Molecular aspects of the H_2 activation on MoS_2 based catalysts — the role of dynamic surface arrangements

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Abstract

In order to model one of the key steps in hydrosulfurization (HDS), density functional calculations of the dissociation of H_2 on the edges of a Co promoted MoS_2 (Co-Mo-S) slab have been performed. The results show that the heterolytic dissociation of hydrogen is not favored, but there appears to exist different homolytic pathways with similar activation barriers. It is shown that the dissociation process couples strongly to flexible sulfur atoms such that dynamic surface reconstructions occur during the adsorption process. By calculating the minimum energy reaction path we find that S atoms at the edge of the MoS_2 slabs can move up to extract one of the H atoms of the dissociating H_2 molecule and transport it to the other side of the slab where it diffuses on. Transition metal sulfides constitute an important class of heterogeneous catalysts and the active part of many enzymes, and we suggest that the catalytic activity of these systems may be closely coupled to the flexibility of the sulfur ligands. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Some of the most important catalysts are transition metal sulfides. The hydrotreating catalysts used in most refinery processes to remove sulfur, nitrogen, and aromatics from oil products consist of MoS_2 promoted by Co or Ni [1]. Many biological catalysts also have transition metal sulfides as the active components. Nitrogenases, hydrogenases, and various reductases are examples of enzymes based on Mo and Fe sulfides [2].

While the processes by which molecules are adsorbed and dissociated on metal surfaces are in many

cases quite well understood due to a combination of kinetics and molecular beam scattering experiments and theoretical modeling [3], the analogous processes on sulfides are only poorly described. For example, if we consider the simple process of hydrogen adsorption on MoS_2, many questions regarding how and where the activation takes place are still unanswered. This has prevented a detailed understanding of the mechanism and kinetics of hydrotreating reactions [1].

It has been known for many years that MoS_2 takes up large quantities of hydrogen [4–6], but the literature is still debating the details of the dissociation process and the form in which hydrogen is present on MoS_2. Two different dissociation schemes have been considered [5,7]. One is the heterolytic dissociation on a sulfur vacancy site to yield Mo-H and Mo-SH

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species. The other is the homolytic dissociation of hydrogen on disulfide groups resulting in the formation of Mo-SH groups. The latter process has been observed on molecular coordination complexes dubois [8]. Spectroscopic studies of MoS_2-based systems have provided evidence for disulfide species [5,9–11] and SH groups [4,12–14], but no such evidence has yet been given for Mo-H species. The FTIR studies have shown that the SH groups are located at the MoS_2 edges [13]. This is in accord with the density functional theory (DFT) studies of Byskov et al. [15] who also found that disulfide species (or sulfur dimers) may also be present at the edges of MoS_2.

In the present letter, we study the hydrogen activation on the edges of small Co-Mo-S structures using density functional theory. We show that at least two different paths are available and that they are both moderately activated. Unlike the H_2 dissociation process on metal surfaces [3], the dissociation on the sulfide involves a complete dynamical movement of the surface atoms in the process. The results show that the "flexibility" of the sulfides is an essential part of the catalytic action of these materials.

Previous theoretical studies of promoted MoS_2 catalysts have been centered on finding the structure of the active catalysts [15–18] and the adsorption and further reaction of thiophene on them [19]. The dissociation pathway of molecular hydrogen on these catalysts has not yet been found, but the adsorption of hydrogen on molybdenum sulfide clusters [7,21,22] and on Ni_3S_2 clusters [23] has been studied.

2. Calculational method and model used

In the present study, we rely on previous experimental and theoretical work to define a simple, but realistic model of the active part of the promoted MoS_2 catalyst [1,15,16]. It is known experimentally that the active sites of the Co promoted MoS_2 catalysts are associated with Co atoms located at the edge of small two dimensional MoS_2 slabs 10–20 Å in diameter [1]. Such structures are referred to as Co-Mo-S structures [1].

A simple model of a Co-Mo-S system is shown in Fig. 1. It consists of MoS_2 strings, two Mo atoms wide and with Co atoms substituted for Mo at one of the edges. By performing calculations on MoS_2 strings which are up to six Mo atoms wide, it has been verified
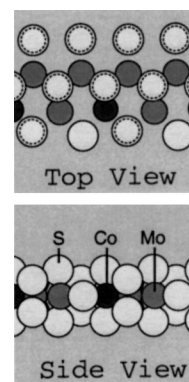

Fig. 1. The calculated equilibrium structure of a single layer MoS_2 slab with every second Mo atom substituted for a Co atom at the S-edge. Both a top and a side view is shown. The slab is chosen as a model of the structures active as catalysts in HDS processes. When Co is present at the edge, the lowest energy structure has S dimers at every second site and an S vacancy at the others. At the vacancies the remaining S atoms has moved up into the plane of the Mo atoms. Very similar results for the S-edge are obtained if sulfur atoms are stripped off the Mo-edge such that the stoichiometry is close to two S atoms per metal atom.

that the basic features of the chemistry at the edges do not depend on the width of the MoS_2 strings [16,20].

The effect of the Co has been shown to lower the binding energy of the S atoms at the edge so that S vacancies are easily created next to the Co atoms [15,16]. It is generally believed for many different transition metal sulfides that S vacancies are responsible for at least part of the catalytic activity of the catalyst [1,15,16].

In our density functional calculations for this system we exploit the periodicity of the model along the chains and repeat the chains periodically separated by vacuum in the other two directions. Along the chains we superimpose a periodicity of two Mo-Mo distances. The Kohn–Sham equations are solved by expanding the wavefunctions in plane waves while describing the ion cores by non-local ultra-soft pseudopotentials [24]. Plane waves with kinetic energies up to 25 Ry and three special k-points have been used to sample the first Brillouin zone. Exchange and correlation effects are described within the generalized gradient approximation [25]. The self-consistent electron density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi-population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay

mixing of the resulting electronic density [26]. All total energies have been extrapolated to $k_B T = 0$ eV. Complete structural relaxation is made for each configuration studied.

In the model studied here where every second Mo edge atom is substituted by Co, the most stable structure has one S vacancy per Co atom [15–16]. When there are no vacancies, the S atoms at the edge dimerize (i.e. form disulfide like species), and when one of the dimer S atoms is removed the other swings up into the plane of the Mo atoms. The edge, we are studying contains both S dimers and the restructured vacancy, cf. Fig. 1. It is of importance in the present context that the dimerization of the S atoms and the edge is present irrespective of the width of the strings [20]. This is in contradiction with the similar calculations of Raybaud et al. [18], a difference that can most likely be traced back to their use of an infinitely thick slab of MoS_2. The small MoS_2 slabs in catalysts are usually only a single layer high [1] making the thick slabs a poor model of the active catalyst. In addition, we find that the calculated vibrational frequency of the S dimer at the edge of a six Mo wide string is in close agreement with the measured value ($483 \, cm^{-1}$ [20] in the DFT calculation to be compared to $529 \, cm^{-1}$ in the Raman experiments of Knözinger and coworkers [5]).

To find the reaction path for dissociation, we use the method described by Ulitsky and Elber [27]. It has proven useful in describing several surface reactions [28–30]. The method which can also be considered as a simplified version of the nudged elastic band method [31], finds iteratively the minimum energy path between a prescribed initial and final state. We study two different dissociation paths, one where the dissociation takes place directly over an S dimer, and one where the dissociation takes place over the vacancy, thus involving both the S atoms and the metal atom more directly. In each case, the final state is the same, see Figs. 2 (7) and 3 (12). This is the lowest energy state of the system with two H atoms at the edge.

3. Results and discussion

We note first that adsorbed H is always found to be more stable as SH groups at the edges [16] than when it is bound directly to the transition metal. In fact, if hydrogen is deliberately placed at one of the metal atoms
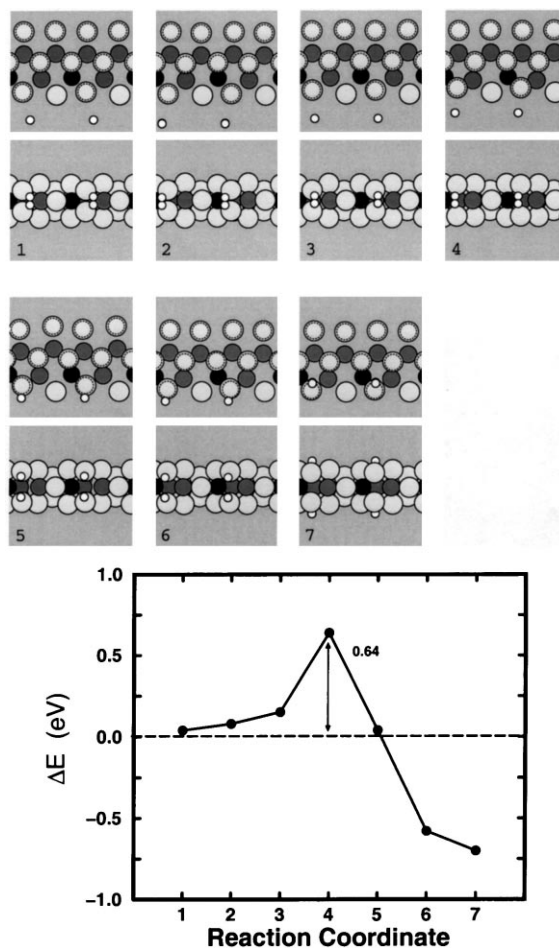

Fig. 2. Snapshots of the minimum energy reaction path for the dimer dissociation process and the calculated energy along the path. The letters in the energy diagram reflect those in the snapshots. For each point along the reaction path all degrees of freedom perpendicular to the path have been minimized.

in the S vacancy, it moves without a barrier ontop one of the S atoms. For this reason, we do not consider H bound to the transition metal as a realistic final state, and such a strictly "heterolytic" process is, therefore, not considered further. We also note that H bound to S atoms on the basal plane of large MoS_2 slabs is unstable relative to H_2 by as much as 0.97 eV [16]. This makes dissociation of H_2 on the basal planes of MoS_2 unlikely under normal conditions in agreement with experimental findings [32–34]. This process is, therefore, not considered further. It is interesting that the formation of sulfhydryl groups was also observed
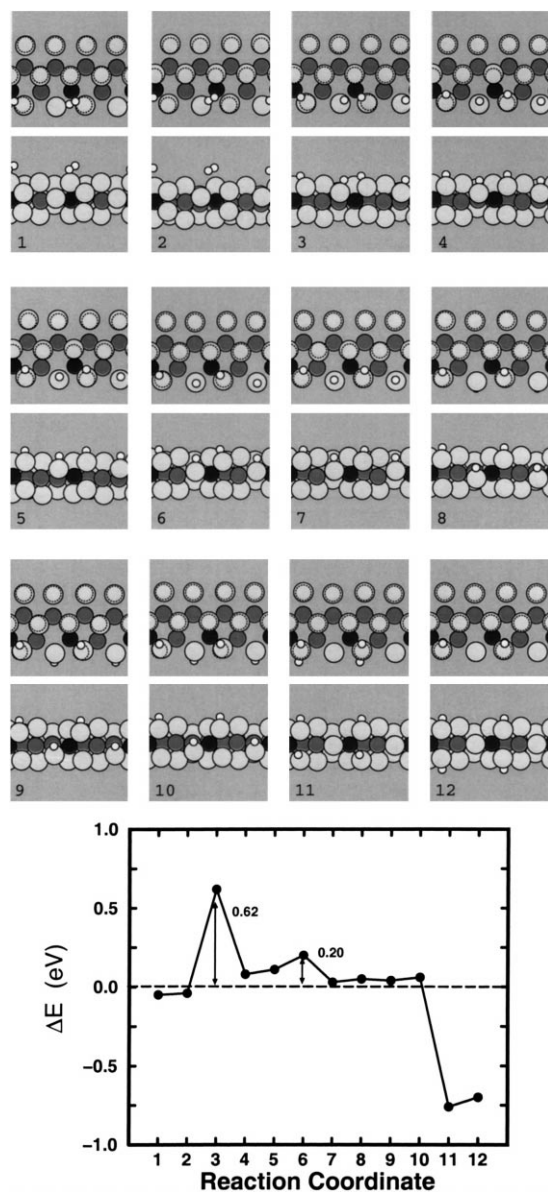
Fig. 3. Snapshots of the minimum energy reaction path for the vacancy dissociation process and the calculated energy along the path. The letters in the energy diagram reflect those in the snapshots. For each point along the reaction path all degrees of freedom perpendicular to the path have been minimized.

upon reaction of hydrogen with a dinuclear disulfide complex [8].

The two different reaction paths are created by choosing different initial states, so that in the first process (which we will term the dimer process) the

H_2 molecule is placed right above an S dimer (Fig. 2 (1)) whereas in the second case (the vacancy process) the H_2 molecule is started out above the vacancy where it can interact directly with the Mo atoms underneath (Fig. 3 (1)). The initial state in this case was found by minimizing the energy of the H_2 molecule outside the slab. In the following we discuss the two processes one by one.

First, consider the dimer dissociation process in Fig. 2. Along the minimum energy path, the H_2 and the S_2 bonds split up in a concerted way. In other words, as the H–H and S–S bonds are split, the two S–H bonds are formed. In the absence of H_2, the energy associated with breaking the S–S bond in the S dimers at the edge is 0.6 eV. This is close to the barrier for the H_2 dissociation process and suggests that the relatively low energy barrier for this process (Fig. 2) comes primarily from the low energy involved in splitting up the S dimer. The presence of an activation barrier for H_2 activation is in accord with experiments [6].

The vacancy process is more complicated, see Fig. 3. Three different elementary processes separated by potential energy barriers are found. First, the H–H bond is broken. This happens by the S atom next to the vacancy moving up and picking up one of the H atoms. The other H atom ends up on one of the S atoms of the nearby S dimer. The dimer also breaks up in this case. The barrier for this step is 0.62 eV. The next step involves the vacancy S atom which picked up one of the H atoms, it moves down through the Mo plane into the plane of the lower S atoms in order to prepare for the delivery of the H atom to the lower S atom of the neighboring S dimer. This process is also moderately activated. The final step is the diffusion of the H atoms from the vacancy S atoms to the lower S atoms of the dimer. This step has only a very minor barrier.

Note that the elementary steps of this complicated process were not an input to the calculation. They are the result of the procedure used for finding the minimum energy path where only the initial and the final states were specified. We cannot rule out that other, even lower energy paths exist, but the procedure clearly points to two feasible reaction routes. They have very similar barriers and we cannot on the basis of the calculations decide which process is fastest. They may both contribute under ordinary reaction conditions. The fact that H_2 can be dissociated at an S dimer

shows that H_2 activation needs not be at the same place where the rest of the catalytic desulfurization takes place. This combined with the relatively low barrier for dissociation and the ease by which H atoms are transferred along the S atoms at the edge (the last step in the vacancy process) means that hydrogen should be readily available at the edges. On unpromoted MoS_2 where there are few S vacancies, we expect the dimer process to dominate whereas the larger vacancy concentration on the Co promoted MoS_2 makes the two processes of more similar importance.

Both reaction paths are characterized by large dynamic restructuring of the surface on which the process is taking place. In the dimer process, the two S atoms at the edge split up during the H_2 dissociation process, thus providing new possibilities for the S atoms to bond to the H atoms in the final state. The vacancy process shows an even more interesting involvement of the S atoms of the surface, since here one S atom acts like an "elevator" by picking up one of the H atoms from the dissociating molecule, swinging around to the other side of the slab and delivering the atom close to its final state. This is very different from the behavior at a metal surface [3]. The origin of the large effects in the sulfide is clearly the large bending flexibility of the metal-sulfur bonds at the edges. The energy of dissociating the S dimer or moving an S atom at the edge of the sulfide is quite small and this provides new degrees of freedom for the reaction to take place.

Movies of the two different hydrogen dissociation paths can be seen on the internet at http://www. fysik.dtu.dk/CAMP/movies/comos_dimer.mpg and http://www.fysik.dtu.dk/CAMP/movies/comos_vacancy.mpg

On the basis of the calculations, we suggest that the flexibility of the S atoms at the edges of MoS_2-like structures is an important part of the unique reactivity of these compounds. In particular, the ability of the surface S atoms of the compound to pick up and transport H atoms may indeed be of vital importance not only for the H_2 dissociation process but also in connection with all the hydrotreating processes where C–S or C–N bonds are broken by the addition of hydrogen or where hydrogen is added to aromatic C–C bonds. Since the catalytically active part of many enzymes are also transition metal sulfide clusters, it is possible that similar effects are of importance for their catalytic activity.

References

[1] H. Topsøe, B.S. Clausen, F.E. Massoth, in: J.R. Anderson, M. Boudart (Eds.), Hydrotreating Catalysis, Science and Technology, Springer, Berlin, 1996.

[2] E.I. Stiefel, in: E.I. Stiefel, K. Matsumoto (Eds.), Transition Metal Sulfur Chemistry, ACS Symp. Ser. 653 (1996) 2.

[3] For a recent review, see e.g. A. Groß, Surf. Sci. Rep. 32 (1998) 291.

[4] C.J. Wright, C. Sampson, D. Fraser, R.B. Moyes, P.B. Wells, C. Riekel, J. Chem. Soc., Faraday Trans. I 76 (1980) 1585.

[5] J. Polz, H. Zeilinger, B. Müller, H. Knözinger, J. Catal. 120 (1989) 22.

[6] W.P. Dianis, Appl. Catal. 30 (1987) 99.

[7] A.B. Anderson, Z.Y. Al-Saigh, W.K. Hall, J. Phys. Chem. 92 (1988) 803.

[8] M. Rakowski-Dubois, M.C. van Der Veer, D.L. Dubois, R.C. Haltiwanger, N.K. Miller, J. Am. Chem. Soc. 102 (1980) 7456.

[9] J.C. Duchet, E.M. van Oers, V.H.J. de Beer, R. Prins, J. Catal. 80 (1983) 386.

[10] G.L. Schrader, C.P. Cheng, J. Catal. 80 (1983) 369.

[11] E. Payen, S. Kasztelan, J. Grimblot, J. Mol. Struct. 174 (1988) 71.

[12] P. Ratnasamy, J.J. Fripiat, J. Chem. Soc., Faraday Trans. 66 (1970) 2897.

[13] N.-Y. Topsøe, H. Topsøe, J. Catal. 139 (1993) 641.

[14] H. Topsøe, B.S. Clausen, N.-Y. Topsøe, J.K. Nørskov, C.V. Ovesen, C.J.H. Jacobsen, Bull. Soc. Chim. Belg. 104 (1995) 283.

[15] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, Catal. Lett. 47 (1997) 177.

[16] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, J. Catal. 187 (1999) 109.

[17] S. Harris, R.R. Chianelli, J. Catal. 86 (1984) 400.

[18] P. Raybaud, J. Hafner, G. Kresse, H. Toulhoat, Surf. Sci. 407 (1998) 237.

[19] P. Raybaud, J. Hafner, G. Kresse, H. Toulhoat, Phys. Rev. Lett. 80 (1998) 1481.

[20] M. Bollinger, K.W. Jacobsen, H. Topsøe, B.S. Clausen, J.K. Nørskov, in preparation.

[21] J.A. Rodriguez, J. Phys. Chem. B 101 (1997) 7524.

[22] A. Sierraalta, F. Ruette, E. Machado, Int. J. Quantum Chem. 70 (1998) 113.

[23] M. Neurock, R.A. van Santen, J. Am. Chem. Soc. 116 (1994) 4427.

[24] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.

[25] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (11) (1992) 6671.

[26] B. Hammer, L.B. Hansen, J.K. Nørskov, Phys. Rev. B 59 (1999) 7413.

[27] A. Ulitsky, R. Elber, J. Chem. Phys. 92 (1990) 1510.

[28] J.J. Mortensen, Y. Morikawa, B. Hammer, J.K. Nørskov, J. Catal. 169 (1997) 85.

[29] J.J. Mortensen, B. Hammer, J.K. Nørskov, Phys. Rev. Lett. 80 (1998) 4333.

[30] J.J. Mortensen, L.B. Hansen, B. Hammer, J.K. Nørskov, J. Catal. 182 (1999) 479.

[31] G. Mills, H. Jónsson, Phys. Rev. Lett. 72 (1994) 1124.

[32] M. Salmeron, G.A. Somorjai, A. Wold, R. Chianelli, K.S. Liang, Chem. Phys. Lett. 90 (1982) 105.

[33] R.T.K. Baker, J.J. Chludzinski Jr., R.D. Sherwood, J. Mater. Sci. 22 (1987) 3831.

[34] B.H. Upton, C.C. Chen, N.M. Rodriguez, R.T. Baker, J. Catal. 141 (1993) 171.