Russian Chemical Bulletin, International Edition, Vol. 54, No. 10, pp. 2259—2263, October, 2005

Full Articles

MoS_2 single slab as a model for active component of hydrodesulfuration catalyst: a quantum chemical study

1. Molecular and electronic structure of $Mo_{12}S_{24}$ macromolecule and its adsorption complex with H_2S

I. I. Zakharov* and A. N. Startsev

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
5 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 3056. E-mail: ivan@catalysis.nsk.su; startsev@catalysis.nsk.su

The molecular and electronic structure of $Mo_{12}S_{24}$ macromolecule as the MoS_2 single slab structure was calculated by the density functional theory (DFT) method with the B3P86 hybrid exchange-correlation functional. The results of calculations point to slight relaxation of coordinatively unsaturated Mo and S atoms, which is consistent with the published data. The calculated width of the forbidden band (0.85—0.98 eV) is comparable with the experimental value (1.30 eV) and similar to that obtained from DFT calculations with periodic boundary conditions (0.89 eV). The surface Mo centers in the $Mo_{12}S_{24}$ macromolecule are more reduced than the internal (Mo^{IV}) atoms. In order to characterize the adsorption capacity of coordinatively unsaturated Mo centers, a $Mo_{12}S_{24} \cdot 6H_2S$ adsorption complex was calculated. The structure and energy characteristics of the adsorption complex point to a weak donor-acceptor interaction of the π-lone pair of H_2S molecule with the surface (reduced) Mo centers. The active center of thiophene hydrodesulfuration catalysts is formed as a result of the oxidative addition of hydrogen followed by occlusion of hydrogen into the MoS_2 matrix.

Key words: quantum chemical calculations, molubdenum disulfide, hydrodesulfuration catalysts.

Molybdenum disulfide MoS_2 is the structural basis for the active component of sulfide catalysts for hydrodesulfuration of petroleum fractions.[1] It is commonly accepted that the active component of finely disperse MoS_2 comprises nanoparticles in the form of layered molybdenum disulfide single slabs of size at most 10—20 Å.[1,2] A single slab of the most stable modification, 2H-MoS_2, is a S—Mo—S sandwich in which molybdenum atoms are at the centers of trigonal prisms formed by six S atoms, each second prism being empty. In the polycrystalline MoS_2 structure single slabs are linked to one another by van der Waals interactions.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2189—2193, October, 2005.

A molybdenum disulfide single slab was first prepared by intercalating lithium between polycrystalline MoS_2 layers (exfoliation technique).[3] Thus, a single slab of layered molybdenum dichalcogenide found a new physical reality in the form of a single-layer dispersion (see Refs 4—6). A 2H-MoS_2 single slab with trigonal-prismatic coordination of Mo atoms has the D_{3h} point symmetry group and its projection on the basal plane looks like a regular hexagon (Fig. 1). Recently,[7] a stoichiometric molecular model for a regular hexagonal structure of MoS_2 single slabs of different size with the general formula $Mo_{3n2}S_{6n2}$ was considered. We believe that it is this model that correctly describes the catalytically active highly disperse MoS_2 particles; recently, it has been the subject of intensive quantum chemical research. For instance, two macromolecules were studied, $Mo_{12}S_{24}$ [8,9] and $Mo_{27}S_{54}$.[10,11] The coordinatively unsaturated surface Mo atoms on the lateral plane of a single slab are usually treated as possible active sites in the course of hydrodesulfuration.[8—11] By analogy with oxides it is accepted the surface transition-metal ions in sulfides are more reduced than internal atoms. However, density functional (DFT) calculations[8,9,11] led to unnatural results, namely, a higher oxidation state (larger positive charge) of coordinatively unsaturated surface Mo ions on the lateral plane of the hexagon compared to internal Mo^{IV} atoms.

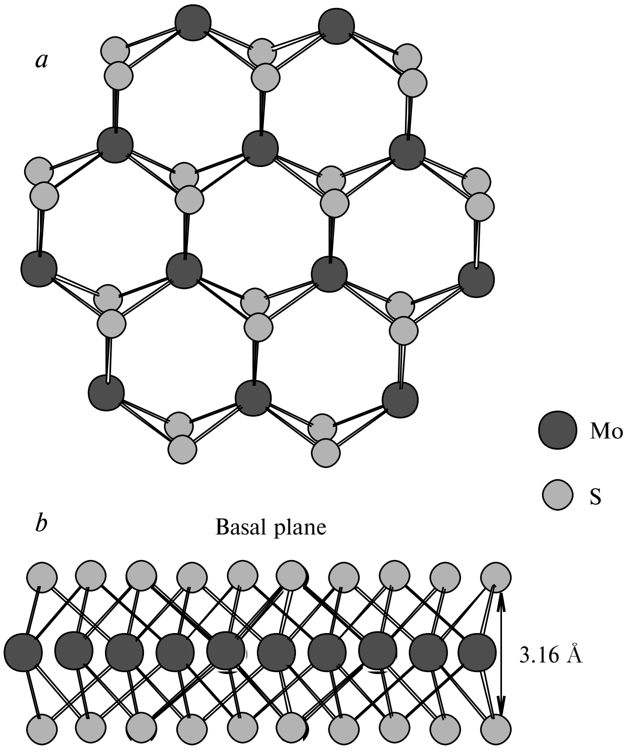

Fig. 1. Molecular structure of $Mo_{12}S_{24}$ cluster with D_{3h} symmetry with the structural parameters of polycrystalline MoS_2 (r(Mo—Mo) = 3.16 Å, r(S—S) = 3.16 Å, r(Mo—S) = 2.41 Å): view from above (a) and side view (b).

In this work we carried out more detailed quantum chemical DFT calculations of the geometry and electronic structure of $Mo_{12}S_{24}$ macromolecule and considered the possibility of adsorption of H_2S molecules on the surface Mo sites on the lateral planes of a MoS_2 single slab.

Calculation Procedure

DFT calculations were carried out with the B3P86 hybrid exchange-correlation functional.[12,13] Geometry optimization of a closed-shell $Mo_{12}S_{24}$ macromolecule (S = 0) was performed using the LANL1 and LANL2 effective potentials for the inner shells of the Mo and S atoms and the extended DZ basis set for the valence orbitals.[14] This version of Gaussian-92 [15] calculations is denoted by B3P86/LANL1-DZ. The atomic charges were calculated using the Mulliken analysis of orbital populations in the minimum basis set for the structure optimized in the extended basis set. This recommendation follows from the results of our theoretical study[16] on the oxidation states of transition-metal ions, because the population analysis with the DZ basis set led to an artifact (which in essence was reported earlier[8,11]). In order to additionally compare the oxidation states of the surface and internal Mo ions on the $Mo_{12}S_{24}$ macromolecule, we also used the energies of the core molecular levels for Mo 4s-electrons.

Results and Discussion

Optimized structure of $Mo_{12}S_{24}$ macromolecule. In accordance with the D_{3h} molecular symmetry all molybdenum atoms in the $Mo_{12}S_{24}$ macromolecule can be divided into three types, namely, tetracoordinate Mo^I atoms on the lateral planes and hexacoordinated outer (Mo^{II}) and internal (Mo^{III}) atoms. Sulfur atoms can also be classified into three groups, namely, unsaturated S^I atoms on the lateral planes and tricoordinate outer (S^{II}) and internal (S^{III}) atoms. The calculated molecular structure of $Mo_{12}S_{24}$ is shown in Fig. 2. The geometric and electronic parameters are listed in Table 1.

Structural differences between the $Mo_{12}S_{24}$ macromolecule and the 2H-MoS_2 single slab are insignificant and concern the relaxation of the surface atoms, Mo^I and S^I. Namely, the Mo^I—Mo^I interatomic distances (r = 3.29 (3.22) Å) are slightly lengthened while the S^I—S^I distances (r = 3.08 (3.16) Å) become somewhat shorter than the corresponding distances in the interior of the macromolecule. Density functional calculations with periodic boundary conditions for the lateral surface (1010)-MoS_2 [17] also confirmed a slight relaxation of coordinatively unsaturated Mo and S atoms. As in the well-known study,[17] the results of our calculations indicate a trend to pairing of the unsaturated S centers with one another (see Table 1); the calculated S^I—S^I distance (r = 3.08 Å) is in good agreement with the published data (r(S^I—S^I) = 3.03 Å).[18] S—S-Pairing was also proved experimentally[19]: a weak band at 529 cm^{-1} in the Raman

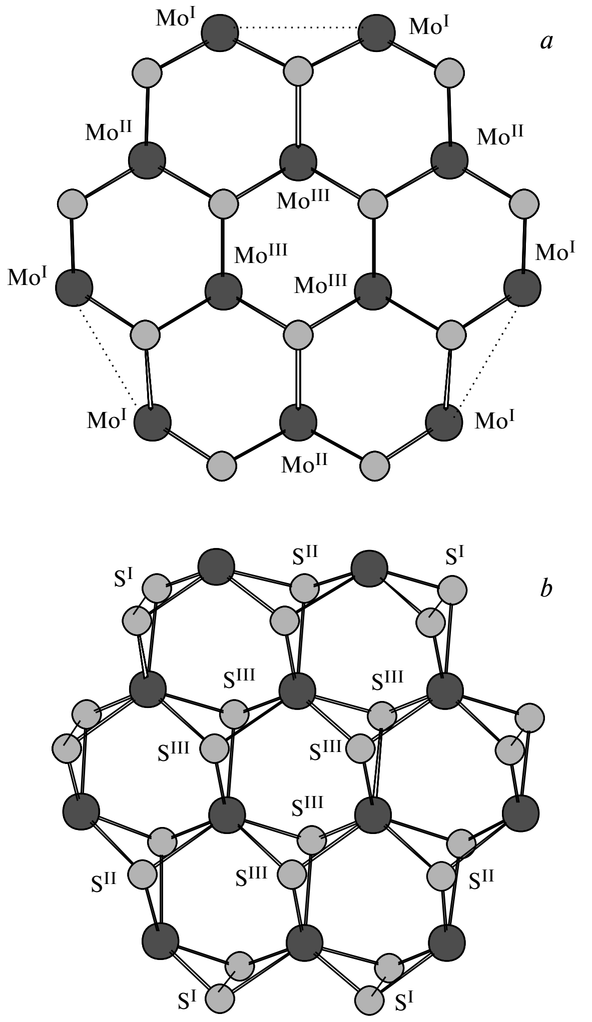

Fig. 2. Molecular structure of $Mo_{12}S_{24}$ cluster as a single slab of polycrystalline MoS_2 obtained from DFT/LANL1DZ (LANL2DZ) calculations: projection on the basal plane (*a*) and view from above (*b*). The geometric parameters of the lateral planes are as follows: $r(Mo^I—Mo^I)$ = 3.29 (3.22) Å and $r(S^I—S^I)$ = 3.08 (3.16) Å. The results of DFT/LANL2DZ calculations are given in parentheses.

Table 1. Results of B3P86/LANL1-DZ and B3P86/LANL2-DZ quantum chemical calculations of the geometric, energy, and electronic characteristics of $Mo_{12}S_{24}$ cluster

Parameter	B3P86/LANL1-DZ	B3P86/LANL2-DZ
Distance	*r*/Å	
$Mo^I—Mo^I$	3.29	3.22
$Mo^I—Mo^{II}$	3.10	3.03
$Mo^I—Mo^{III}$	3.16	3.03
$Mo^{III}—Mo^{III}$	3.16	3.20
$Mo^I—S^I$	2.33	2.37
$Mo^I—S^{II}$	2.43	2.38
$Mo^{II}—S^I$	2.40	2.43
$Mo^{II}—S^{III}$	2.44	2.49
$Mo^{III}—S^{II}$	2.43	2.47
$Mo^{III}—S^{III}$	2.41	2.44
$S^I—S^I$	3.08	3.16
$S^{II}—S^{II}$	3.06	3.33
$S^{III}—S^{III}$	3.06	3.19
Atom	*q*	
Mo^I	+0.13	+0.30
Mo^{II}	+0.44	+0.39
Mo^{III}	+0.61	+0.41
DFT energy/a.u	−347.78370	−1061.36960
μ/D	0	0
ε_i(HOMO) − ε_i(LUMO)/eV	0.98	0.85

Note. Parameters of the adsorption complex $Mo_{12}S_{24} \cdot 6H_2S$ are as follows: $r(Mo—SH_2)$ = 2.73 Å, r(S—H) = 1.379 Å, the H—S—H angle is 94.6°, α = 96.3°, the DFT energy is −416.74280 a.u., μ = 0 D, $\Delta\rho(SH_2)$ = 0.11 *e*, and ΔH = 19.0 kcal mol^{-1}. Gas-phase characteristics of H_2S molecule are as follows: r(S—H) = 1.377 Å, the H—S—H angle is 94.1°, the DFT energy is −11.46285 a.u., and μ = 1.82 D.

spectra of the MoS_2 catalyst was attributed to S—S vibrations. Note that earlier[8,11] the positions of S atoms were optimized only in the basal plane; therefore, the trend to pairing of unsaturated S-centers (see above) was not reported in these studies. For instance, only the calculated Mo—S distances (r = 2.32—2.42 Å) are available from study.[8] The authors of another study[11] pointed that the calculated Mo—S distances (r = 2.33—2.46 Å) are comparable with the distances in the MoS_2 crystal and that the $Mo^I—Mo^I$ distances are somewhat shorter than in the crystal.

Electronic structure of $Mo_{12}S_{24}$ macromolecule. When studying the electronic structure of the MoS_2 single slab, the coordinatively unsaturated Mo centers are of prime interest. According to published data,[17] these centers are characterized by high density of electronic states in the forbidden band and can determine the reactivity of the lateral plane in the interactions with electron-donor molecules (thiophene, H_2S). According to calculations,[8,11] the coordinatively unsaturated Mo centers bear the largest positive charges, which seems to be an indication of possible reactivity of these centers as active MoS_2 sites in the thiophene hydrogenolysis reaction. Nevertheless, it was reasonably mentioned[11] that the results of orbital population analysis strongly depend on the basis set employed in the calculations. In the text above we mentioned an artifact, namely, the highest oxidation state of the surface Mo centers in the $Mo_{12}S_{24}$ [8] and $Mo_{27}S_{54}$ [11] macromolecules. Therefore, in order to compare the oxidation states of the surface and internal Mo ions in the $Mo_{12}S_{24}$ macromolecule, we analyzed the orbital populations according to Mulliken with the minimum basis set (see Table 1) and used the energies of the core molecular levels for Mo 4s-electrons (Fig. 3). Our calculations led to excellent correspondence between the calculated

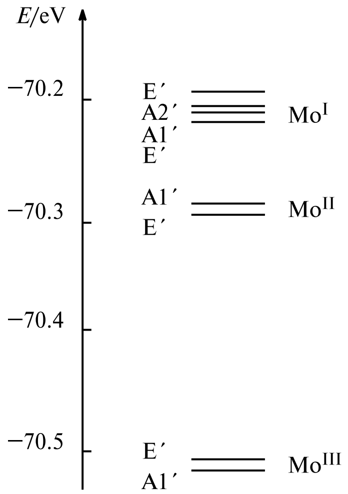

Fig. 3. Energies of core Mo 4s energy levels in $Mo_{12}S_{24}$ cluster with D_{3h} symmetry calculated by the DFT/LANL2DZ method. The core level symmetry is given on the left and the type of the Mo atom, which gives the largest contribution of the electron density to this level, is given on the right.

charges and the oxidation state of the Mo atoms with respect to the energies of the core levels. Deeper-lying core levels of the internal Mo^{III} atoms correspond to larger positive charges of these atoms ($q(Mo^{III}) = +0.61$ (+0.41)), whereas the surface coordinatively unsaturated Mo^I sites have the smallest positive charge ($q(Mo^I) = +0.13$ (+0.30)), thus being more reduced than the internal Mo^{III} centers. These results substantiate the recommendations reported earlier.[16]

Molecular and electronic structure of adsorption complex $Mo_{12}S_{24}\cdot 6H_2S$. In order to characterize the adsorption ability (or Lewis acidity) of the coordinatively unsaturated Mo^I centers, we carried out calculations of the adsorption complex of $Mo_{12}S_{24}$ macromolecule with six H_2S molecules to retain the MoS_2 single slab symmetry. The calculated band gap (energy difference between the highest occupied and lowest unoccupied MOs, ε_i(HOMO) − ε_i(LUMO)) equals 0.98 (0.85) eV. This is comparable with the experimental value (1.30 eV), being in good agreement with the results of DFT calculations[17] with periodic boundary conditions for the MoS_2 single slab (0.89 eV). Note that the ε_i(HOMO) − ε_i(LUMO) difference calculated for $Mo_{27}S_{54}$ macromolecule is only 0.15 eV.[11] The DFT/LANL1DZ calculated molecular structure of the adsorption complex is shown in Fig. 4 (for its characteristics, see Note to Table 1). The local structure of the adsorbed H_2S molecule is first of all characterized by the donor-acceptor interaction between the π-lone pair of H_2S and the surface (reduced) Mo^I centers, because the calculated angle (α) between the molecular plane of HSH and the $Mo^I...SH_2$ adsorption bond slightly exceeds a value of 90° (see Table 1). This is consistent with theoretical concepts of higher reactivity of the π-lone pair of H_2S compared to that of the σ-lone pair[20] and with the experimental data on bent coordination of thiophene in transition metal complexes.[21] The results obtained, that is, a low heat of H_2S adsorption ($\Delta H = -19$ kcal mol^{-1}), long equilibrium distance $Mo^I...S$ in the complex (2.73 Å), low degree of electron density transfer from the H_2S molecule to the $Mo_{12}S_{24}$ macromolecule ($\Delta\rho = 0.1$ e), and insignificant changes in the geometry of the adsorbed H_2S molecule compared to the gas-phase structure point to weakness of the donor-acceptor interaction in the complex. In essence, they confirm a recently drawn conclusion[22] that the results obtained by optimization of the adsorbate geometry on the surface metal center indicate a low degree of electron density transfer from the H_2S molecule to the sulfide catalyst and that this interaction should be treated as physisorption. In other words this implies a low reactivity of coordinatively unsaturated surface Mo^I centers in the reactions with electron-donor molecules (thiophene, H_2S) and suggests that the active component is formed as a result of oxidative addition of hydrogen to the surface metal atoms present in the sulfide catalysts of hydrodesulfuration.[2] According to the results of calculations for the simplest models of the active centers of sulfide catalysts,[23] the surface site exhibits a much higher chemisorption activity after occlusion of hydrogen in the MoS_2 matrix than before it. Similar calculations of dissociative adsorption of H_2 on the $Mo_{12}S_{24}$ macromolecule followed by chemisorption of H_2S are now in progress; their results will be published in the next communication.

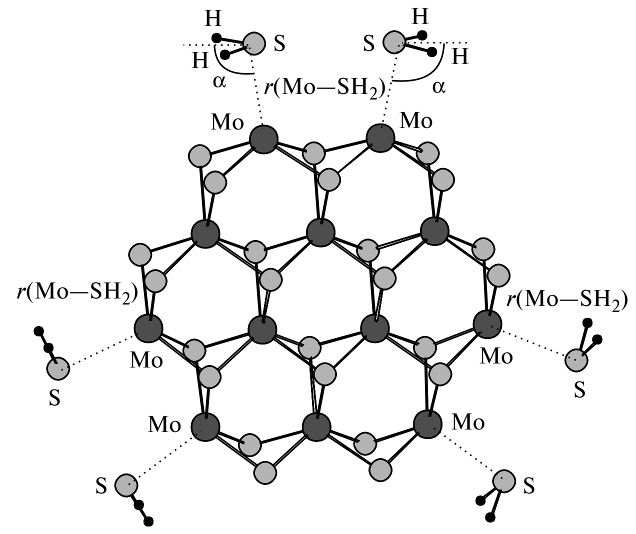

Fig. 4. Molecular structure (D_{3h} symmetry) of adsorption complex of $Mo_{12}S_{24}$ with six H_2S molecules obtained from DFT/LANL1DZ calculations. Local structure of adsorbed H_2S molecule ($r(Mo—SH_2) = 2.73$ Å, α = 96.3°) characterizes a weak donor-acceptor interaction of the π-lone pair of H_2S with the surface (reduced) Mo^I centers.

This work was financially supported by the Council on Grants at the President of the Russian Federation (Program for the State Support of Leading Scientific Schools in the Russian Federation, Grant NSh 1140.2003.3) and the Russian Foundation for Basic Research (Project No. 01-03-32417).

References

1. A. N. Startsev, *Catal. Rev. Sci. Eng.*, 1995, **37**, 353.
2. A. N. Startsev and I. I. Zakharov, *Usp. Khim.*, 2003, **72**, 579 [*Russ. Chem. Rev.*, 2003, **72** (Engl. Transl.)].
3. P. Joensen, R. F. Frindt, and S. R. Morrison, *Mater. Res. Bull.*, 1986, **21**, 457.
4. E. Benavente, M. A. Santa Ana, F. Mendizabal, and G. Gonzalez, *Coord. Chem. Rev.*, 2002, **224**, 877.
5. A. S. Golub´, Ya. V. Zubavichus, Yu. L. Slovokhotov, and Yu. N. Novikov, *Usp. Khim.*, 2003, **72**, 138 [*Russ. Chem. Rev.*, 2003, **72** (Engl. Transl.)].
6. A. S. Golub´, Ya. V. Zubavichus, N. D. Lenenko, Yu. L. Slovokhotov, M. Dano, and Yu. N. Novikov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2191 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2293].
7. X. Ma and H. H. Schobert, *J. Mol. Catal. A: Chem.*, 2000, **160**, 409.
8. P. Faye, E. Payen, and D. Bougeard, *J. Catal.*, 1998, **179**, 560.
9. P. Faye, E. Payen, and D. Bougeard, *J. Catal.*, 1999, **183**, 396.
10. Y.-W. Li, X.-Y. Pang, and B. Delmon, *J. Phys. Chem. A*, 2000, **104**, 11375.
11. H. Orita, K. Uchida, and N. Itoh, *J. Mol. Catal. A: Chem.*, 2003, **195**, 173.
12. J. P. Perdew, *Phys. Rev.*, 1986, **B33**, 8822.
13. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.
14. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
15. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *Gaussian 92/DFT, Revision G. 2*, Gaussian, Inc., Pittsburgh (PA), 1993.
16. I. I. Zakharov, A. N. Startsev, G. M. Zhidomirov, and V. N. Parmon, *J. Mol. Catal. A: Chem.*, 1999, **137**, 101.
17. P. Raybaud, J. Hafner, G. Kresse, and H. Toulhoat, *Surf. Sci.*, 1998, **407**, 237.
18. P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, and H. Toulhoat, *J. Catal.*, 2000, **189**, 129.
19. J. Polz, H. Zeilinger, B. Muller, and H. Knozinger, *J. Catal.*, 1989, **120**, 22.
20. I. I. Zakharov, V. I. Avdeev, and G. M. Zhidomirov, *Surf. Sci.*, 1992, **227**, 407.
21. R. J. Angelici and M. A. Reynolds, *Abstrs Int. Symp.* "*Molecular Aspects of Catalysis by Sulfides*" *(St. Petersburg, Russia, October 6—9, 1998)*, Novosibirsk, 1998, OP-2.
22. A. Sierraalta, A. Herize, and R. Anez, *J. Phys. Chem. A*, 2001, **105**, 6519.
23. I. I. Zakharov and A. N. Startsev, *Tez. dokl. VI Ros. konf.* "*Mekhanizmy kataliticheskikh reaktsii*" [*Abstrs VIth Russ. Conf. "Mechanisms of Catalytuc Reactions*"] *(Moscow, October 1—5, 2002)*, Novosibirsk, 2002, PP-76 (in Russian).

Received November 23, 2003