Catalysis Letters 47 (1997) 177–182

Sulfur bonding in MoS_2 and Co–Mo–S structures

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Received 3 April 1997; accepted 11 July 1997

The structure and bonding in small MoS_2 structures with and without Co is studied theoretically using self-consistent density functional theory with a non-local exchange-correlation energy. The structures model the catalysts used extensively in hydrotreating. We study in detail the structure and binding energies as a function of the amount of sulfur. The calculations show that extensive reconstructions occur at the two types of MoS_2 edges where the sulfur dimerizes and occupies non-lattice positions. These structures are shown to be in good agreement with available experimental data. We also study the energy required to form sulfur vacancies, which are believed to be the active sites for many hydrotreating reactions. The presence of Co atoms at the edges is shown to lead to a significant lowering of the metal–sulfur binding energy. This imposes an increase in the concentration of active sites for the reactions and may thus explain the promoting effect of Co.

Keywords: sulfur bonding, MoS_2 structures, Co–Mo–S structures

1. Introduction

Hydrodesulfurization (HDS) of oil fractions is an important refining process [1–4]. The importance is related to the increased demand to convert heavier and more sulfur-rich feed stocks and to the need to make oil products more environmentally acceptable by reducing the sulfur content. Consequently, there is a demand for introducing so-called deep HDS, which will require new processing schemes and more active catalysts. In order to aid the development of new HDS catalysts, several useful structure–activity relationships have been established for both unpromoted and promoted catalysts [1]. For the unpromoted catalysts, the activity has been attributed to sites at the MoS_2 edges, whereas for Co or Ni promoted catalysts, the Co–Mo–S and Ni–Mo–S structures are responsible for the activity. For all these systems and for transition metal sulfides in general, the metal–sulfur biding energy has been suggested to be one of the key parameters determining the activity [5,6], even though the specific role of the sulfur binding energy has varied in the different studies. It is generally believed that completely sulfided catalysts will be unable to adsorb the sulfur-containing molecules, and that sulfur vacancies must be created to provide catalytically active sites. The number of sulfur vacancies is therefore a key measure of the catalytic activity, and this number is closely correlated to the sulfur binding energy [6].

Several questions remain unanswered regarding the structure of the active MoS_2 and Co–Mo–S (Ni–Mo–S), and a key problem has been that the active structures are present as small nano-crystals, which cannot be characterized by diffraction methods. The conclusions regarding the three-dimensional structure have therefore to a large extent been based on radial distribution functions determined by extended X-ray absorption fine structure (EXAFS) (see ref. [7] for a review). This has provided insight into the overall structure, but it does not allow unique conclusions, and several different views have appeared regarding the detailed structure of Co–Mo–S, see e.g. refs. [7,8].

In order to shed further light on the structure of the active catalysts and their interaction with sulfur, we have carried out a range of self-consistent density functional theory (DFT) calculations for the MoS_2 and Co–Mo–S structures. Our results provide evidence for new structures of the basic MoS_2 unit, allowing an improved understanding of several experimental observations. The calculations also show how Co added to the MoS_2 structure lowers the S binding energy at the edges and thereby provides more active sites.

2. Calculational method

In the last few years, it has become possible to calculate semi-quantitatively adsorption energies and surface reaction activation energies for realistic systems [9,10]. This development is based on density functional theory and a combination of new, non-local exchange-correlation functionals [11], better numerical algorithms [12,13] and faster computers. In the present letter, we apply this technique to the structure and bonding in small Mo and Co–Mo sulfides.

Our results are all based on fully self-consistent DFT calculations. The exchange-correlation energy is treated using the generalized gradient approximation (GGA)

[11], and the ionic cores are described by pseudopotentials [14].

The details of the calculations are as follows: The pseudo-wave functions are expanded in plane waves. For the MoS_2 system, the cutoff energy is 40 Ry, and for systems including Co, which has more tightly bound valence d electrons, the cutoff is 50 Ry. The calculations are performed with 3 $\boldsymbol{k}$-points in the irreducible Brillouin zone. For all configurations, a full structure relaxation has been carried out. The occupation numbers are Fermi distributed with an electronic temperature of $kT = 0.025$ eV, and the total energies are extrapolated to $T = 0$ K. Convergence in cutoff and number of $\boldsymbol{k}$-points have been checked. We also verified that for bulk Mo metal, Co metal and MoS_2, the method gives equilibrium lattice constants (3.11 Å , 2.52 Å, and $d_{\mathrm{Mo-Mo}} = 3.12$ Å, respectively) in excellent agreement with experiments (3.15 Å [15], 2.51 Å [16], and 3.16 Å [17]). Likewise, Toulhoat et al. have recently shown that DFT-GGA calculations give a good description of the bonding in bulk transition metal sulfides [18].

Bulk MoS_2 consists of S–Mo–S layers held together by van der Waals forces. The catalytically active MoS_2 structures are known to be present as two- or three-dimensional nano-crystals with particle diameters around 10 Å [1], and the catalytically active sites are believed to be at the edges. We use a model consisting of single layer, one-dimensional MoS_2 chains, two Mo atoms in cross section. These chains expose the two types of edges present in MoS_2; the Mo-terminated $(10\bar{1}0)$ edge (termed Mo-edge in figure 1a) and the S-terminated $(\bar{1}010)$ edge (termed S-edge in figure 1a).

The model has the advantage that periodic boundary conditions can be applied along the chains. In the other two directions, we also impose periodic boundary conditions by repeating the chains with a periodicity of 12 Å perpendicular to the MoS_2 planes, and 11 Å perpendicular to the edges. The set up of the calculation and the super cell used is shown in figure 1. The super cell size is held fixed in all calculations.

Since the S- and Mo-edges have different dipole moments, a dipole layer is added between the chains in order to correct for this difference. The calculated lattice constant of an infinite MoS_2 (bulk) system is used as starting input in the present calculations.

In the following, we first consider the MoS_2 structure and subsequently study the effect of adding Co.

3. Structure and bonding of the MoS_2 catalyst

In order to find the equilibrium structure of the MoS_2 chain, we set up a number of different structures and allow these to relax to find the minimum energy configuration. We define the sulfur binding energy, ΔE_S, as:

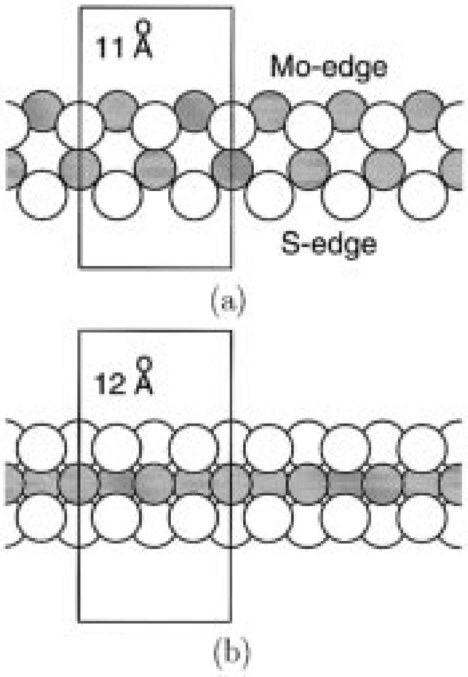

Figure 1. Illustration of the stoichiometric MoS_2 model. The white circles denote S atoms, and the light grey ones are Mo atoms. The super cell is indicated by a rectangular box. The S–Mo–S chains are separated by vacuum. (a) Top view. (b) Side view, seen from the S terminated edge.

$$\begin{aligned}\Delta E_S = {} & E(\text{chain with vacancy}) - E(\text{chain}) \\ & - E(H_2) + E(H_2S)\,. \end{aligned} \tag{1}$$

ΔE_S is referred to the energy of H_2 and H_2S in the gas phase and it is therefore the reaction enthalpy for the reaction:

$$H_2(g) + S{*} \rightleftharpoons H_2S(g) + {*} \tag{2}$$

Here $S{*}$ denotes the “adsorbed” S atom, and $*$ is an S vacancy. We neglect effects of zero point energies throughout this work. They are small on the scale of energies considered here.

We start by adding the maximum number of S atoms possible to the structure in figure 1. The S-edge is already full, but at the Mo-edge, we can add another two S atoms per Mo-edge atom. The resulting, relaxed structure is shown from the Mo-edge side and the S-edge side in figures 2a and 3a, respectively. Here it is seen that the S atoms have a tendency to dimerize at both edges. At the S-edge, there is a local minimum in which the S atoms are close to the perfect lattice position. However, this configuration is metastable relative to the dimerized structure. At the Mo-edge, the non-dimerized structure is extremely unstable since the S atoms coordinate to only a single Mo atom.

We now investigate sulfur bonding to the Mo-edge in more detail. By removing the S atoms one by one and calculating ΔE_S for each removal, we can identify the structure which is stable under usual gas phase H_2/H_2S

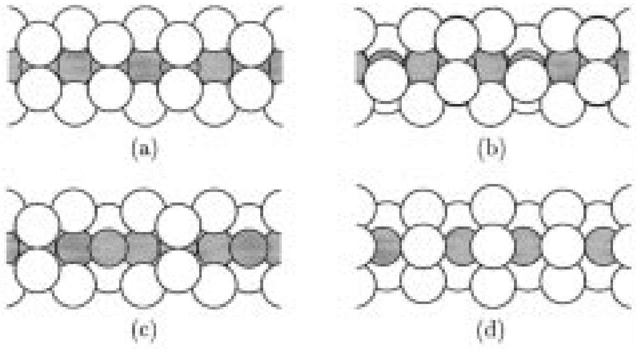

Figure 2. Illustration of MoS_2 structures. Side view, seen from the Mo-edge side. The white circles denote S atoms, and the light grey ones are Mo atoms. (a) Two S atoms added per Mo-edge atom. (b) One S atom per super cell is removed from structure a. (c) The remaining S-dimer atom is removed from structure b. (d) One S atom is removed from the S dimer in structure b.

ratios. In addition, this gives us information of the energy required to remove S atoms from this most stable structure, which may further be related to the probability of creating active sites on the catalyst.

The S atoms in the dimerized Mo-edge structure in figure 2a, are very stable. The energy required to remove an S atom from a dimer at the Mo-edge is 126 kJ/mol as shown in table 1. In this calculation, we have restrained the neighboring dimers to keep their position along the chain (but otherwise allowed to relax completely), and the relaxed structure is shown in figure 2b. We do this to mimic the removal of single S atoms at a long Mo-edge. Due to the periodic boundary conditions imposed, we are actually removing an S atom from every second dimer, and if this structure is allowed to relax freely the whole edge restructures. This is not feasible under usual working conditions, since the large ΔE_S means that the vacancy concentration at the Mo-edge is extremely small.

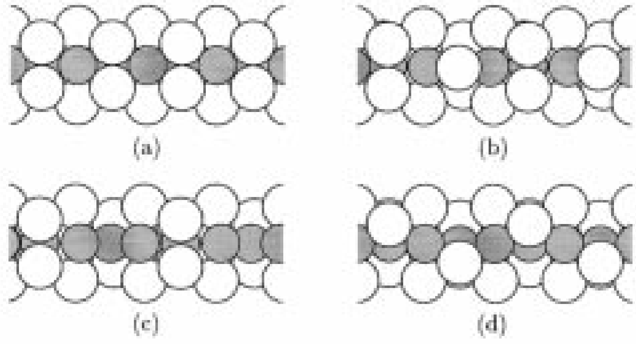

Figure 3. Illustration of MoS_2 structures. Side view, seen from the S-edge side. The white circles denote S atoms, and the light grey ones are Mo atoms. (a) The dimerized S-edge. (b) One S atom per super cell is removed from structure a. (c) The remaining S-dimer atom is removed from structure b. (d) One S atom is removed from the S dimer in structure b.

Table 1
Calculated sulfur binding energies for the MoS_2 structures shown in figure 2. Removal from Mo-edge. "initial" refers to the initial structure in figure 2, and "final" is the obtained structure after removal of an S atom

Mo-edge		
initial	final	ΔE_S (kJ/mol)
a	b	126
b	c	143
b	d	−19

Removal of the second S atom from the S dimer results in the configuration depicted in figure 2c. This also requires a large energy of 143 kJ/mol, see table 1.

If we instead remove one S atom from every dimer, i.e. remove two S atoms from the Mo-edge in each unit cell, the structure shown in figure 2d emerges. It can be seen that the edge is completely restructured. The S atoms have moved sideways, and each S now binds to two Mo atoms. In table 1 it is seen, that ΔE_S for this process is negative with respect to H_2 and H_2S in the gas phase, −19 kJ/mol. It must be emphasized, that in order to reach this point the first S atom has to be removed, which requires a much larger energy; 126 kJ/mol, see table 1.

We conclude that it is energetically expensive to remove S atoms from the Mo-edge. Under normal reaction conditions, the Mo-edge will be covered by S dimers as shown in figure 2a.

We next consider the stability of the S atoms at the S-edge. When calculating the sulfur binding energy, the Mo-edge with the dimer termination of figure 2a is applied. The first S atom removed from the S-edge has a binding energy, ΔE_S, of 47 kJ/mol, see table 2.

Here the S atoms already coordinate to two Mo atoms and the possibility of a restructuring parallel to the edge like in figure 2d is not present; hence it is not necessary to impose constraints on the calculation due to the small unit cell used. Removing more than one S atom per super cell costs more than 100 kJ/mol. The relaxed structures after removal of one or two S atoms from the S-edge are shown in figures 3b and 3c, respectively. The S vacancy creation, in which structure a is the initial and b is the final configuration, is accompanied by large relaxations

Table 2
Calculated sulfur binding energies for the MoS_2 structures shown in figure 3. Removal from S-edge. "initial" refers to the initial structure in figure 3, and "final" is the obtained structure after removal of an S atom

S-edge		
initial	final	ΔE_S (kJ/mol)
a	b	47
b	c	326
b	d	148

of the S atoms underneath the vacancy as seen in figure 3b. After the vacancy is created, the S atom beneath the S vacancy moves to a position in the plane of the Mo atoms. Removal of one S atom from each S dimer on the S-edge yields the structure shown in figure 3d.

In addition, we have tried removing three-coordinated S atoms from the basal plane of bulk (two-dimensional) MoS_2. ΔE_S for this process is 263 kJ/mol. These sites are thus not expected to be active in HDS, in agreement with surface science experiments [19].

We therefore conclude that the working catalyst will most probably have "filled", sulfur dimerized Mo-edges, and the S sites at the S-edges are mainly filled and dimerized. Vacancies created at the S-edges apparently provide the most easily accessible active sites.

The structure of figures 2a and 3a is quite different from the usual model of the active MoS_2 structure [1]. The structure is non-stoichiometric and has S restructuring at both edges. The structure we find is, however, completely compatible with available experimental observations. EXAFS typically shows a sulfur coordination number of six [1,17]. This does not support a stoichiometric model with bare Mo-edges, but it follows immediately from the present model, in which both edges have sulfur dimers. Experimental evidence for such structures has previously been provided based on X-ray photoelectron spectroscopy (XPS) experiments [20].

The calculated bond lengths are furthermore in reasonable agreement with results from EXAFS experiments. A top view of the MoS_2 structure without vacancies is shown in figure 4, and the calculated interatomic distances are presented in table 3. The atom numbers in figure 4 specify the atoms in table 3.

The average bond lengths deduced from EXAFS experiments, are $d_{\mathrm{Mo-S}} = 2.41$ Å [17] and $d_{\mathrm{Mo-Mo}} = 3.16$ Å [17]. The calculated Mo–S bond lengths vary around the calculated bulk MoS_2 value of 2.38 Å, close to the experimental value. Only the Mo–Mo distance across the chain appears too low. We suggest that this discrepancy is due to the relatively narrow model we use; the MoS_2 structures observed experimentally are typically broader. If we had placed one more MoS_2 row, the contraction would probably be less pronounced, and the width of the chain would resemble the diameter of an industrial catalyst particle more. Such calculations are, however, even more computationally demanding.

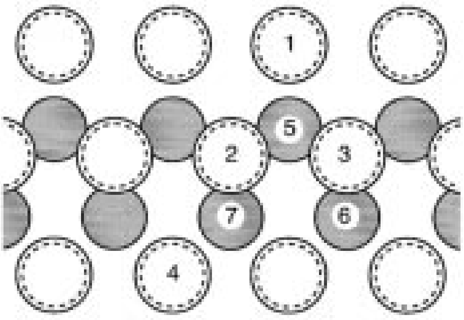

Figure 4. The MoS_2 configuration without vacancies. Top view. The white circles denote S atoms, the light grey ones are Mo atoms, and the dashed circles are S atoms in the bottom layer. Selected atoms are numbered.

Table 3
Calculated bond lengths for the MoS_2 structure without vacancy, shown in figure 4. The atom numbers refer to the ones in figure 4

Bond lengths (Å)	
Mo(5)–S(1)	2.43
Mo(5)–S(2)	2.40
Mo(5)–S(3)	2.40
Mo(6)–S(3)	2.34
Mo(7)–S(2)	2.34
Mo(7)–S(4)	2.42
Mo(7)–Mo(5)	2.85
Mo(7)–Mo(6)	3.12

4. The effect of Co

We now turn to the possible role of Co as a promoter for the HDS reaction. It has been established experimentally that the Co atoms are substituted into the MoS_2 edges, and that the promoting effect scales linearly with the amount of this Co–Mo–S edge structure [1].

The exact location of the Co atoms has not been established experimentally with certainty. We have started by calculating the energy difference between Mo substituted with Co at the Mo-edge and at the S-edge, and we find the latter to be more stable by 68 kJ/mol Co.

We hence continue by studying the effect of Co substituted at the S-edge. A key question is the effect of Co on the S vacancy formation energy; if Co lowers ΔE_S, the number of active sites will increase, explaining (at least partly) the promoting effect [6]. In table 4, we present ΔE_S for the Co containing structure. Clearly, the S atoms at the S-edge will be most strongly perturbed by the addition of Co at this edge, and since this sulfur is the most easily removed, even without Co, it is natural to concentrate on the S-edge sulfur.

Table 4
Calculated sulfur binding energies for the Co–Mo–S structures. The relaxed structures show the same type of relaxations as the ones in figure 3. Removal from S-edge. "initial" refers to the initial structure, and "final" is the obtained structure after removal of an S atom

S-edge		
initial	final	ΔE_S (kJ/mol)
a	b	−34
b	c	222
b	d	99

A comparison of the values in table 4 with the ones for the MoS_2 structure, see table 2, reveals a reduction in ΔE_S when S vacancies have a Co neighbor. In fact, the "first" S atom is unstable with respect to H_2S in the presence of H_2. We therefore suggest that the Co–Mo–S structure generally has coordinatively unsaturated Mo sites, except under extremely sulfiding conditions.

The configuration of the Co–Mo–S structure with one S atom removed from every super cell is depicted in figure 5. The Mo-edge has dimerized S, while the S-edge has S dimers and restructured S vacancies. The Co–Mo–S structure we deduce from the calculations is also in good agreement with available experimental evidence. To compare bond lengths, a top view of the Co–Mo–S configuration without and with vacancies is illustrated in figure 6. The corresponding interatomic distances are given in table 5, and the atom numbers refer to the ones in figure 6.

The experimental values of the bond lengths for the Co–Mo–S structure are $d_{\mathrm{Mo-S}} = 2.41$ Å [17], $d_{\mathrm{Co-S}} = 2.21$ Å [1] and $d_{\mathrm{Co-Mo}} = 2.85$ Å [8]. It is seen from table 5, that the calculated values are in good agreement with experimental observations, in particular for the more stable structure with vacancies. When we consider the Co–S and Co–Mo distances, the problems related to the narrow chain model discussed in section 3 are not present, because the Co is located at the edge and the lack of "bulk" Mo in the calculation will not be important.

When Co is substituted into the structure, the metal–sulfur bond lengths in general decrease, especially the ones in which the S is directly coordinated to Co, i.e. the bonds metal(7)–S(2) and metal(7)–S(4); compare tables 3 and 5.

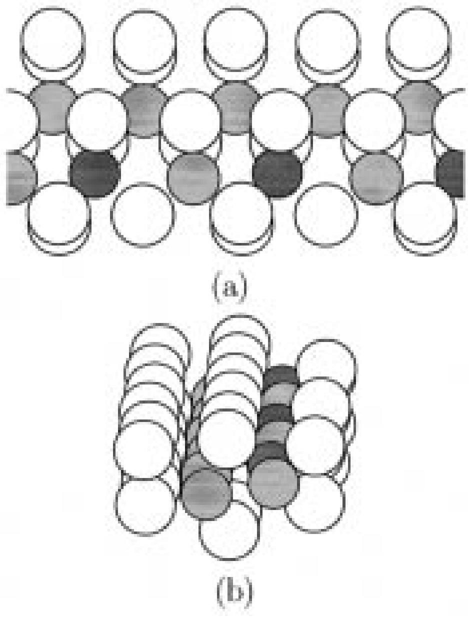

Figure 5. The active Co–Mo–S configuration. Top view. The white circles denote S atoms, the light grey ones are Mo atoms, and the dark grey circles are Co atoms. (a) Top view, slightly tilted. (b) Side view, slightly tilted.

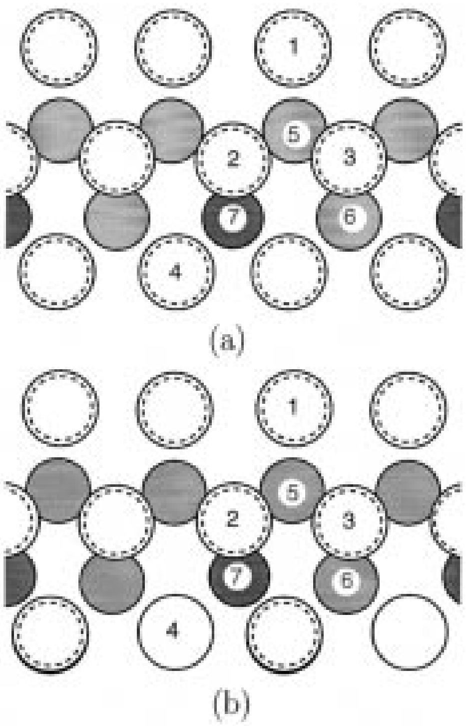

Figure 6. Illustration of two Co–Mo–S configurations. Top view. The white circles denote S atoms, the light grey ones are Mo atoms, and the dark grey circles are Co atoms. The dashed circles are S atoms in the bottom layer. Selected atoms are numbered. (a) Without vacancies. (b) With vacancies.

Table 5 shows that the bond lengths are in general shortest in the Co–Mo–S structure with the vacancy. When a vacancy is created, the atoms move closer together to maintain the same electronic density as before [21]. Thus the bond lengths decrease. In particular it is seen that the Co–Mo bonds are shortened when S is

Table 5
Calculated bond lengths for the Co–Mo–S structure without and with vacancies, illustrated in figure 6. The atom numbers refer to the ones in figure 6

Bond	Bond lengths (Å)	
	without vacancy	with vacancy
Mo(5)–S(1)	2.42	2.41
Mo(5)–S(2)	2.38	2.37
Mo(5)–S(3)	2.39	2.41
Mo(6)–S(3)	2.35	2.32
Co(7)–S(2)	2.21	2.20
Co(7)–S(4)	2.34	2.24
Co(7)–Mo(5)	2.87	2.72
Co(7)–Mo(6)	3.12	2.88

removed. This is in accordance with the bond energy model [6], which suggests that the stability of the S vacancy in the Co–Mo–S structure is related to an increased Co–Mo interaction in the absence of the S atom.

We have seen a good agreement between the bond lengths for the vacancy containing Co–Mo–S structure and experimental values and observed a high concentration of active sites, and we hence propose figure 5 to be a model of the active Co–Mo–S catalyst.

It is interesting to note that although the structure of figure 5 is different from the square pyramidal structure of Co–Mo–S favored in most recent papers on the topic, see e.g. ref. [1] for a review, nice agreement with experiment is found.

5. Conclusions

The conclusions of our calculations can be summarized as follows:

– It is possible to calculate sulfur binding energies on transition metal sulfides. Average bond lengths agree quite well with experimental values.

– A microscopic model of the MoS_2 catalyst has been suggested.

– Extensive reconstruction takes place at all MoS_2 edges, and the calculations have provided evidence for the presence of sulfur located in non-lattice positions. In particular we find that the edge S dimerizes.

– Substitution of some Mo atoms at the edge with Co atoms leads to a significant lowering of the sulfur binding energy. This may in part explain the promoting effect of Co and the role of the Co–Mo–S structure.

– We propose a model for the Co–Mo–S structure which has "inherent" vacancies. Bond lengths between atoms near the vacancy are shorter than the average values.

Having established that the present method is able to describe the structure and bonding of the MoS_2 and Co–Mo–S structures in HDS catalysts, it is clear that the possibility is now open for a detailed study of the reaction mechanisms in hydrodesulfurization. The first step must be to study the effect of adsorbed hydrogen. The presence of S–H groups could perhaps result in a preference for a slightly different structure than the "pure" sulfides studied here, and the hydrogen could for instance lift the dimerization. In addition, adsorption of hydrocarbons containing hetero-atoms, hydrogenation, and hetero-atom–C bond breaking at the sulfur vacancies of the Co–Mo–S structure can now be studied.

Acknowledgement

The present work was in part financed by The Danish Research Councils through The Center for Surface Reactivity and grant #9501775. Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Foundation.

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