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# Density Functional Approach of a $\gamma$-Alumina Supported $MoS_2$ Hydrotreating Catalyst

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**The present paper reports on the influence of the support on the active phase in hydrodesulfurization (HDS). An $Mo_{12}S_{24}$ cluster appears to be a suitable model of the active phase for a DFT approach; it was docked to an elementary model of alumina. This study shows that the $MoS_2$ sheet perpendicular or nearly perpendicular to the alumina surface is the stable configuration. However the creation of bonds between the active phase and the support does not modify the charge of the unsaturated molybdenum atoms considered as active sites in HDS.** © 1998 Academic Press

*Key Words:* **density functional; hydrotreatment; molybdenum disulphide.**

## INTRODUCTION

Hydrodesulfurisation (HDS) is one of the most important catalytic processes used to remove sulfur from petroleum fractions. The increasing demand to convert sulphur-rich feed stocks and the environmental demand for further reductions in the sulphur content of oil products lead to a need for more efficient processes and more active catalysts. The most used catalyst for HDS is $Co(Ni)Mo/Al_2O_3$ which consists of well-dispersed molybdenum disulfide nanocrystallites supported by a $\gamma$-alumina and associated with promotors atoms like Co or Ni. $MoS_2$ is a layered compound and it has been shown that these actives phases are composed of one or several sheets (1). The optimum value of 0.28 of the atomic ratio $Co/Co + Mo$ has been determined experimentally (1). Despite the numerous works dedicated to these solids the exact nature of the interaction of these disulfide crystallites with the support as well as of their orientation on the support are still unclear (2,3). Modelling techniques are one possible approach to get a better insight into the nature of the interactions of the active phases with the carrier in order to develop more efficient catalysts.

In two previous papers we used molecular mechanics techniques in order to investigate the orientation of the $MoS_2$ sheets on alumina (4) and silica (5) supports. It turned out that the stacking of sheets containing 39 molybdenum atoms induces a screening effect between the layers as soon as three sheets are stacked together or as soon as one sheet isolates the next one from the support. It was further shown that the $MoS_2$ layers prefer to lie parallel to the support, but nonbonded crystallites of the active phase standing perpendicularly to the support could also exist as metastable species, particularly when these crystallites were composed of several $MoS_2$ sheets. These results were obtained by considering only the nonbonded electrostatic and Van der Waals interactions between the $MoS_2$ layers and the support. Preliminary trials which concentrated on the interaction of different surfaces of $MoS_2$ with several surfaces of alumina led to the conclusion, with the help of molecular mechanics, that periodic covalent interaction of both compounds is improbable due to the strong incommensurabilities appearing at the interface (6). We therefore decided to check the possibility of the existence of localized covalent interactions. As the periodic properties of the solid are not involved in this approach it seemed reasonable to treat clusters. In order to handle clusters of significant size the computational work was performed using the DFT approach which permits the study of larger systems than Hartree–Fock treatments. The aim of this paper is to report the results obtained with such a complementary approach, taking into account the possibility of existence of covalent bonds between the active phase and the support. The next section will present the computational method used in the paper. The results are then reported sequentially: a cluster $Mo_{12}S_{24}$ is defined as a model of the active phase, afterwards this cluster is put in interaction with aluminium atoms through oxygen bridges representing its interaction with a $\gamma$ alumina support.

## COMPUTATIONAL TECHNIQUES

The DFT calculations were performed with the package Amsterdam Density Functional, ADF, version 2.0.1 (7) on SGI workstations with R4400 and R10000 processors. The local density approximation (LDA) to the

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**TABLE 1**

**Description of the Basis of Atomic Orbitals**

| | Frozen core | STO-DZ exponents | Polarization exponents |
|---|---|---|---|
| Hydrogene | | 1s: 0.76; 1.28 | 2p: 1.25 |
| Oxygene | 1s | 2s: 1.70; 2.82 | 3d: 2.00 |
| | | 2p: 1.30; 3.06 | |
| Aluminium | 1s-2p | 3s: 1.05; 1.70 | 3d: 1.20 |
| | | 3p: 0.70; 1.35 | |
| Sulphur | 1s-2p | 3s: 1.60; 2.60 | 3d: 1.50 |
| | | 3p: 1.15; 2.15 | |
| Molybdenum | 1s-3d | 4s: 3.25; 4.85 | |
| | | 4p: 2.65; 4.35 | |
| | | 4d: 1.30; 3.05 | |
| | | 5s: 1.00; 1.80 | 5p: 1.36 |

exchange-correlation functionals is parametrized according to Vosko *et al.* (8). The nonlocal gradient corrections were used as post-SCF treatment according to Becke (9) for exchange and to Perdew (10) for correlation. All atoms were described by Slater-type orbitals (STO) basis sets implemented in ADF. All the calculations reported in this paper were performed with the basis set and the frozen-core approximation defined in Table 1. The default convergence criteria of ADF were used for the SCF process as well as for the geometry optimization. The charges reported are issued from the standard Mulliken analysis. Other descriptions of the charge distribution like the Hirshfeld scheme or the Voronoy charges, calculated in ADF, were also considered but, although the absolute values are different, they lead to the same conclusions and will not be reported here.

## RESULTS AND DISCUSSION

### *The $Mo_{12}S_{24}$ Cluster*

Two disulfide model clusters have recently been calculated using the DFT method. The first one, studied by Mitchell *et al.* (11), consisting of three molybdenum atoms is the cluster $Mo_3S_9H_6$ in which the octahedral environment is obtained by saturating each molybdenum atoms by one hydrogen atom and one SH group. The second one of similar size studied by Weber *et al.* (12) is the $Mo_3S_7^{4+}$ cluster. They estimated the energy of the Mo-S bonds as a function of their position in the cluster. The neutral cluster $Mo_3S_9H_6$ contains molybdenum atoms with the oxidation number +IV. The main drawback of this model is the fact that no molybdenum atom has an environment similar to the one in bulk $MoS_2$. In the second cluster no perturbation is introduced by the saturating hydrogen atoms, but it is highly charged. The molybdenum atoms should therefore have properties different from those of bulk $MoS_2$. In order to analyze these effects we studied several clusters containing from 3 to 10 Mo atoms, some of which were saturated with H-atoms on sulfur and others containing unsaturated Mo atoms. The neutral cluster $Mo_{12}S_{24}$ was found as the most representative of the active phase because its size corresponds to the size of the active phase determined by high resolution electron microscopy (HREM) (2,3). Moreover it contains Mo-atoms with unsaturated coordination. These coordinatively unsaturated sites (CUS) (13, 14) obtained by reductive elimination reactions at relatively low temperature are usually considered as involved in the HDS mechanism. Finally, assuming the oxidation states +IV and −II for Mo and S, respectively, this cluster is the first neutral species which could be built without saturating H-atoms. Several models have been proposed in the literature to explain the promoting effect of cobalt (1). The most recognized of these is the CoMoS model in which the promotor atoms lie at the edges of the disulfide slabs (15). In this cluster the ratio 0.5 of the tetracoordinated Mo atoms to the total number of molybdenum atoms is of the same order of magnitude as the experimental optimal ratio of cobalt atoms to the total number of atoms (Co/Co + Mo) estimated to 0.28 which characterizes, at least qualitatively, the number of Mo edge atoms.

The preliminary results concerning the cluster treated with a DZ basis in the LDA approximation were improved with the use of the DZP basis for the sulfur atoms and a Becke–Perdew nonlocal contribution (NL-P) (9,10). The atom types are identified in Fig. 1 which gives a representation of this cluster from which the lower layer of sulfur atoms has been omitted. The main structural data deduced for the optimized geometry are gathered in Table 2. The bond lengths are in good agreement with the experimental values, with a difference of only 0.026 Å for the internal $Mo_i$-$S_i$ bond. Moreover, the standard Mulliken analysis, reported in Table 3, shows that the outer sulfur atoms $S_2$ have the highest negative charge, while the tetracoordinated molybdenum atoms are the most positive. Therefore, we can consider that the use of the DZP basis at

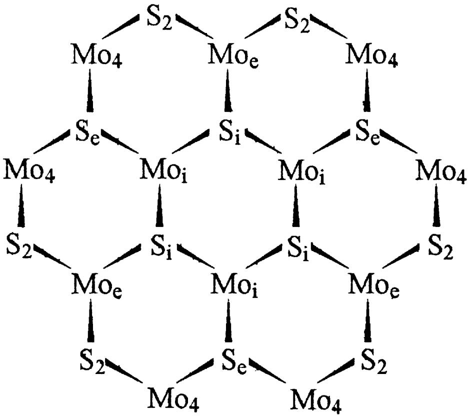

**FIG. 1.** Schematic representation of the $(Mo_{12}S_{24})^0$ cluster.

**TABLE 2**

**Main Data of the $Mo_{12}S_{24}$ Cluster at the Optimized Geometry**

| Bond | Bond length (Å) |
|---|---|
| $Mo_i$-$S_i$ | 2.392 |
| $Mo_i$-$S_e$ | 2.414 |
| $Mo_e$-$S_i$ | 2.414 |
| $Mo_e$-$S_2$ | 2.380 |
| $Mo_4$-$S_e$ | 2.350 |
| $Mo_4$-$S_2$ | 2.315 |
| Mo-S in bulk $MoS_2$ | 2.418 |

*Note.* See Fig. 1 for the indexing.

the NL-P level offers a satisfactory compromise for further work in which the interaction over oxygen bridges of $MoS_2$ with aluminium atoms, representing the alumina support, is simulated.

### *Interaction with the Alumina*

The analysis of the crystal structure of $\gamma$ alumina and bulk $MoS_2$, as well as molecular-mechanical docking trials for the most stable surfaces show that complete atomic rows of both materials can hardly fit to create a stable interface. Therefore, we will test the possibility of localized interactions through Mo-O-Al bridges. In order to estimate the influence of such an interface the cluster shown in Fig. 2b was considered. This cluster should carry a negative charge (−2) which was neglected because, at a real alumina interface, the bulk support, which is in fact a disordered solid with numerous vacancies, can be assumed to buffer the local charges carried by the $MoS_2$ sheets. The coordination of the aluminium atoms in this model is different from the coordination in the $\gamma$ alumina; However if this model with Al atoms in a trivalent environment cannot be considered as a model of the support it can be used to study the influence of the support on the active phase. The cluster $Al_2O_5H_2$ (Figure 2a) was thus calculated as neutral, without inclusion of diffuse orbitals, to serve as a reference for the comparison between $Mo_{12}S_{24}$ and supported $Mo_{12}S_{24}$.

The geometry optimisation of the interface was performed in two steps by first varying the Mo-O bond length and then changing the mutual orientation of both fragments. The fragments were not relaxed for either optimisation in

**TABLE 3**

**Mulliken Charges for Molybdenum and Sulfur Atoms of the Isolated Fragments and the Optimized Models**

| | Isolated fragments | Perpendicular sheet Mo-O-Al = 180° |
|---|---|---|
| $Mo_{12}S_{24}$ | | |
| $Mo_2$ | 0.606 | 1.001 |
| $Mo_3$ | 0.532 | 0.520 |
| $Mo_4$ | 0.590 | 0.568 |
| $Mo_8$ | 0.590 | 0.587 |
| $Mo_9$ | 0.606 | 0.612 |
| $Mo_{10}$ | 0.606 | 0.607 |
| $Mo_{11}$ | 0.532 | 0.532 |
| $S_3$ | −0.307 | −0.337 |
| $S_5$ | −0.325 | −0.317 |
| $S_7$ | −0.325 | −0.323 |
| $S_9$ | −0.211 | −0.202 |
| $S_{17}$ | −0.211 | −0.212 |
| $S_{19}$ | −0.307 | −0.316 |
| $S_{21}$ | −0.325 | −0.321 |
| Support | | |
| $O_2$ | −0.590 | −0.911 |
| $Al_2$ | 1.412 | 1.410 |
| $O_3$ | −0.894 | −0.918 |
| $O_{hyd}$ | −0.741 | −0.774 |
| H | 0.366 | 0.367 |

*Note.* Atom numbers according to Fig. 2.

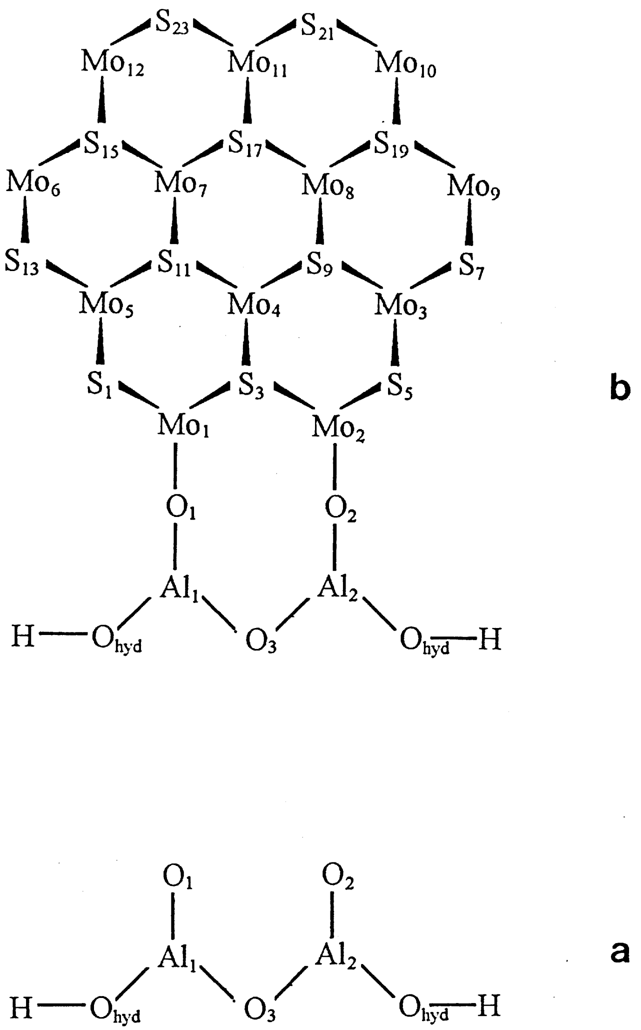

**FIG. 2.** (a) Simplified model of the support; $O_{hyd}$ represents an oxygen atom belonging to an OH group. (b) $(Mo_{12}S_{24})^0$ cluster interacting with aluminium atoms through oxygen bridges.

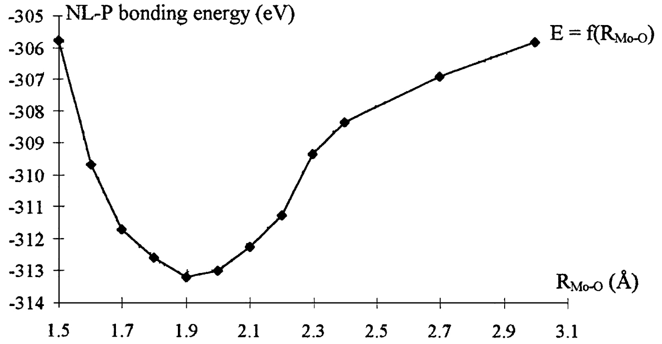

**FIG. 3.** NL-P bonding energy of the $Mo_{12}S_{24}$ cluster docked to the support surface as a function of the Mo-O bond length.

order to reduce the amount of memory and of computational time required to perform the calculation. The first calculation used the C2v symmetry, while the second one was performed according to the Cs symmetry.

Figure 3 shows the potential curve corresponding to the first step, calculated using the corrected NL-P approximation (9, 10). The optimal bond length of 1.92 Å is similar to the value of 1.85 Å deduced from inelastic electron tunneling spectroscopy (IETS) by Diemann *et al.* (16). Taking into account the fact that two bonds are represented in the curve, we can extract the force constant of one Mo-O bond, which turns out to be $2837 \pm 243$ kJ $mol^{-1}$ $Å^{-2}$ or $4.7 \pm 0.4$ mdyn $Å^{-1}$. Such a value is in agreement with those obtained for Mo-O bonds (17). The comparison of the bonding energies of the isolated components with the energy of the optimized cluster yields a stabilization energy of 11.105 eV (about 1100 kJ $mol^{-1}$). The basis set superposition error (BSSE) upon creation of two Mo-O bonds with the support was estimated by calculating each part of the $Mo_{12}S_{24}Al_2O_5H_2$ cluster in the complete basis. The bonding energy of $Mo_{12}S_{24}$ with $Al_2O_5H_2$ "ghosts" orbitals shifts by −0.57 eV from −251.58 eV to −252.15 eV (i.e., 0.23%) while the energy of $Al_2O_5H_2$ shifts by 0.01 eV from −50.13 to −50.14 eV (0.02%). The BSSE of 0.57 eV can be considered as negligible. The stabilization energy therefore indicates a strong and stable interaction when the Mo-O-Al bonds are created.

In the second step the two angles Al-O-Mo at the interface are simultaneously bent between 180° and 90°, simulating an $MoS_2$ sheet turning from a perpendicular toward a parallel position with respect to the support surface. Figure 4 indicates that the potential is nearly flat between 180° and 120° and becomes extremely repulsive for more acute angles. This means that the most stable bent position of an $MoS_2$ sheet with respect to the alumina surface is represented by an AlOMo angle of about 135° in very good agreement with the experimental value of ca 140° obtained by Diemann *et al.* by IETS (16). With such a flat potential, large-amplitude oscillations can occur at sufficiently high temperatures. The form of the potential and, thus, also the oscillating behaviour will depend on the long-range steric and electrostatic hindrances which would originate with a larger model of $\gamma$-alumina representing a broader surface, instead of a line of Al atoms. It appears, thus, that a $MoS_2$ sheet perpendicular or nearly perpendicular to the alumina surface is the stable configuration, if Mo-O bonds exist.

No variation in the bond lengths were observed for this stable geometrical configuration except a small distortion at the interface due to the interaction with the support. It is interesting to examine the electronic distribution of such a model in order to elucidate more information on the effect

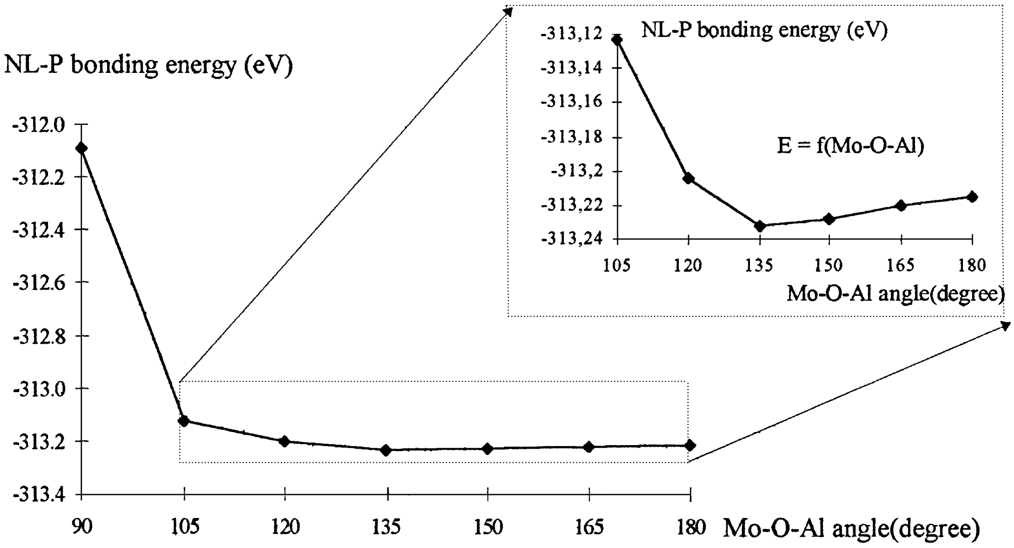

**FIG. 4.** NL-P bonding energy of the $Mo_{12}S_{24}$ cluster docked to the support surface as a function of the Mo-O-Al angle.

of the carrier on the $MoS_2$ active phase, bearing in mind that we had neglected the expected charge on the model. Table 3 presents the Mulliken charges of the isolated fragments and of the model. Obviously the modification of the $MoS_2$ active phase induced by the formation of bonds with the aluminium atoms is only noticeable in the immediate vicinity of the molybdenum atoms directly bonded to the support. The charge differences for the second nearest neighbour atoms are less than $5 \times 10^{-3}$ and $9 \times 10^{-3}$ electronic charges for molybdenum and sulfur atoms, respectively. The charge of the free unsaturated molybdenum atoms ($Mo_6$,$Mo_{12}$,$Mo_{10}$, $Mo_9$), considered as the active sites, are not modified at all upon the creation of bonds with the support.

## CONCLUSION

This paper presents a DFT approach of $Mo_{12}S_{24}$, a model of $MoS_2$ crystallites, and discusses possible interactions with a $\gamma$-alumina support. It has been shown that covalent bonds with the support can stabilize this cluster in an orientation slightly bent with respect to the support. Such a bonding does not require periodic interactions over long rows of atoms. The creation of such bonds does not influence the charge distribution of the $MoS_2$ cluster except at the interface.

As a general conclusion it is possible to state that $\gamma$-alumina only acts as a dispersant for the active phase. The cluster is only slightly distorted by its interaction with the support and this distortion cannot be considered as the basis for the catalytic process, if we consider that the active sites are the molybdenum coordinatively unsaturated atoms. These particular sites exist on the cluster $Mo_{12}S_{24}$ which appears to be a good model to study the reactivity of the $MoS_2$ phase. Work on this cluster is currently in progress in the interest of a fuller understanding of the reactivity of the $MoS_2$ crystallites.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Massoth, F., Topsoe, H., and Clausen, B., *in* "Catalysis Science and technology" (J. R. Anderson and M. Boudart, Eds.). Springer Verlag, Berlin, 1996.
2. Payen, E., Hubaut, R., Kasztelan, S., Poulet, O., and Grimblot, J., *J. Catal.* **147**, 123 (1994).
3. Stockmann, R. M., Zandbergen, H. W., Van Langeveld, A. D., and Moulijn, J. A., *J. Mol. Catal.* **102**, 147 (1995).
4. Faye, P., Payen, E., and Bougeard, D., *J. Chem. Soc., Faraday Trans.* **92**(13), 2437 (1996).
5. Faye, P., Payen, E., and Bougeard, D., *Stud. Surf. Sci. Catal.* **106**, 281 (1997).
6. Faye, P., thesis, Université des Sciences et Technologies, Lille, France, 1997.
7. G. te Velde, *in* "Amsterdam Density Functional, User's Guide," Scientific Computing & Modelling, Theoretical Chemistry Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands, 1995.
8. Vosko, S. H., Wilk, L., and Nussair, M., *Can. J. Phys.* **58**, 1200 (1980).
9. Becke, A. D., *Phys. Rev. A* **38**, 3098 (1988).
10. Perdew, J. P., *Phys. Rev. B* **33**, 8822 (1986).
11. Mitchell, P. C. H., and Plant, C., *Bull. Soc. Chim. Belg.* **104**, 293 (1995).
12. Weber, J., "Structure et réactivité des systèmes organométalliques par la DFT. Visualisation graphique des résultats," 4ème Université d'Eté Physico-Chimie Théorique, Mittelwihr, 1995.
13. Wambeke, A., Jalowiecki, L., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **109**, 320 (1988).
14. Kasztelan, S., Toulhoat, H., Grimblot, J., and Bonnelle, J. P., *Appl. Catal.* **13**, 127 (1984).
15. Candia, R., Sorensen, O., Villadsen, J., Topsøe, N. Y., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93**, 783 (1984).
16. Diemann, E., Weber, Th., and Müller, A., *J. Catal.* **148**, 288 (1994).
17. Rocchiccioli-Deltcheff, C., Thouvenot, R., and Fouassier, M., *Inorg. Chem.* **21**, 30 (1982).