

Adsorption of thiophene on RuS₂: An *ab initio* density-functional study

V. Smelyansky, J. Hafner, and G. Kresse

Institut für Theoretische Physik and Center for Computational Material Science, Technische Universität Wien, Wiedner Hauptstraße 8-10, A-1040 Wien, Austria

(Received 9 April 1998)

The adsorption of thiophene on stoichiometric and reduced (100) surfaces of RuS₂ has been studied using *ab initio* density-functional molecular dynamics. On the stoichiometric surface, the thiophene molecule is shown to adsorb in a tilted η^1 position where the S atom of the molecule forms a bond with the surface Ru atom similar to that in the bulk RuS₂, but there is no activation of the molecule. Formation of sulfur vacancies on the surface creates a chemically active surface and possibility of thiophene adsorption in the η^2 position, where the molecule is activated. These findings are in good agreement with recent experimental evidence of a drastic increase in catalytic activity of the reduced RuS₂ surface and should contribute to a better understanding of unique catalytic properties of RuS₂ for thiochemistry applications. [S0163-1829(98)51328-8]

The interaction of the heterocyclic molecule thiophene (C₄H₄S) with a transition-metal-sulfide surface has long served as a model of the industrially important hydrodesulfurization (HDS) process.¹ The HDS process is a catalytic reaction between an organosulfur compound and hydrogen to form hydrocarbons and H₂S. Transition-metal disulfides are well-known catalysts for hydrotreating catalysis, with the activity varying by orders of magnitude depending on the metal. Ruthenium disulfide is the most active and most selective catalyst for the HDS process, 13 times catalytically more active than the industrially used Mo sulfide. It is therefore plausible that the nature of the catalytic properties of transition metal sulfides can be more clearly elucidated in the case of RuS₂.

The key step of the HDS process, namely the C-S bond cleavage, is still far from being completely understood. An important first step towards an improved understanding is the knowledge of the initial mode of bonding of thiophene to the surface. Previous theoretical studies of HDS catalysis focused mainly on the thiophene adsorption on MoS₂ using semiempirical techniques.^{2,3} In a recent paper,⁴ however, *ab initio* molecular dynamics has been successfully applied to study the adsorption of thiophene on the catalytically active surface of MoS₂.

The electronic structure of RuS₂ was first theoretically studied by pseudopotential calculations.^{5,6} Despite its obvious importance, there were no theoretical studies of the surface electronic structure and related properties of RuS₂, until a recent Hartree-Fock (HF) type calculation.⁷ The present study relies on a state-of-the-art density-functional (DFT) method for simultaneous calculation of the total energy and electronic structure of the substrate-adsorbate system and should lead to a better understanding of catalytic properties of the RuS₂ surface from the theoretical point of view.

For our calculations we use the Vienna *Ab Initio* Simulation Program (VASP).⁸⁻¹¹ It is based on finite-temperature local-density functional theory as developed by Mermin.¹² We use the exchange-correlation functional based on the quantum Monte Carlo calculations of Ceperley and Alder as parametrized by Perdew and Zunger.¹³ Nonlocal corrections are introduced in the form of the generalized-gradient expansion

proposed by Perdew *et al.*¹⁴ In the finite-temperature form of DFT the variational quantity is the electronic free energy. It also leads to a broadening of the one-electron levels that is very helpful for improving the convergence of Brillouin-zone integrations for metallic systems.

The calculations are performed in a plane-wave basis. The electron-ion interaction is described by fully nonlocal optimized ultrasoft pseudopotentials.^{15,16} Extensive tests of the ultrasoft pseudopotentials for transition metals have been presented before.¹⁷

The minimization of the electronic free energy is performed using an efficient iterative matrix diagonalization routine based on a sequential band-by-band residual minimization method.^{10,11,18} Alternatively, a preconditioned band-by-band conjugate-gradient (CG) minimization has been used.^{8,9} An improved Pulay mixing^{10,19} has been used to update charge density and potential.

The optimization of the atomic geometry (ionic coordinates, volume, and shape of the unit cell) is performed via a conjugate-gradient minimization of the total energy, using the Hellmann-Feynman forces on the atoms and stresses on the unit cell, applying appropriate corrections for the Pulay stress. For a more detailed description of the technique, we refer to the papers by Kresse *et al.*⁹⁻¹¹

The ultrasoft pseudopotentials have been constructed on the basis of scalar relativistic solutions for atomic reference configurations. Typical cutoff energies for the plane-wave expansion of the eigenstates can be as low as 250 eV, as confirmed by detailed convergence tests and comparisons with all electron calculations.¹⁷ During the geometry optimizations, k point grids varying from 11 special points for the bulk to 2 special k -points for the surface have been employed for Brillouin-zone integration using the linear tetrahedron method with Blöchl corrections.²⁰⁻²²

We have obtained a theoretical lattice constant for bulk RuS₂ (cubic lattice, FeS₂ type) $a_{th} = 5.68$ Å, in good agreement with the experimental value $a_{exp} = 5.61$ Å. Other theoretical values from the HF calculations⁷ overestimate the experimental value to a larger extent (see Table I). Our calculated value for the internal parameter u is in perfect agreement with experiment, in contrast with the HF calculations.

TABLE I. Lattice constant a and internal parameter u for bulk RuS₂ from DFT and HF calculations.

| | Expt. ^a | Theory present work | Theory ^b HF with S 3d | Theory ^b HF without S 3d |
|---------|--------------------|------------------------|-------------------------------------|--|
| a (Å) | 5.61 | 5.68 | 5.72 | 5.78 |
| u | 0.388 | 0.3875 | 0.395 | 0.391 |

^aReference 23.

^bReference 7.

Our calculated energy band structure is in excellent agreement with all-electron FLAPW calculations, which we performed to test the accuracy of our pseudopotentials. The material is a semiconductor with an indirect band gap $E_g = 0.8$ eV (experimental value is $E_g = 1.2$ eV).

Before presenting our theoretical results for the surface properties and adsorption of thiophene, let us briefly discuss relevant experimental data. The surface structure of the RuS₂ (100) surface has been recently studied by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM).²⁴ The LEED patterns showed remarkable stability and chemical inertness of the surface under ambient conditions. Compared to other semiconductors, the RuS₂ (100) surface is extremely unreactive towards air constituents such as carbon and oxygen. Further studies using STM confirmed these results. The (100) cleavage planes were found to be atomically flat even months after cleavage, further demonstrating extreme stability of the surface. From the STM images it is evident that the surface is completely unreconstructed, in sharp contrast with most semiconductors. Recent experimental studies²⁵ focused on the catalytic properties of RuS₂ for HDS. The study of the reduction process of ruthenium disulfide has shown that as much as 50% of the total sulfur content can be removed from the surface without any noticeable structural or morphological modification of the surface. At the same time, as long as the stability of the catalyst is preserved, an increase in the degree of desulfurization of the surface leads to a dramatic increase of its catalytic activity from practically zero for the stoichiometric surface to the maximum at a sulfur coverage of 50%.

We model the (100) RuS₂ surface with a periodic stoichiometric slab consisting of four monolayers of Ru each surrounded by two monolayers of S, resulting in 24 atoms per unit cell. All calculations have been performed at the theoretical equilibrium lattice parameter using two special k points. The width of the vacuum layer was 12 Å. After testing for convergence, only the three top layers (one Ru monolayer and two adjacent S monolayers) were allowed to relax.

The stoichiometric (100) surface is very stable and shows practically no reconstruction, in agreement with experiment²⁴ and previous Hartree-Fock calculations.⁷ The surface retains its semiconducting character, although some surface states can be found in the gap region (see Fig. 1). These states are mostly metallic d states of the outermost Ru atoms. We also considered a reduced surface with two S surface vacancies in the top S monolayer and a Ru to S ratio of 1:1. Similarly to the stoichiometric surface, there was no reconstruction, in agreement with experiment.²⁵ We estimate the energy of the vacancy formation to be 1.4 eV per atom.

Thiophene adsorption on the stoichiometric (100) RuS₂

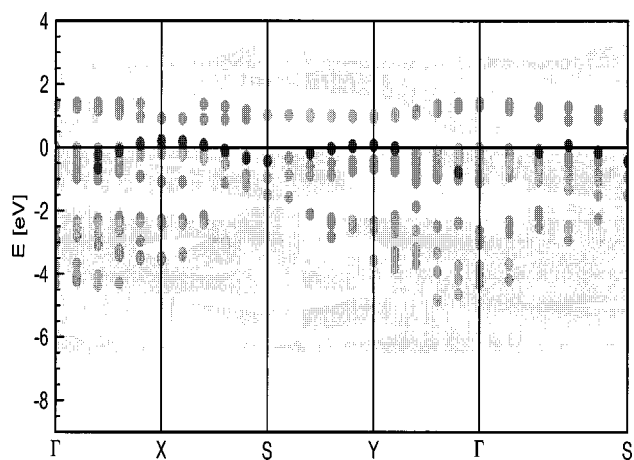


FIG. 1. Surface band structure of RuS (100) (dots). Darker dots correspond to more surface localized states. Shaded areas represent the projected bulk band structure.

surface was studied using various starting geometries with subsequent relaxation of the atoms of the molecule and the top surface layers to their most energetically favorable positions. Surprisingly, the geometry with thiophene in a tilted η^1 position yields a positive adsorption energy of 0.43 eV. Here the S atom of the molecule forms a bond with the surface Ru atom continuing the network of Ru-S bonds in bulk RuS₂ (see Fig. 2). To check for the accuracy of the adsorption energy calculations and to eliminate the possibility of steric hindrance effects, we repeated the calculations with the molecule adsorbed on the (2×1) surface, thus effectively modeling lower thiophene coverage on the surface. The result is the same adsorption geometry with a very similar adsorption energy of 0.38 eV. Again, there is no indication of activation of the molecule (see Table II). Finally, to make sure that our adsorption energy corresponds to a true minimum and not to some metastable configuration, the entire system was gradually heated in a Nosé thermostat to 700 °C. We found no reconstruction of the surface and no change in the adsorption geometry.

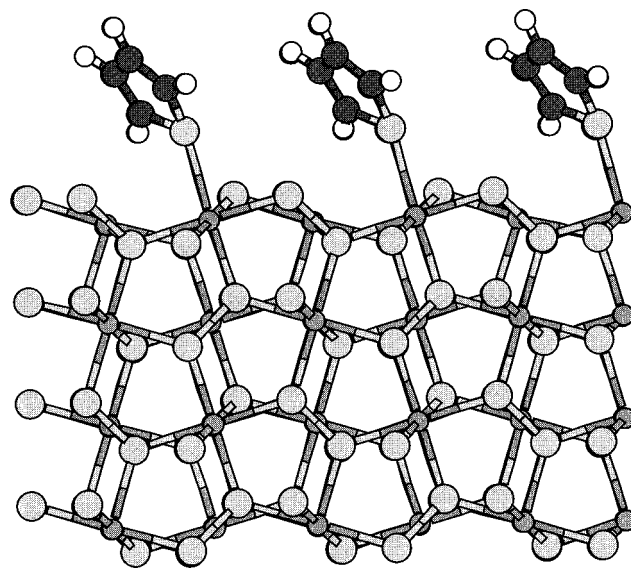


FIG. 2. Thiophene adsorbed on the stoichiometric RuS (100) surface (side view of the slab used in the calculations).

TABLE II. Bond lengths in Å and bond angles in degrees for the free thiophene molecule (experiment and theory) and for the molecule adsorbed on the (100) RuS₂ (theory).

| | Expt. ^a | Theory | Adsorbed | | |
|-------------------------------|--------------------|--------|--------------|---------------|-----------------|
| | | | Low coverage | High coverage | Reduced surface |
| SC ₂ | 1.714 | 1.722 | 1.727 | 1.718 | 1.806 |
| C ₂ C ₃ | 1.378 | 1.389 | 1.384 | 1.366 | 1.393 |
| C ₃ C ₄ | 1.427 | 1.434 | 1.436 | 1.424 | 1.426 |
| C ₂ H ₆ | 1.069 | 1.089 | 1.092 | 1.084 | 1.115 |
| C ₃ H ₇ | 1.081 | 1.094 | 1.093 | 1.087 | 1.078 |
| $\overline{C_5SC_2}$ | 92.57 | 92.26 | 93.14 | 92.25 | 92.26 |
| $\overline{SC_2H_6}$ | 120.25 | 120.25 | 120.23 | 120.28 | 117.75 |
| $\overline{C_3C_4H_7}$ | 124.07 | 120.18 | 124.20 | 124.21 | 122.73 |

^aReference 26.

To model adsorption of thiophene on a reduced RuS₂ surface, we consider a defect surface with the top S atoms removed and start from the same initial geometries as in the case of stoichiometric surface. Now the tilted η^1 position is not most energetically favorable, but an η^2 position is with an adsorption energy of 0.1 eV (see Fig. 3). In this geometry, the surface-induced modifications of the molecular bonds are evident (see Table II). The most pronounced changes are to the SC₂ bond (bond length is increased by 0.09 Å), while the SC₅ bond length remains essentially the same as in the case of the free molecule. In addition, the difference in the C₂C₃ and C₃C₄ bond lengths is decreased from 0.05 to 0.03 Å, indicating a reduced aromatic character of the molecular ring. The origin of these changes can be clearly seen on the charge difference plot (Fig. 4). There is a strong charge depletion around the S atom of the molecule, combined with the corresponding charge influx to the surface metal atoms, illustrating donor properties of the thiophene molecule, and to the C₂ atom of the molecule, demonstrating a back donation from the surface to the molecule. So the formation of

sulfur vacancies on the surface creates a chemically active surface, as found in the experiment.²⁴

In conclusion, we have studied the adsorption of thiophene on the stoichiometric and reduced (100) surfaces of RuS₂ by an *ab initio* molecular dynamics method. Quite surprisingly, thiophene readily adsorbs on the stoichiometric surface in the tilted η^1 position, but there are no signs of activation of the molecule. Calculations for a (2x1) surface show that the adsorption geometries and energies do not change significantly with thiophene coverage. In agreement with experiment, we found activation of the molecule adsorbed on a reduced surface, indicating high chemical activity with respect to bond breaking. In this case, a molecule adsorbs in an η^2 position with an adsorption energy of only 0.1 eV.

These findings confirm the experimental results concerning the unusually high HDS reactivity of the RuS₂ surface and shed some light on the nature of the process. We believe

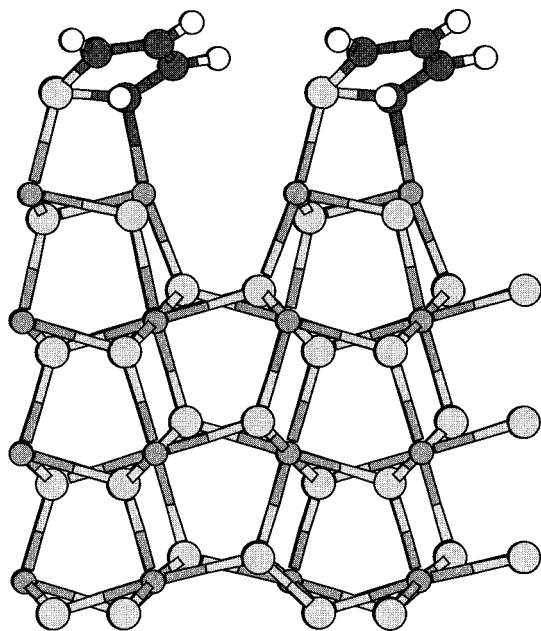


FIG. 3. Thiophene adsorbed on the reduced RuS (100) surface.

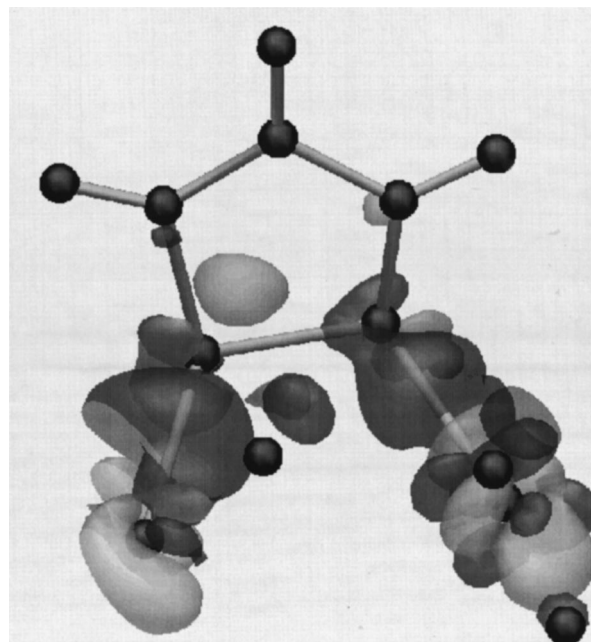


FIG. 4. Charge flow from the molecule to the surface. Lighter areas correspond to the areas of charge depletion, darker areas show charge influx.

the origins of this lie in (a) the very high stability of the surface and its resistance to external contamination, leading to a high selectivity of the surface reactions; (b) the ability of the sulfur-covered surface to adsorb thiophene (and presumably other organosulfur species), thus preparing for the subsequent reactions when the surface is desulfurized by hydrogenation; (c) the very low adsorption energy for thiophene combined with activation of the molecule in an η^2 position, indicating the possibility for easy desorption of the intermediate reaction products. Compared to the case of thiophene on the MoS₂, we note a much lower adsorption energy, but also a substantially lower cost of removing S from the surface. Hence the higher catalytic activity of RuS₂ as compared to MoS₂ is in agreement with the Sabatier principle,²⁹ predicting maximum catalytic activity at intermediate metal-sulfur bond strength.

So far, we completely ignored the important question of coadsorption and dissociation of hydrogen. Experimentally, there is ample evidence that hydrogen plays a crucial role in

the HDS reaction on the RuS₂ surface.²⁷ In addition, molecular chemisorption of hydrogen and H₂S on the stoichiometric (100) RuS₂ surface has been recently studied by the HF method.²⁸ Both species have been shown to adsorb in a tilted geometry similar to that found in the present study. Also, there is a need to investigate the catalytic properties of other surfaces, most importantly the (111) surface, which is usually even more catalytically active than the (100) surface. These are the main goals of our future work. Given the success of our method in the accurate and efficient description of complex adsorbate-substrate systems, there is every reason to expect that it will yield many interesting results in this area.

This work has been supported by the Austrian Science Foundation under Project No. P11353-PHYS. Fruitful discussions with P. Sautet and M. E. Grillo within the Groupe de Recherche Européen "Dynamique moléculaire quantique appliquée a la catalyse" (CNRS) are gratefully acknowledged.

-
- ¹M. Lacroix *et al.*, in *Heterogeneous Catalysis and Fine Chemicals II*, edited by M. Giusnet *et al.* (Elsevier, Amsterdam, 1991), p. 277.
- ²M.C. Zonneville and R. Hoffman, *Surf. Sci.* **199**, 320 (1988).
- ³R. Pis Diez and A.H. Jubert, *J. Mol. Catal.* **83**, 219 (1993).
- ⁴P. Rabaud, J. Hafner, G. Kresse, and H. Toulhoat, *Phys. Rev. Lett.* **80**, 1481 (1998).
- ⁵N.A.W. Holzwarth, S. Harris, and K.S. Liang, *Phys. Rev. B* **32**, 3745 (1985).
- ⁶P. Raybaud, J. Hafner, G. Kresse, and H. Toulhoat, *J. Phys.: Condens. Matter* **9**, 11 085 (1997); **9**, 11 107 (1997).
- ⁷F. Fréchar and P. Sautet, *Surf. Sci.* **336**, 149 (1995).
- ⁸G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 5858 (1993).
- ⁹G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14 251 (1994).
- ¹⁰G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ¹¹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11 169 (1996).
- ¹²N.D. Mermin, *Phys. Rev.* **137**, A1141 (1965).
- ¹³J.P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹⁴J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ¹⁵D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1980).
- ¹⁶G. Kresse and J. Hafner, *J. Phys.: Condens. Matter* **6**, 8245 (1994).
- ¹⁷E.G. Moroni, G. Kresse, J. Hafner, and J. Furthmüller, *Phys. Rev. B* **56**, 15 629 (1997).
- ¹⁸D.M. Wood and A. Zunger, *J. Phys. A* **18**, 1343 (1985).
- ¹⁹P. Pulay, *Chem. Phys. Lett.* **73**, 393 (1980).
- ²⁰O. Jepsen and O.K. Anderson, *Solid State Commun.* **9**, 1763 (1971).
- ²¹M. Methfessel and A.T. Paxton, *Phys. Rev. B* **40**, 3616 (1989); **9**, 1763 (1971).
- ²²P. E. Blöchl, O. Jepsen, and O.K. Andersen, *Phys. Rev. B* **49**, 16 223 (1994).
- ²³O. Sutarno, O. Knopp, and K.I.G. Reid, *Can. J. Chem.* **45**, 1391 (1967).
- ²⁴H. Colell, M. Bronold, S. Fiechter, and H. Tributsch, *Surf. Sci. Lett.* **303**, 361 (1994).
- ²⁵M. Breyse, C. Geantet, M. Lacroix, J.L. Portefaix and M. Vrinat, in *Hydrotreating Technology for Pollution Control Catalysts, Catalysis and Processes*, edited by M.L. Occelli and R. Chianelli (Marcel Dekker, New York, 1997).
- ²⁶P.B. Liescheski and D.W.H. Rankin, *J. Mol. Struct.* **178**, 227 (1988).
- ²⁷S. Yuan, T. Decamp, M. Lacroix, C. Mirodatos, and K. Breyse, *J. Catal.* **132**, 253 (1991).
- ²⁸F. Fréchar and P. Sautet, *Surf. Sci.* **389**, 131 (1997).
- ²⁹P. Sabatier, *Ber. Dtsch. Chem. Ges.* **44**, 1984 (1911).