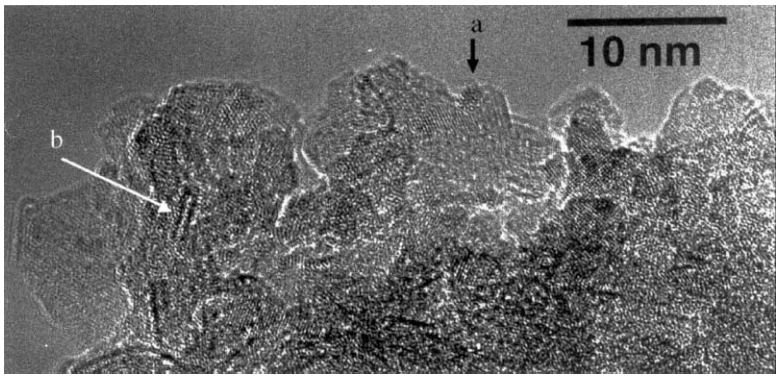

Figure 1. High resolution TEM image of 675 K sulphided NiMo/alumina. One of the nanometer-sized entities is indicated by an arrow labelled a, one small stack of slabs is indicated by an arrow labelled b.

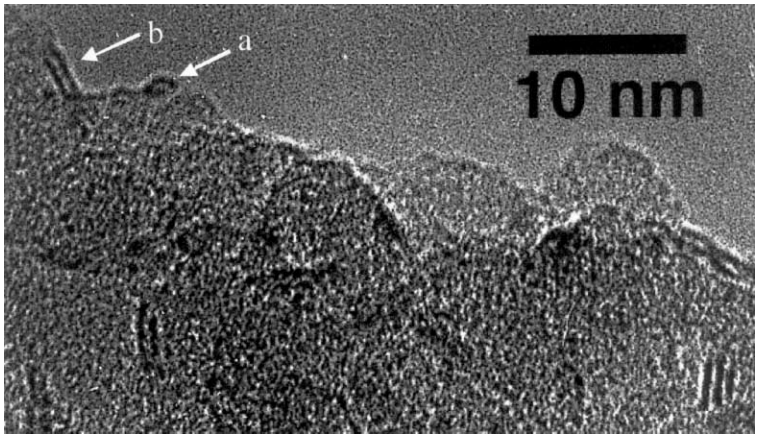

Figure 2. High resolution TEM image of 675 K sulphided Mo/silica. One of the nanometer-sized entities is indicated by an arrow labelled a, one small stack of slabs is indicated by an arrow labelled b.

Table 1
Sulphidation temperatures and TEM observations of the model catalysts.

Sulphidation T (K)	Spot size (nm)	Slab size (nm)
350	1.2	–
400	1.3	–
450	1.3	–
500	1.6	2–3
675	1.7	2–15

is shown in figure 1. One of the spots is indicated with an arrow labelled a. A small stack of slabs is indicated with an arrow labelled b. The lattice of the alumina is also clearly visible in this image as parallel lines.

Even for pure Mo sulphided catalysts, spots are sometimes observed. Figure 2 is an example of a sulphided Mo/silica catalyst where both spots and slabs are present simultaneously. One of the spots is indicated with an arrow labelled a. A small stack of slabs is indicated with an arrow labelled b.

3.2. Model catalysts

The two examples described above already show that the formation of spots is possible for various systems of

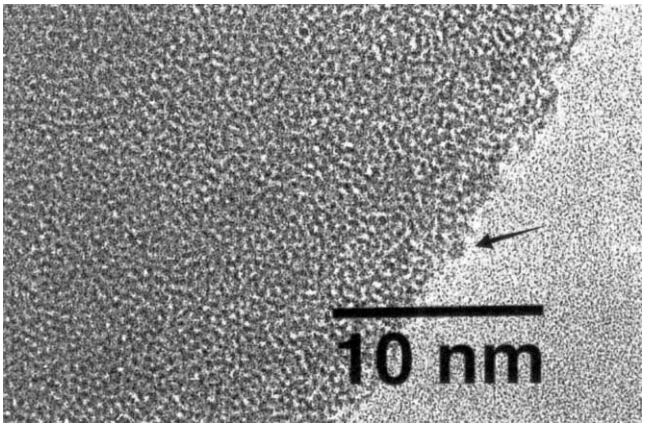

Figure 3. High resolution TEM image of 350 K sulphided CoMo/Stöber silica sphere. The arrow indicates one of the nanometer-sized entities.

Mo-based sulphided catalysts. In order to investigate their formation properly, a series of model catalysts has been prepared, consisting of sulphided CoMo on Stöber silica spheres. Small portions of the same batch of CoMo-loaded Stöber silica spheres were sulphided at different sulphidation temperatures. Each sample obtained in this way was studied using TEM and XPS. The sulphidation temperatures used are listed in table 1. Figures 3 through 7 show HRTEM

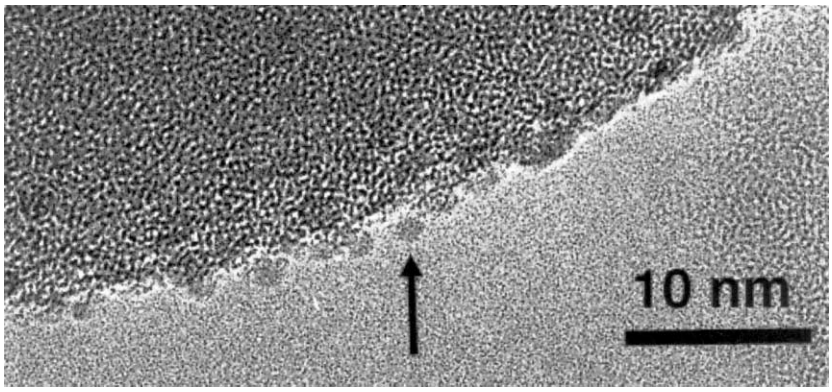

Figure 4. High resolution TEM image of 400 K sulphided CoMo/Stöber silica sphere. The arrow indicates one of the nanometer-sized entities.

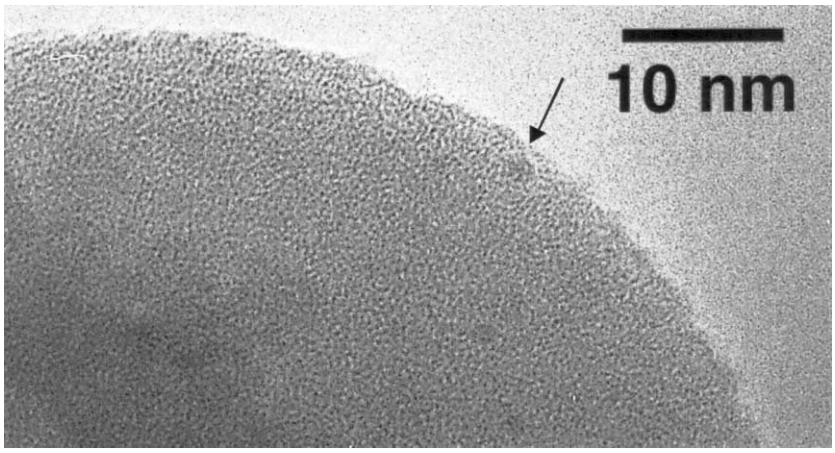

Figure 5. High resolution TEM image of 450 K sulphided CoMo/Stöber silica sphere. The arrow indicates one of the nanometer-sized entities.

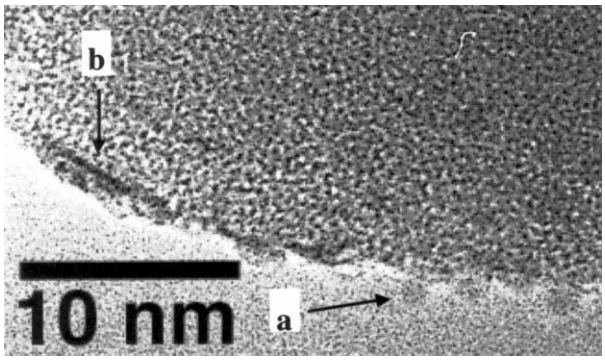

Figure 6. High resolution TEM image of 500 K sulphided CoMo/Stöber silica sphere. One of the nanometer-sized entities is indicated by an arrow labelled a, one small slab is indicated by an arrow labelled b.

images of the sulphided samples at the various sulphidation temperatures.

The HRTEM images clearly show the development of the (oxy)sulphidic phase with increasing sulphidation temperature. At low sulphidation temperature (350 K), a low density of 1.2 nm small particles is found on the silica spheres. With increasing sulphidation temperature, the size and density of these spots increase. Starting at a sulphidation temperature of 500 K, some small slabs (2–3 nm in length) are observed next to the spots, and a sulphidation temperature of 675 K gives rise to the presence of substantial amounts of slabs up to about 15 nm in length, still next to spots. EDX elemental analysis shows that areas that show spots in the TEM images contain Mo, Co and S next to Si and O. This indicates that at the 10 nm scale no segregation of Mo and Co has occurred.

Table 2
Summary of conclusions from XPS.

Sulphidation *T* (K)	Mo	Co
350	Partially reduced	Oxidic
400	Largely sulphided	Oxidic
450	Almost fully sulphided	Partly sulphided
500	Fully sulphided	Fully sulphided
675	Fully sulphided	Fully sulphided

The XPS data, summarised in table 2, also show the development of the (oxy)sulphidic phase. For Mo, XPS spectra of the oxidic catalyst precursor reveal only Mo 3d peaks at a binding energy corresponding to a Mo^{6+} species. At 350 K, a shoulder develops at a binding energy of 229.5 eV, which indicates that Mo is already partially reduced. At 450 K, the majority of the Mo is transformed to a species with a binding energy of 229.2 eV, indicating that Mo is mostly in an (oxy)sulphidic form. The important point to note is that sulphidation of Mo takes place between 350 and 450 K, while the larger part has already been converted to the sul-

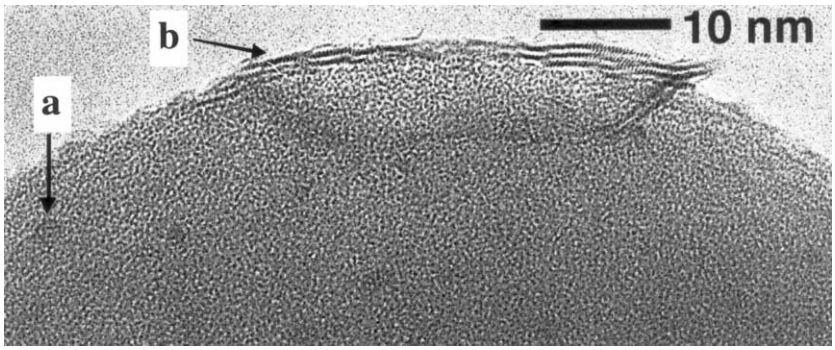

Figure 7. High resolution TEM image of 675 K sulphided CoMo/Stöber silica sphere. One of the nanometer-sized entities is indicated by an arrow labelled a, one stack of slabs is indicated by an arrow labelled b.

phidic state at 400 K. At 675 K, the Mo is fully sulphided. The Co 2p spectra of the oxidic catalyst precursor as well as those after sulphidation at 350 and 400 K are characteristic of oxidic cobalt, with a main peak at 781.5 eV. Spectra of catalysts sulphided at 500 K and higher show a Co 2p peak at 779.0 eV binding energy, fully characteristic of sulphidic cobalt, while the catalyst sulphided at 450 K is in the transition between the two states. Thus, complete sulphidation of Co in these catalysts takes place between 450 and 500 K. Due to charging of the silica support material, the quality of the XPS spectra is not optimal. However, they closely resemble the high-quality spectra published for the same CoMo system on a SiO_2/Si(100) (conducting) model support [10], and we refer to the latter for detailed interpretation.

We propose that the development of the sulphided phase in CoMo/silica catalysts proceeds to the well-known slabs *via* nanometer-sized entities. At sulphidation temperatures where these spots predominate, XPS shows partially sulphided Co and Mo to be present. EDX elemental analysis shows that areas where only spots are observed contain both Co and Mo next to sulphur. This is an indication that the spots do not consist of segregated CoS_x. Areas where only slabs are observed show EDX elemental analysis spectra that are very similar to the spectra of areas where only spots are observed. For the catalysts studied here, no large particles of segregated CoS_x have been found.

4. Conclusions

Depending on the exact preparation conditions of the catalyst under study, Mo-containing (oxy)sulphidic nanometer-sized entities are observed instead of or next to the well-known slabs of MoS_2-like material. These nanometer-sized entities can only be observed using HRTEM when a quasi *in situ* preparation procedure is employed, as they are very sensitive to air and/or moisture.

For a CoMo/silica model system, a series of catalysts shows the development of the spots from 1.2 to 1.7 nm upon increasing the sulphidation temperature from 350 to 675 K. Additionally, slabs are observed from a sulphidation temperature of 500 K. The slabs also increase in size upon increasing the sulphidation temperature.

Practical Mo-based sulphidic catalysts sometimes also show spots next to slabs. This is illustrated for a NiMo/alumina and for a Mo/silica catalyst.

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