Hydrodesulphurization of Thiophenes using Transition Metal Sulphides

by

Timotheus Servaas Smit

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Abstract

Transition metal sulphides (TMS) are widely used as hydrodesulphurization (HDS) catalysts for thiophenic species occurring in oil. Although the removal of sulphur from oil is of great industrial importance and has been studied extensively, it is still not known how an HDS catalyst functions at a fundamental level. Open questions in HDS catalysis include (1) the nature of the dependence of the activity of monometallic TMS on the position of the metal atom in the periodic table (periodic effect) and (2) the origin of the unusually high activity of certain mixed TMS (promotion effect). The rational design of new catalysts requires a thorough understanding of these issues.

Density functional electronic structure calculations on model catalyst clusters and catalyst-thiophene complexes have made it possible to identify the rate-limiting step in the overall HDS process, to propose a new HDS reaction mechanism, and to develop a *unified theory of periodic and promotion effects* in TMS HDS catalysis with direct implications for catalyst design. Both effects are above all electronic: the quality of the active site directly affects the activity of the catalyst.

Periodic effects can be explained on the basis of differences in the rate of the rate-limiting step in the HDS process, not through differences in the number of active catalytic sites. A theoretical activity parameter I, based on the strength of the interaction between sulphur $3p$ and metal d electrons in monometallic TMS, correlates well with HDS activity. I depends strongly on the oxidation state of the transition metal and the metal-sulphur bond length.

The promotion effect in mixed TMS, such as nickel(cobalt)molybdenum sulphides, arises from electron transfer from nickel(cobalt) to molybdenum. This transfer corresponds to the removal of σ antibonding metal d - sulphur $3p$ electrons from nickel(cobalt), resulting in a high intrinsic catalytic activity. Molybdenum sulphide merely acts as a support for the promotor elements nickel and cobalt.

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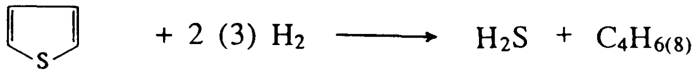
Chapter 1

Introduction

Depending on its geographic origin, crude oil may contain up to 5 wt % sulphur, 2 wt % nitrogen and small amounts of heavy metals such as nickel and vanadium [85]. The presence of sulphur and nitrogen in fossil fuels is harmful to the environment: the oxides which are formed when fuel is burned contribute to acid rain. A further reason for removing sulphur and nitrogen from oil is that many catalysts which are used in the refining process do not tolerate their presence. Hence the removal of sulphur is a crucial step in the processing of oil. Sulphur contaminates oil in various forms: elemental sulphur, (di)sulphides, thiols and thiophene, C_4H_4S, and its derivatives, such as (di)benzothiophene, dihydrothiophene, tetrahydrothiophene, etc.. Of these, thiophenic species are the most difficult to desulphurize, since the sulphur atom is part of a relatively stable aromatic ring. The prototypical reaction for thiophene hydrodesulphurization (HDS) is



$$+ 2\ (3)\ H_2 \longrightarrow H_2S + C_4H_{6(8)}$$

thiophene

The process is typically carried out at 300 - 400 ^oC and 0.7 - 5 MPa hydrogen pressure in an H_2/H_2S environment. Butadiene, butene and butane are formed. Transition metal sulphides (TMS), such as MoS_2 and WS_2, have the ability to catalyze the HDS process of thiophenic species, and have been used for over 60 years for this purpose.

Given its enormous importance for the petroleum industry and the role of oil in the global economy, it is not surprising that the HDS of thiophenes (and particularly thiophene) has been studied extensively by experimentalists and theoreticians alike. It has long been known that mixtures of cobalt-, nickel-, tungsten-, and molybdenum-sulphides are relatively cheap, yet quite active; these catalysts are used in virtually every refinery in the world, cobaltmolybdenum sulphide being probably the most commonly used industrial HDS catalyst. What is not known is why these catalysts are so unusually active: Prins *et al.* [73] recently concluded that the question of how an HDS catalyst functions is completely open again. Since a fundamental understanding of the HDS process is absolutely crucial for the rational design of new catalysts, HDS remains an area of active research. Determination of the structure of the catalyst and identification of the complex surface reactions at work during HDS remain major challenges for surface chemistry, complicated by the fact that many experimental techniques are not representative of reactor conditions. Like other areas of chemistry, catalysis research has benefited greatly from the advent of quantum chemistry. HDS is no exception. Collaboration between various disciplines of chemistry is inspired by the ever greater demands on HDS catalysts, as air-pollution legislation continues to become stricter.

With an eye towards designing new catalysts, two issues are particularly important. It is vital that we understand firstly why certain monometallic TMS are more active than others (periodic effects), and secondly why the above-mentioned mixtures of sulphides are so much more active than the individual components (promotion effects). However, it would have been impossible to explain these effects without a thorough understanding of the basic HDS reaction mechanism. This thesis therefore initially focuses on the catalytic mechanism, using density functional electronic structure calculations [69] on model catalytic clusters and thiophene-catalyst complexes. After a brief review of the literature on HDS catalysis (chapter 2) and a section on research objectives (chapter 3), density functional theory and the multiple-scattered wave method [41] will be discussed in chapter 4. The conventional theory of the HDS mechanism is treated next in chapter 5 [97, 99]. An alternative mechanism is proposed and investigated in chapter 6 [98]. Chapters 5 and 6 thus provide the groundwork for a unified theory explaining *both* periodic and promotion effects, presented in chapter 7 [95]. This will be followed by a brief discussion (chapter 8) and summary of the main results and conclusions (chapter 9). The implications for HDS catalysis and for related catalytic processes and compounds will be discussed in chapter 10.

Chapter 2

Review

Despite the wealth of experimental information from Mössbauer spectroscopy, X-ray diffraction, extended X-ray absorption fine structure (EXAFS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), nuclear magnetic resonance (NMR) and other experimental techniques, many aspects of HDS catalysis remain poorly understood. Theoretical studies also frequently lead to conflicting conclusions. The brief review of the literature given in this section summarizes the current understanding of the catalytic process with particular emphasis on those areas where consensus has not yet been reached among the many researchers active in this field. Following a discussion of the basic HDS reaction mechanism (section 2.1), the focus will shift to periodic and promotion effects in HDS catalysis (section 2.2). The review presented in this chapter is only an introduction into HDS catalysis, highlighting important unsettled issues of immediate importance for the design of new catalysts. Further details of specific aspects of the HDS process are provided in subsequent chapters. For more information, the reader is referred to a number of excellent recent review articles [32, 72, 73, 113, 118].

2.1 Fundamental HDS mechanism

Considerable insight into the nature of the HDS process has been gained from studies on monometallic MoS_2, in which the Mo atoms are located at the center of a

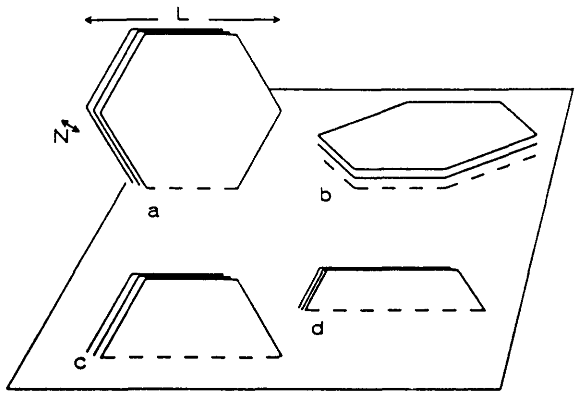


Figure 2-1: Side- (a, c and d) and edge-bonding (b) of MoS_2 crystallites to the support. From ref. [20].

trigonal prism of sulphur atoms. Layers of Mo are sandwiched between layers of sulphur. The MoS_2 sheets are stacked on top of each other with weak Van der Waals bonding between them (MoS_2 is also an excellent lubricant). The crystallites are commonly supported on high-surface-area carbon or $\gamma - Al_2O_3$, either through basal plane bonding or edge plane bonding, figure 2-1.

Voorhoeve [112] suggested that catalysis occurs along the edges of MoS_2 sheets. Edge sulphur atoms are more weakly bonded to Mo than basal plane sulphur atoms. Consequently, some of the metal atoms may be exposed. Experimental studies indicate that exposed metal atoms are the catalytically active sites. Salmeron *et al.* [84] showed that the basal planes of MoS_2 are catalytically inactive. Sputtering increases the HDS activity [21], presumably through the formation of anion vacancies, thus exposing the metal atoms. It was shown by Tauster and co-workers [105] that the activity of MoS_2 for the HDS of dibenzothiophene does not correlate to the BET (Brunauer, Emmett and Teller) surface area, but instead correlates to O_2 uptake. For RuS_2 however, which has the more uniform pyrite structure, the catalytic activity correlates both to BET surface area *and* to O_2 uptake. Kasztelan *et al.* [48, 49] correlated the activity of the catalyst directly to the size and the shape of the TMS cluster. Cluster dimensions uniquely determine the number of corner and edge surface sites. By assigning different intrinsic catalytic activities to different types of sites, a value

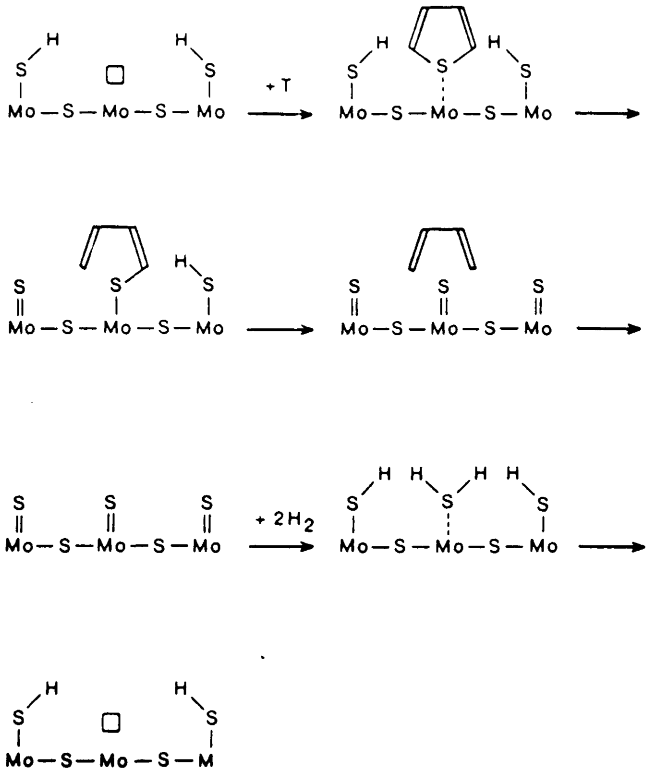


Figure 2-2: Schematic representation of the HDS mechanism proposed by Lipsch and Schuit [58, 59]. See text for details. From ref. [72].

for the total catalytic activity may be obtained.

While it is generally agreed that sulphur vacancies on the surface of the catalyst play a crucial role in the HDS process, there is no consensus on the catalytic mechanism. Even concerning the first step in the HDS process, the adsorption of the thiophene molecule onto the surface of the catalyst, there is little agreement among various researchers in this field. Several binding modes have been put forward. The thiophene molecule may lie perpendicular to the surface, η_1- bound through its sulphur atom, or it may be oriented parallel to the catalyst surface, η_5-bound through all five atoms of the aromatic ring. Both binding modes occur for organometallic molecules with thiophene ligands, the latter slightly more frequently. Alternatively, thiophene may be η_2-bound through adjacent sulphur and carbon atoms. All three binding mechanisms have in common that they rely on sulphur vacancies on the surface of the catalyst. There is no consensus on which one(s) is(are) in fact operative. Given that experimental measurements and theoretical calculations have been interpreted to support all three cases, it is clear that they do not provide conclusive evidence for a specific binding mode. However, in what follows I will argue that η_1 binding is probably operative; this is the mechanism that has been modeled in chapter 5. [1]

It is important to recognize that the specific binding mechanism will depend on such factors as the exact surface/edge structure of the catalyst (different types of sites are present on the catalyst, so that several binding modes may occur simultaneously), sample preparation, the degree of surface coverage, the hydrogen pressure, temperature, etc.. It is possible that thiophene initially adsorbs in a parallel manner, but then tilts away as more molecules are adsorbed [77]. It has also been suggested that a perpendicular geometry is favoured only after hydrogenation of thiophene. Given the multitude of factors influencing the experiments, caution must be exercised when comparing data from different studies. Furthermore, many experiments are performed under ultra high vacuum, whereas reactor conditions require high hydrogen pressures. Despite these limitations, the available *experimental* data suggest, in my opinion, that η_1-binding is operative. For example,using NMR spectroscopy, Blake *et al.* [3] found that thiophene is adsorbed in a vertical position, since hydrogen exchange occurred only at the carbon atoms adjacent to the sulphur atom of thiophene. Also, dihydrothiophene has been suggested as an intermediate in the HDS process [58, 59]. Xu *et al.* [117] recently studied the HDS of dihydrothiophene and found that it is adsorbed perpendicularly to the surface of the catalyst.

Less ambiguity may be expected from *theoretical* studies. Joffre *et al.* [39, 40] performed EHT calculations on the adsorption of thiophene on model MoS_2 clusters

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[1] It will be shown in chapters 5 and 6 that adsorption of thiophene is not the rate-limiting step in the HDS process and that it does not involve strong metal-sulphur interactions. The absence of these interactions has important consequences for the overall HDS mechanism and for the explanation of periodic effects in HDS catalysis. The fact that they do not occur for the adsorption mechanism where they are, a priori, most likely, viz. perpendicular adsorption, makes that the conclusions for perpedicular adsorption can be extended to other adsorption mechanisms (but not vice versa). Thus studying perpendicular adsorption offers important advantages over studying alternative adsorption mechanisms.

representing one-, two-, and three-vacancy sites on the surface. It was found that in the case of one-site adsorption, only perpendicular adsorption of thiophene is (weakly) attractive. $DV-X\alpha$ calculations by Rong *et al.* [79, 80, 81] also point to weak adsorption in a perpendicular fashion. This is supported by extended Hückel calculations on MoS_2 by Zonnevylle *et al.* [120]. Although strong thiophene-catalyst repulsion was observed for parallel adsorption of thiophene, this mechanism is favoured by Zonnevylle *et al.*, since activation of the carbon-sulphur bonds is observed only for parallel adsorption. As cleavage of the carbon-sulphur bonds is necessary at some point along the HDS recation path, this is taken as evidence that η_5 binding is operative. However, IR measurements by Qin *et al.* [74] on adsorbed thiophene show that the electronic structure is almost identical to that of free thiophene, indicating that activation of the carbon-sulphur bonds does not occur upon adsorption.

Finally, it must be remembered that thiophene is the prototype for many sulphur-containing compounds. If a particular adsorption mechanism is operative for thiophene, it does not imply that thiophene derivatives adsorb in a similar manner. Geometric constraints may limit the number of possible adsorption modes, but η_1 adsorption appears to be compatible with most thiophenic species. Whereas the main products of thiophene HDS are butadiene (for low H_2 pressures) and butane (for high H_2 pressures), HDS of dibenzothiophene leads to the formation of biphenyl.

In light of the experimental evidence, the results of quantum chemistry calculations and the adsorption of derivatives of thiophene, this thesis focuses (initially) on perpendicular adsorption of thiophene. This is the so-called one-point end-on mechanism, proposed by Lipsch and Schuit [58, 59] in the early 70's (figure 2-2). In its simplest form, co-adsorbed hydrogen assists in the cleavage of the carbon-sulphur bonds in thiophene and in the removal of the sulphur atom, regenerating the orginal sulphur vacancy through the formation of H_2S. As for adsorption, there is no consensus yet on many other aspects of this process. For example, it is not known whether hydrogen preferentially attacks sulphur or carbon in thiophene. $CNDO$ calculations by Ruette and Ludeña [82] show that a situation where the hydrogen atom is shared by neighbouring sulphur and carbon atoms is energetically favoured over complete hydrogenation of either sulphur or carbon. This suggests that the HDS reaction goes through a complicated series of transition states. A concerted mechanism is operative, much more complex than the simple model proposed by Lipsch and Schuit. There is also no agreement on whether or not hydrogenation precedes desulphurization [119]. For example Rong *et al.* [80] infer from their $DV - X\alpha$ calculations that thiophene is probably first hydrogenated and then desulphurized. The nature of adsorbed hydrogen and its precise kinetic role are not yet fully understood. Both are areas of active research [66].

Satterfield and Roberts [86] have shown that the kinetics of thiophene desulphurization at atmospheric pressure and 235 to 265 $^{\circ}C$ on a commercial sulphided $CoMo/Al_2O_3$ catalyst in a differential reactor is best described by a Langmuir-Hinshelwood type expression of the form:

$$-r = \frac{kP_T P_H}{(1 + K_T P_T + K_S P_S)^2} \tag{2.1}$$

T refers to thiophene, S to hydrogen sulphide and H to hydrogen. It follows that the HDS process is inhibited by H_2S.

Despite the lack of consensus on the fundamental HDS mechanism, this has not traditionally been the focus of industrial research in this field. Until fairly recently, catalysts were developed mainly on a trial and error basis, emphasizing the fabrication of catalysts, rather than a detailed understanding of how they work. (Industrial research is usually not inspired by a particular desire to advance pure scientific knowledge, but instead based on economic motives.) TMS catalysts are commonly made through sulphidization of an oxidic precursor. E.g. $CoMo/Al_2O_3$ may be produced through impregnation of γ-Al_2O_3 with an aequeous solution of ammoniamolybdate and cobalt nitrate. After drying and calcination, the resulting MoO_3 is sulphided in a mixture of H_2 and H_2S. Lu *et al.* [63] and Kuo *et al.* [53] have recently shown that the catalytic activity and selectivity are strongly affected by the presulphidization conditions. The nature of the support may also affect the dispersion of the catalyst, thus directly affecting catalytic activity through the number of sites [48, 49]). The support may furthermore interact electronically with the TMS, thus influencing the intrinsic catalytic activity of the sites [2, 76].

The previous discussion demonstrates that much remains unknown about the fundamental HDS mechanism and TMS catalysts in general. Consequently, it is far from clear how one might improve the quality of the catalyst, the ultimate objective of industrial research in HDS catalysis. The quality of a catalyst is determined by its *selectivity* (percentage of useful products), and by its *activity.* The periodic and promotion effects introduced in chapter 1 both relate to the *activity* of HDS catalysts and will be briefly discussed in the next section.

2.2 Open questions in HDS catalysis: periodic and promotion effects

It has long been known that the activity of monometallic TMS depends strongly on the position of the transition metal in the periodic table, figure 7-1. Consensus for an explanation for this periodic effect has not yet been arrived at. One theory, advocated by Topsøe and co-workers [68, 107] and henceforth referred to as the *structural* theory, holds that the activity differences between various TMS can be explained through different numbers of active sites. The rate of the rate-limiting step in the HDS process is less important. If correct, a detailed understanding of the HDS process is largely irrelevant for the design of new catalysts. What is needed is a catalyst with many active surface sites. A competing *electronic* theory [13, 29, 30, 31] holds that HDS activity differences are determined mainly by differences in the quality of the active site. The number of different sites is still important and for example explains activity differences between different samples of the same material, but it can not account for activity differences between different TMS. A remarkable correlation between the electronic structure of TMS and their activity as HDS catalysts was published by Harris and Chianelli more than ten years ago [29, 30, 31]. However, the correlation was largely empirical and based only on the electronic structure of the monometallic TMS. Since the detailed HDS mechanism was not studied (thiophene was never included in any of the calculations), it is still not clear why the particular electronic parameters identified should correlate so well to HDS activity. Detailed knowledge of the HDS reaction mechanism is a necessary prerequisite for understanding the observed correlation, identification of the rate-limiting step and its chemistry being particularly important: if periodic effects are indeed electronic, then it is likely that direct involvement of the metal atom in the rate-limiting step lies at its basis. [2]

A full understanding of periodic effects is clearly important for future catalyst design. Equally important from a design perspective are so-called promotion effects. As mentioned in the introduction, soon after TMS started being used as HDS catalysts, it was discovered that *mixtures* of nickel-, cobalt-, molybdenum- and tungstensulphides combine low cost with relatively high activity. Cobaltmolybdenum sulphide is the preferred catalyst for HDS, nickelmolybdenum sulphide for hydrodenitrogenation (HDN). Typically, the $Co(Ni) : Mo$ ratio is roughly 1:4. Since the activity of these mixed sulphides is higher than that of $CoS(NiS)$ and MoS_2 separately, $Co(Ni)$ are said to be promotor elements.

The nature of promotion is also not fully understood [72]. Detailed knowledge about the structure of the catalyst is required in order to explain this effect. Topsøe and coworkers [106, 108, 109] have shown that $Co(Ni)$ in a $CoMo(NiMo)/Al_2O_3$ catalyst can be present in three distinct forms: as $Co_9S_8(Ni_3S_2)$ crystallites on the support, as cobalt (nickel) ions decorating the edges of MoS_2 (the so-called $Co-Mo-S$ phase), or adsorbed into the $\gamma - Al_2O_3$ lattice. It is believed that the unusually high HDS activity is related to the $Co - Mo - S$ phase [116]. Recently, EXAFS measurements by Bouwens *et al.* [6, 7, 8, 9] and Louwers *et al.* [61, 62] have provided detailed information on the position of the promotor elements along the edges of MoS_2 and WS_2 (see section 4): promotion is probably related to $Co(Ni)$ ions in close contact with $Mo(W)$. However, this does not indicate whether promotion is a structural or electronic effect. In fact, both the structural and electronic theory of

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[2] It should be noted that only specific aspects of the HDS process may be related to periodic effects. For example, the controversy surrounding the adsorption mechanism (η_1 vs. η_5) may be irrelevant from the point of view of catalyst design (but interesting from an academic viewpoint), if adsorption is not rate-limiting or if it does not involve the metal atom.

periodic effects have been used to also explain promotion effects. Clearly, at most one can be correct. Furthermore, while appealing, there is no guarantee that one theory can explain both phenomena.

Chapter 3

Research Objectives and Strategy

It may be inferred from the previous review that the question of how an HDS catalyst functions is indeed completely open again, as was recently concluded by Prins *et al.* [72, 73]. There is no consensus on (1) the basic reaction mechanism, (2) the origin of the dependence of HDS activity on the position of the transition metal in the periodic table, and (3) the nature of the promotion effect for mixed TMS. Further research is clearly needed, as it is likely that the design of new catalysts will benefit greatly from a comprehensive understanding of these issues. Development of a unified theory for periodic and promotion effects in TMS catalysts is not only of great industrial importance, it also represents the frontier of current research in HDS catalysis. That, in my opinion, is the holy grail of HDS catalysis and the ultimate objective of this thesis.

Proponents of the electronic and structural theories both claim to have compelling "evidence" in support of their theories. Interpretation of experimental data is, however, inherently subjective and slight differences in experimental conditions may have important repercussions for the validity of the conclusions. Consequently, it will be insufficient to merely endorse one of the current theories, or to formulate an entirely new theory. Acceptance of one theory implies rejection of the alternatives; to do so requires falsification. Thus both theories have to be examined, even if one hypothesizes that one or the other is correct. If the structural theory is thought to be correct, then one should focus first and foremost on the catalyst alone (for example in an attempt to determine the *number* of catalytically active sites), but also demonstrate the flaws of the electronic theory. Alternatively, if the electronic theory is adopted as a working hypothesis, the interaction of thiophene with the catalyst will be the focus of attention (for example in order to determine the rate-limiting step and its rate, hence the *quality* of the active site), but arguments must still be provided for rejection of the structural theory. [1] That is the approach taken in this thesis. The interaction of thiophene with the catalyst and the basic HDS reaction mechanism is the starting point of this research. [2] Combined with (1) a critical examination of the structural and electronic theory, and (2) calculations on all first, second and third row TMS, a new theory of periodic and promotion effects will be developed.

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[1] Consequently, the exact nature of the hypothesis has little impact on a research strategy. This is rather fortunate as the choice of hypothesis is often based on such vaguely defined concepts as scientific "intuition" and "reasonableness".

[2] Recall that the analysis of Harris and Chianelli was based solely on the electronic structure of the catalyst, thiophene was not included in any of their calculations.

Chapter 4

Density Functional Theory and the Multiple-Scattered Wave Method

A brief introduction of density functional theory and the multiple-scattered wave method will be given in this chapter. Both methods are widely used in physics and chemistry and many excellent review articles and books have appeared in the literature [41, 47, 50, 69], to which the reader may refer for more details.

4.1 Density functional theory

Although the structure and properties of any polynuclear and multi-electron system are determined by the motions of nuclei and electrons and the interactions between them, often the nuclear dynamics and electronic structure alone provide valuable information about the physics and chemistry of that system. A formal separation of nuclear and electronic coordinates may be achieved through application of the Born-Oppenheimer approximation [5]. Even when this is done it is a formidable task to solve the remaining electronic problem for a static nuclear configuration. In general, a complicated N-electron wave function $\Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, ..., \vec{x}_N)$ ($\vec{x}$ includes both spatial ($\vec{r}$) and spin (σ) coordinates) must be found. In the *Hartree* approximation Ψ is represented as a single product of one-electron wave functions, but this does not satisfy the antisymmetry requirement (Pauli-principle). In the *Hartree-Fock* approximation, a single Slater determinant of one-electron wave functions is used to represent Ψ [102]. From a variational analysis for the Hartree-Fock total energy, a set of *coupled* one-electron equations can be derived [1]:

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla_1^2\psi_{i\sigma}(\vec{r}_1)+ \quad & V(\vec{r}_1)\psi_{i\sigma}(\vec{r}_1) + \textstyle\sum_j e^2 \int \frac{|\psi_{j\sigma}(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|} d\vec{r}_2 \psi_{i\sigma}(\vec{r}_1) - \\ & [\textstyle\sum_j e^2 \int \frac{\psi^*_{j\sigma}(\vec{r}_2)\psi_{i\sigma}(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|} d\vec{r}_2]\psi_{i\sigma}(\vec{r}_1) = \varepsilon_i \psi_{i\sigma}(\vec{r}_1) \end{aligned} \tag{4.1}$$

The last term on the left hand side of this equation represents the *exchange*. The $\psi_{i\sigma}$ are one-electron wave functions (not to be confused with the total N-electron wave function Ψ); the ε_i are the corresponding one-electron energies. By expanding the one-electron wave functions in terms of basis functions, the mathematical problem is transformed into a matrix eigenvalue problem. In *ab initio* Hartree-Fock theory, the matrix elements are computed exactly. Otherwise the method is said to be *semi-empirical.* A solution for the electronic structure is obtained through self-consistent iteration. Higher accuracy can be obtained by expressing Ψ as a combination of determinants. The term *correlation* is used for the energy difference between the exact total energy of an electronic system and the Hartree-Fock total energy (by definition therefore, Hartree-Fock theory does not include correlation effects).

Slater realized that by statistically approximating the exchange term, a set of *uncoupled* equations arises that is much simpler to solve [90]. In his $X\alpha$-method [91, 92, 93], the complicated exchange term is replaced by a term dependent only on the local electron density ρ. This is in effect the earliest and simplest density-functional method. Hohenberg and Kohn [37] justified the use of the electron density as a basic variable in electronic structure calculations. It was shown that the ground state energy of a many-electron system is a functional of the density and that it attains a minimum for the (correct) physical ground-state density. Following the Hohenberg-Kohn paper, Kohn and Sham [51] derived the one-electron equations, analogous to the Hartree-Fock equations, which make density functional theory a practical scheme:

$$[-\frac{\nabla^2}{2} + v_{eff}(\vec{r})]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r}) \tag{4.2}$$

$$v_{eff}(\vec{r}) = v(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}' + v_{xc}(\vec{r}) \tag{4.3}$$

$$\rho(\vec{r}) = \sum_i \sum_\sigma |\psi_i(\vec{r}, \sigma)|^2 \tag{4.4}$$

$$v_{xc} = \frac{\partial E_{xc}[\rho]}{\partial \rho(\vec{r})} \tag{4.5}$$

The Kohn-Sham theory in principle fully incorporates exchange *and* correlation effects through the exchange-correlation potential, $v_{xc}(\vec{r})$, and is thus superior to Hartree-Fock theory. However, an explicit expression for the exchange-correlation functional $E_{xc}[\rho]$ is needed. The search for an accurate functional is one of the main challenges in density functional theory. The simplest approximation is the local density approximation, in which the exchange-correlation potential is a function of the local electron density only

$$E_{xc}^{LDA}[\rho] = \int \varepsilon_{xc}[\rho(\vec{r})]\rho(\vec{r})d\vec{r} \tag{4.6}$$

giving

$$v_{xc}^{LDA}(\vec{r}) = \frac{\partial E_{xc}^{LDA}}{\partial \rho(\vec{r})} = \varepsilon_{xc}(\rho(\vec{r})) + \rho(\vec{r})\frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \tag{4.7}$$

Many forms for the exchange-correlation-functional have been proposed, including gradient-energy terms (to account for the inhomogeneity of the electron gas), non-local terms, etc. [11, 27, 34, 71].

A fundamental difference between Hartree-Fock and density-functional theory is the meaning of the one-electron orbital energies. In Hartree-Fock theory, these represent ionization potentials (Koopmans' theorem [52]). In density functional theory, orbital energies are a measure of the orbital electronegativities [64]. Ionization potentials may be found through application of Slater's transition state procedure [92, 115].

Both Hartree-Fock and density functional theory are widely used in chemistry and physics, but their relative merits are still strongly disputed. Theoretical considera-

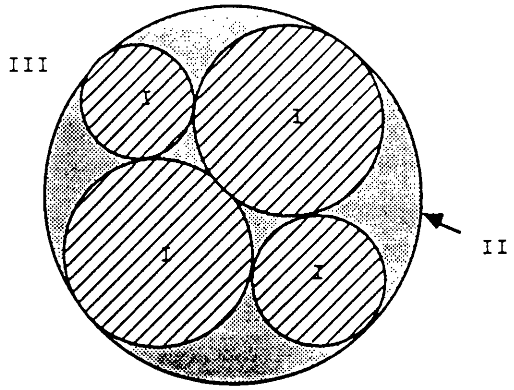

Figure 4-1: Partitioning of a molecular cluster. See text for details.

tions aside, density-functional methods tend to be less computationally demanding, an important quality for the purposes of this research.

4.2 The multiple-scattered wave method

In density functional formalism, solving the electronic structure corresponds to solving the uncoupled Kohn-Sham equations. A number of methods is available, which must be judged on the basis of speed and accuracy. The multiple-scattered wave method (MSW) is relatively fast, particularly for high-symmetry environments [17], and has been successfully applied to many problems in materials science and chemistry, including catalysis [42, 43, 44, 45, 46, 65, 94]. This method, modified for overlapping spheres [36], has been used throughout the calculations presented in this thesis. A brief general introduction and a comparison to other quantum chemistry methods available is given here.

In the MSW method, the space of a polyatomic cluster is partitioned into three regions: (I) atomic: overlapping spheres centered on the constituent atoms, (II) interatomic: the region between the atomic spheres and an outer sphere surrounding the entire cluster, and (III) extramolecular: the region outside the outer sphere (figure 4-1). The potential is spherically averaged in the atomic and extramolecular regions (the so-called muffin-tin approximation), volume-averaged in the interatomic region. The

Kohn-Sham equations are solved separately in each region. The solutions, represented as expansions in spherical harmonics, are matched continuously and with continuous first derivatives across the boundaries separating the various regions. This procedure leads to a rapidly convergent set of secular equations which are solved numerically for the molecular orbitals and energies. With the occupied orbitals a new charge density and potential can be constructed (eq. 4.4). The entire computational procedure is repeated until self-consistency is achieved. In the process of iterating towards self-consistency, large fluctuations may occur in the energy levels of the orbitals. As a result it may be necessary to repopulate the orbitals between subsequent iterations, thereby introducing significant changes in the potential. In this process, repeated switching of the highest occupied and lowest unccupied molecular orbitals (HOMO and LUMO) is sometimes encountered. To avoid this problem, fractional occupation numbers for the orbitals have in some cases been used in the calculations reported in this thesis. Occupying the orbitals according to a Fermi-Dirac distribution does not significantly affect the character of the orbitals, but greatly improves the speed of convergence of the calculations [99].

The MSW method has often been combined with Slater's $X\alpha$ method [91, 93], but one is free to use different exchange-correlation functionals. In the calculations reported in this thesis, the exchange-correlation potentials of Hedin and Lundqvist [34] and Ceperley and Alder [11] have been used. If the polyatomic cluster carries a net charge, the stabilizing Madelung potential of a crystalline or surface environment can be mimicked through the use of a Watson sphere [114]. This may result in a shift of the manifold of molecular orbital energy levels and appropriate corrections have to be made, as has been done throughout this thesis.

The performance of the MSW method is in general good, especially for calculating one-electron properties. In case of poor agreement with experiment, failure is attributed to the muffin-tin approximation, rather than to the density functional approximation [38]. The accuracy can be improved by optimizing the choice of atomic sphere radii [38, 67] and by the use of overlapping spheres [36] (as used in this thesis). Recently, Takai and Johnson [103, 104] have proposed an optimization procedure taking into account both the minimization of total energy and the virial theorem. In spite of these improvements, the use of the muffin-tin approximation may lead to the incorrect charge density. This applies in particular to "open" systems and low-symmetry structures, where the accuracy of the potential in the interatomic region may be questioned. It is also well-known that total energy figures are only approximate within the MSW framework [15, 38]. While full-potential quantum chemistry methods are more accurate and often incorporate geometry optimization, they are also much more computationally intensive. For certain applications, such as the determination of the ground state geometry of a particular compound, the greater accuracy is essential and can not be sacrificed. One of the goals of this thesis, however, is to identify the *basic* HDS mechanism, through calculations on *model* clusters. These clusters are chosen to represent basic chemistry. "Chemical accuracy" is not required. The necessarily approximate nature of the model clusters implies that an approximate quantum chemistry method suffices: there is no justification for striving for greater numerical accuracy in the determination of inherently approximate parameters, particularly if it sacrifices computational speed. Hence the MSW method has been chosen on the basis of its computational speed, the expert advise available and its proven success in HDS catalysis (the method was also used by Harris and Chianelli [29, 30, 31]). As a result, it has been possible to carry out a systematic investigation of *all* TMS. However, as computers continue to become cheaper and more powerful, computational speed will become less relevant an argument in the choice of a quantum chemistry method in the near future. Consequently, the shift to full-potential ab initio methods is expected to continue.

It should be noted that the programs allow for rapid visualization of individual molecular orbitals, an extremely useful feauture if one is interested in orbital topologies and interactions.

Chapter 5

HDS Mechanism

5.1 Introduction

In this chapter the basic HDS reaction mechanism is investigated. For reasons explained in chapter 2, the focus is on the η_1-binding mode. The identification of the rate-limiting step in the HDS process and the involvement of the metal atom in that step will be emphasized.

Within the framework of this one-point end-on mechanism, the question remains what the precise mechanism is through which *adsorption* of the thiophene molecule onto the catalyst takes place. Since the transition metal atom is exposed at the sulphur surface vacancies, one is led to believe that metal-sulphur interactions are responsible for binding the thiophene molecule to the catalyst [29, 30]. A number of (molecular orbital) studies have been devoted to the nature of this bonding, addressing the question whether σ or π *metal*-sulphur bonding governs the adsorption process. Duben [18] reported Hückel molecular orbital calculations on adsorption complexes in which the transition metal sulphide was represented as a single metal atom. Similarly Zdražil [118] modeled the sulphide as a single protonic center. The extreme simplicity of these models excludes the possibility of sulphur-sulphur interactions and severely limits the validity of the conclusions.

In the calculations reported in this chapter, the surface of a TMS has been modeled as an MS_5^{-n} cluster (an octahedral cluster where one of the sulphur atoms has been omitted). Starting separately from the electronic structure of thiophene (section 5.2) and the electronic structure of this simple model for the surface of a TMS catalyst (section 5.3), a model for the adsorption complex will be developed. Electronic structure calculations have been performed on this model for various thiophene-catalyst separations, mimicking the gradual end-on adsorption of thiophene. A similar series of calculations has been carried out for complexes of thiophene and Ni-promoted MoS_2, for which Bouwens *et al.* recently reported accurate EXAFS data [8]. In both cases metal-suphur interactions are found to be weak during adsorption of the thiophene molecule onto the surface of the catalyst. Strong $p\pi$ interactions between the sulphur atom in thiophene (which will henceforth be referred to as S_T) and the *sulphur* atoms in the catalyst are however observed, leading to weak binding of thiophene to the catalyst. It is concluded that adsorption is not the rate-limiting step in the overall HDS process (section 5.4). The fact that *adsorption* of thiophene onto the catalyst is not dominated by metal-sulphur bonding suggests an alternative *adsorption* mechanism, which does not require vacancies on the surface of the catalyst. This possibility will be explored in chapter 6.

The inclusion of hydrogen into the simple adsorption complex provides some (limited) insights into its role in the HDS process. This is the subject of section 5.5. The calculations indicate *when* and *how* metal-sulphur interactions become important during the HDS process. Only small differences in the strength of metal-sulphur bonding are observed for various TMS-thiophene complexes, but the differences are significant for TMS-dihydrothiophene complexes. This suggests that hydrogenation of the thiophene molecule must take place before, or in conjunction with, desulphurization and also that the dependence of catalytic activity on the position of the transition metal in the periodic table is an electronic effect, determined by the rate of the rate-limiting desulphurization step. It prompts a new look at the calculations and analysis of Harris and Chiannelli in which electronic parameters of the bulk TMS are correlated to HDS activity [29, 30]. This is the topic of chapter 7, where a new theory of periodic effects in TMS HDS catalysts will be presented.

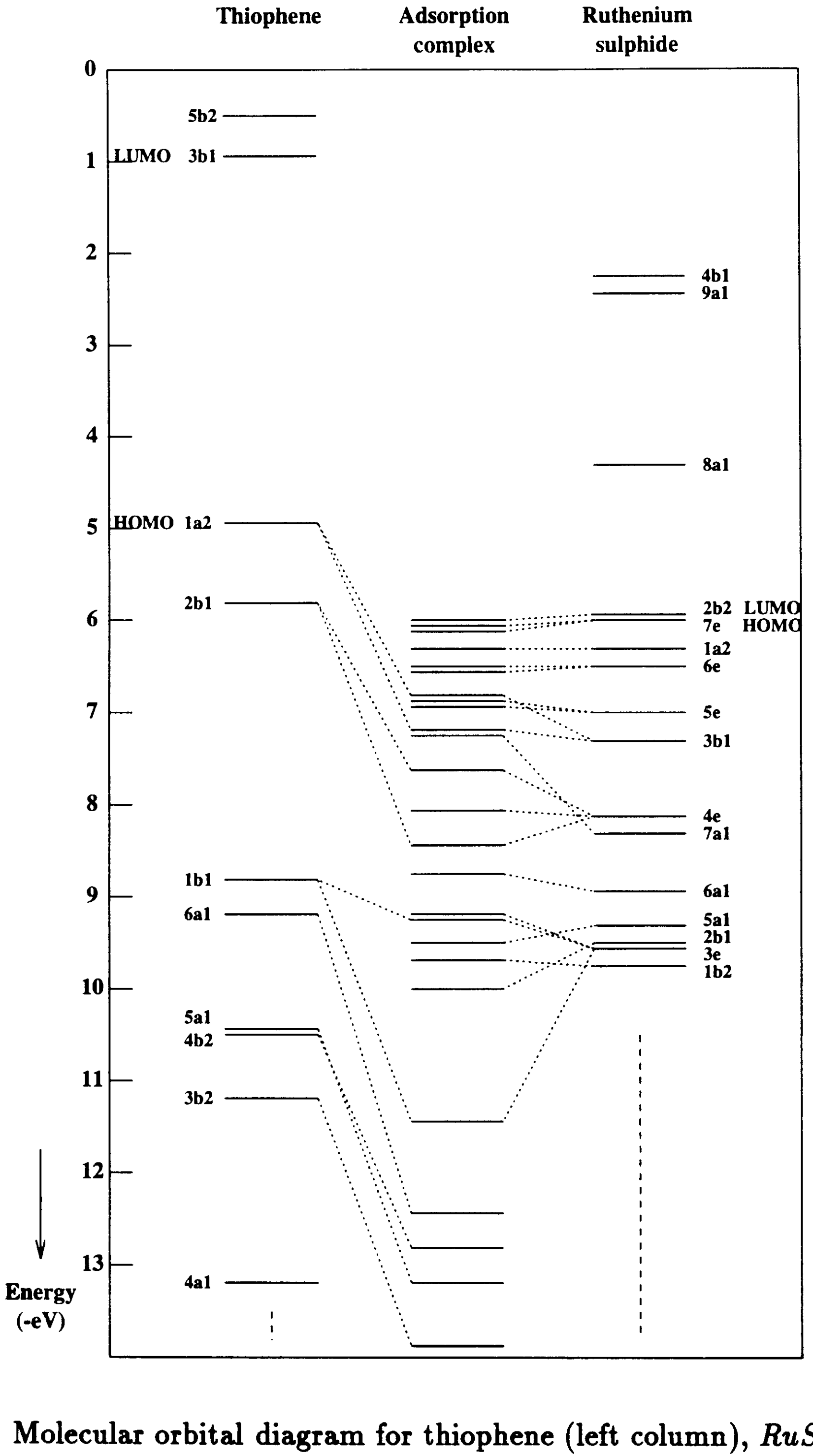

Figure 5-1: Molecular orbital diagram for thiophene (left column), RuS_5^{-6} (right column), and for the RuS_5^{-6}-thiophene adsorption complex (middle). The positions of the highest occupied and lowest unoccupied orbitals (HOMO and LUMO) are indicated. For thiophene the orbital labels correspond to the irreducible representations of the C_{2v} point group, C_{4v} for RuS_5^{-6}.

5.2 Thiophene: (electronic) structure and implications for the HDS process

(Electronic) Structure

Thiophene, C_4H_4S, is a planar molecule, with a two-fold rotation axis and two symmetry planes [33]. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are combinations of p-contributions from the various ring atoms, perpendicular to the plane of the molecule. Many electronic structure calculations for thiophene have been reported, using a variety of quantum chemistry methods (for a review, see [35]). A molecular orbital energy level diagram, obtained using the scattered-wave method, is given in figure 5-1, left column. Orbital labels correspond to the irreducible representations of the C_{2v} point group. By including spherical harmonics of order 2 on the sulphur atom, d-orbitals have effectively been included [1] . The reader is reminded of the fact that energy eigenvalues represent orbital electronegativities in density functional theory, not ionization potentials [64]. The latter can be found using Slater's transition state procedure [115], giving e.g. values of -8.0 eV and -8.9 eV for the first and second ionization potentials, in reasonable agreement with ESCA measurements by Gelius *et al.* [24] (-9.0 and -9.3 eV).

The LUMO has b_1 character and lies well above the HOMO (-0.9 eV). This orbital is antibonding between adjacent carbon and sulphur atoms. Perhaps the most remarkable feature of the HOMO (-4.9 eV, irreducible representation a_2) is the fact that it has no component on the sulphur atom. A contour plot for this orbital is given in figure 5-2a, a schematic representation is included. The orbital characteristics are summarized in table 5.1, where the contributions form the various atoms are separated into s, p, d and f components. The next highest orbital lies about 1 eV below the HOMO and has b_1 character. Although it is antibonding between sulphur and carbon, figure 5-2b, it is often referred to as the out-of-plane sulphur

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[1] There has been considerable debate about the importance of d-functions on the sulphur atom (see e.g. Gelius *et al.* [25]). Very little difference was found from the results presented here if only p-functions were used.

Level	*Energy (-eV)*	*Charge*	*Character*			*Charge*	*Character*		
			%s	%p	%d		%s	%p	%d
$1a_2$	4.9	44% C_1	0	100	0	15% C_2	0	91	9
		3% S_1	0	0	100	1% H_1	0	100	0
		0% H_2	0	100	0	35% int	0	0	0
		2% out	0	0	95				
$2b_1$	5.8	5% C_1	0	74	26	33% C_2	0	99	1
		27% S_1	0	99	1	0% H_1	0	100	0
		1% H_2	0	100	0	33% int	0	0	0
		2% out	0	6	71				
$1b_1$	8.8	18% C_1	0	98	2	10% C_2	0	97	2
		38% S_1	0	98	2	0% H_1	0	100	0
		0% H_2	0	100	0	33% int	0	0	0
		1% out	0	61	19				
$6a_1$	9.2	16% C_1	4	85	11	19% C_2	6	85	9
		50% S_1	7	92	2	1% H_1	89	11	0
		10% H_2	91	9	0	0% int	0	0	0
		3% out	6	83	10				

Table 5.1: Orbital characteristics for the four highest occupied orbitals of thiophene. "Int" refers to the intersphere region, "out" to the outersphere region. For details of the scattered wave method, see chapter 4 and ref. [41].

"lone pair", because of the large sulphur $3p$ contribution. The other lone pair, $6a_1$, lies in the plane of the molecule, figure 5-2c. The orbital energy is approximately 3.4 eV lower than the energy of the $2b_1$ orbital. The $1b_1$ orbital (-8.8 eV) also has a large out-of-plane sulphur component, but is bonding between carbon and sulphur.

Implications for the adsorption of thiophene onto TMS catalysts

In frontier orbital theory [22], the orbitals in the vicinity of the Fermi level, particularly the HOMO and the LUMO, play a crucial role when a molecule takes part in a chemical reaction. If the thiophene LUMO ($3b_1$, figure 5-1,antibonding between carbon and sulphur) were to be occupied during the adsorption process, it would clearly weaken the carbon-sulphur bond, hence induce $C - S_T$ cleavage. Since adsorption is often described in terms of the Blyholder model [4], i.e. electron donation from an occupied adsorbate orbital to the surface and backdonation from the surface into an empty adsorbate orbital, Zonnevylle *et al.* [120] use the population of the thiophene $3b_1$ orbital as the main criterion for determining the HDS activity of various adsorption geometries. Extended Hückel calculations indicate that its population is significantly higher for η_5-binding than for η_1-binding. Hence it is concluded that the η_5-binding mode is more active, despite the fact that the binding energy indicates repulsion between adsorbate and adsorbent for η_5-binding but weak attraction for η_1-binding, and contrary to the findings of some transition metal surface studies [3, 117]. Occupation of the $3b_1$ orbital is however not the only way of weakening the sulphur-carbon bonds. This may also be achieved as a result of hydrogenation of the carbon atoms [80]. The low occupation of the thiophene LUMO in η_1-binding may therefore be alternatively interpreted as an indication that adsorption and hydrogenation are distinct phases in the overall HDS process. It does not imply that η_1-binding is not operative.

The fact that the LUMO does not participate in adsorption should not be surprising, given the substantial energy gap between the HOMO and the LUMO (approximately 4 eV). Since the gap between the two sulphur lone pairs is similarly large, roughly 3 eV, it is likely that only the $1a_2$ and $2b_1$ levels will strongly participate in

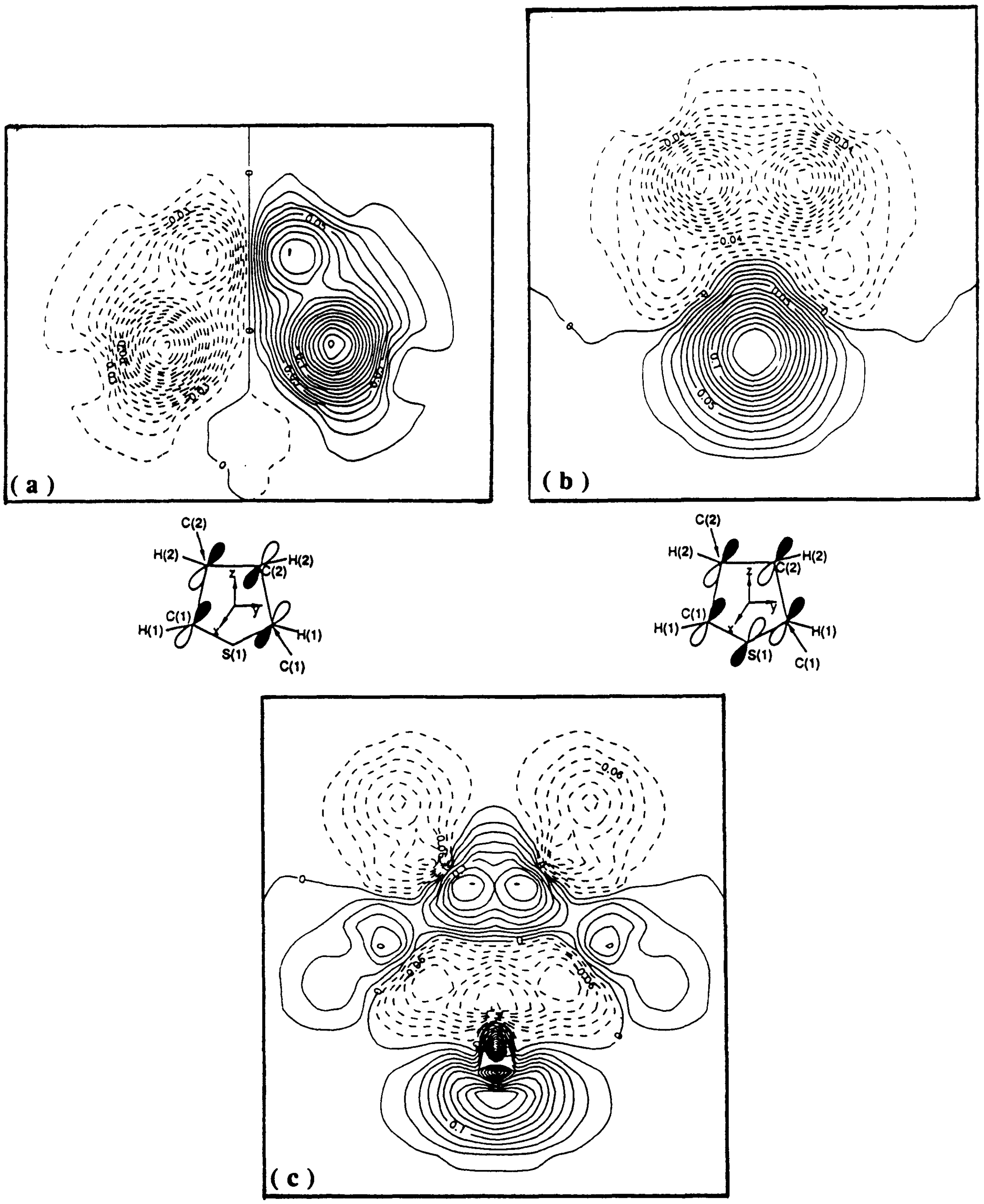


Figure 5-2: Contour plots for the two highest occupied molecular orbitals of thiophene, $1a_2$ (a) and $2b_1$ (b), and for the $6a_1$ orbital (c), see figure 5-1. Schematic representations are included. The $1a_2$ and $2b_1$ orbitals are given 1 a.u. above the plane of the molecule. Maximum contour values are 0.18 and 0.14 respectively, the contour interval is 0.01. Dotted lines indicate negative values, solid lines refer to positive values. The $6a_1$ orbital is shown in the plane of the molecule. The maximum contour value is 0.28, minimum -0.16. The contour spacing is 0.02.

η_1-binding. The very large sulphur p_z-component of the $2b_1$ orbital makes this orbital the most likely candidate for dominating the η_1-adsorption process. The antibonding nature between S_T and C_1 (nomenclature of symmetry-unique atoms corresponds to figure 5-3) will also facilitate the breaking of the sulphur-carbon bond at some point along the HDS reaction path.

The above argument is based on the topology of specific thiophene orbitals. For wider applicability to other thiophenic compounds the electronic structure of these derivatives must be similar to that of thiophene. Spectroscopic measurements show that this is indeed the case as far as the local electronic configuration on the sulphur atom is concerned [26, 78] The sulphur "lone pairs" are not significantly affected by the addition of more aromatic rings. However, steric effects limit the number of binding modes for thiophene derivatives, as mentioned in chapter 2. This suggests that it suffices to study the one-point end-on adsorption of thiophene in order to understand the basic chemistry of the HDS process of thiophenic species.

An argument that is also frequently used in support of η_1-binding is the electrostatic attraction between the positively charged metal atom of the catalyst and the supposedly negatively charged sulphur atom in thiophene. In terms of its charge however, the thiophene sulphur atom is highly uncharacteristic. Most quantum chemistry calculations show that it is positively charged, or at best neutral [25, 35]. This is supported by experimental measurements of the dipole moment of thiophene [28]. Any electrostatic attraction between this sulphur atom and the exposed metal atom must therefore result from a dipole-monopole interaction, i.e. from polarization of the lone pairs on the sulphur atom. In this context it is likely that the out-of-plane lone pair is important in the adsorption process. The involvement of the in-plane lone pair is expected to be less, as it strongly tied up in the electron system of the aromatic ring.

In summary, frontier orbital theory, orbital topologies and electrostatics all assign particular significance to the out-of-plane sulphur lone pair on the thiophene molecule in the HDS process.

5.3 The (electronic) structure of model and real TMS catalysts

5.3.1 Model catalysts

A simple model for the surface of TMS catalysts

The binary TMS have either octahedral (e.g. RuS_2) or trigonal prismatic symmetry (e.g. MoS_2), with the exception of PdS and PtS, for which Pd and Pt are in a square planar environment. Since both supported and unsupported TMS can catalyze the HDS reaction, the catalytic activity is believed to arise from the sulphide, rather than from the support. It is also well-known that the catalytic activity depends on the position of the transition metal in the periodic table [70]. In an attempt to correlate the electronic structure to the experimentally observed activities, Harris and Chianelli carried out scattered-wave calculations on octahedral TMS clusters, MS_6^{-n} [29, 30, 31]. Despite the fact that this model represents the *bulk* catalyst whereas the catalytic reaction is supposed to take place at the *surface*, and furthermore *all* TMS were modeled as having octahedral symmetry, remarkably good correlation between experimental catalytic activities and a theoretical activity parameter was obtained for first and second row TMS (no results were reported for third row elements). It was concluded that it is the ability of the metal atom to bond covalently to sulphur which determines the catalytic activity of the TMS. This suggests (but does not imply) that adsorption is the rate-limiting step in the overall HDS process, but leaves open the exact nature of the interaction between the thiophene molecule and the catalyst.

One of the sulphur atoms in the octahedron is replaced by a vacancy (explicitly included in our calculations), so as to model the edge/surface rather than the bulk. In doing so, the symmetry is lowered from O_h to C_{4v}. This is a very simple model: as noted previously, many TMS do not possess octahedral symmetry and even if they do, some degree of surface reconstruction is to be expected. However, these limitations are not expected to affect the *basic* chemistry which these calculations aim to identify. On the other hand, the simplicity of the model and its relatively high symmetry do influence the speed of the calculations favourably [17].

The second and third row TMS are considerably more active than the first row sulphides. Since maximum catalytic activity is obtained for RuS_2 for the second row elements (although this depends in part on the normalization of experimental data [70]), this is the TMS for which calculations have been performed. After a detailed discussion of the electronic structure of an RuS_5^{-6} cluster, the adsorption of thiophene onto RuS_5^{-6} will be discussed in secion 5.4.

Electronic structure

An energy level diagram for RuS_5^{-6} is given in figure 5-1, right column. The HOMO and LUMO ($7e$ and $2b_2$) are both π antibonding between the metal and sulphur atoms in the cluster, through metal d and sulphur p contributions. The $1a_2$ orbital, which lies immediately below this pair of orbitals, is a non-bonding combination of sulphur p contributions in the xy plane (no metal component). This orbital serves as a reference level and has been assigned the same energy as the $3p$ level in atomic sulphur, viz. -6.3 eV. All the levels from $1a_2$ down to $6a_1$ are based on sulphur $3p$ states. This manifold of levels corresponds to the sulphur $3p$ band in the bulk TMS. The metal contribution to these orbitals is small (e.g. 6 percent for $4e$), except for the $6a_1$ orbital which has substantial $Ru - 4s$ character (15 percent). Metal d - sulphur p bonding orbitals lie below the sulphur $3p$ band. Further down one finds sulphur s states, etc. Above the π antibonding levels lie two σ metal-sulphur antibonding orbitals ($9a_1$ and $4b_1$). The $8a_1$ level, which is situated between the π and σ antibonding levels, is a direct consequence of the inclusion of the vacancy in the cluster. Its character is similar to that of the $9a_1$ level.

Implications for the adsorption of thiophene and the geometry of the adsorption complex

As the number of orbitals near the Fermi level is rather large, it might appear that many different orbitals can participate in the adsorption process, resulting in a very complex interaction mechanism. However, orbitals can interact only if the product of

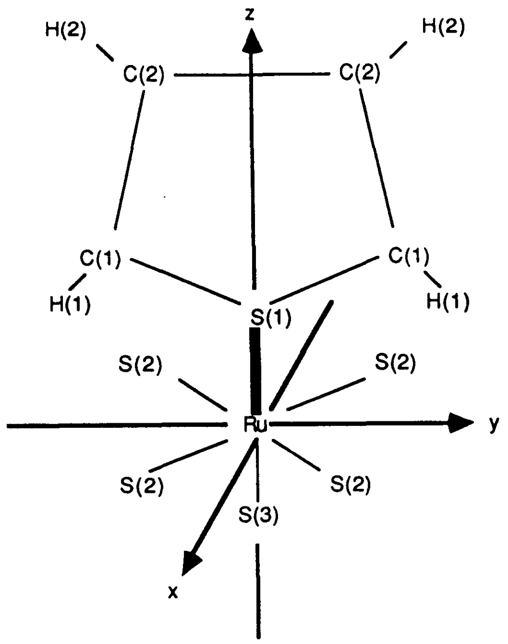


Figure 5-3: Schematic representation of the thiophene-catalyst adsorption complex.

their irreducible representations contains the fully symmetric, a_1, representation. The highest possible symmetry for the thiophene-catalyst complex is that of the thiophene molecule, C_{2v}, if the end-on mechanism is operative. If the plane of the molecule coincides with the xz-plane of the catalyst (see figure 5-4: the $C(1) - S_T - C(1)$ bonds would be located directly above the $S(2) - Ru - S(2)$ bonds), the C_{4v} irreducible representations (a_1, a_2, b_1, b_2 and e) reduce to a_1, a_2, a_2, a_1 and $b_1 + b_2$ respectively. If alternatively the catalyst is rotated by 45^0 (as shown in figure 5-3), they correspond to a_1, a_2, a_2, a_1, $b_1 + b_2$ respectively. It is assumed that the symmetry of the adsorption complex is preserved during adsorption.

It follows that the thiophene HOMO can interact only with catalyst (C_{4v}) a_2 orbitals for the former geometry, or with either (C_{4v}) a_2 or b_1 orbitals for the latter geometry. The only catalyst orbital with (C_{4v}) a_2 character is a non-bonding combination of sulphur $p_{x/y}$ contributions. Any involvement of this orbital in the adsorption process must be considered extremely unlikely. The b_1 orbital closest to the Fermi level ($3b_1$) is a combination of sulphur $3p$ contributions in the xy plane, without any metal content.

The out-of-plane sulphur lone pair (described at length in the previous section and the most likely candidate for dominating the adsorption process) can interact *only* with catalyst e orbitals, regardless of the choice of model. The topologies of these orbitals suggest that the strength of the interaction will probably be maximized if the second choice for the geometry of the thiophene-catalyst complex is adopted, as in figure 5-1. This is the model for which calculations have been carried out for various thiophene-catalyst separations.

Only the catalyst HOMO has a large metal contribution and might explain activity differences between various TMS *if* adsorption is rate-limiting in the overall HDS reaction. This orbital, shown in figure 5-4a in the xz plane and in figure 5-4b in a plane spanned by a line through two neighbouring sulphur atoms and the z-axis, is antibonding between Ru and S, but weakly bonding between neighbouring sulphur atoms. The other e-orbitals in the vicinity of the Fermi level belong to the sulphur $3p$ band.

The simplicity of the model catalyst made it relatively easy to identify interaction partners for the two highest occupied thiophene orbitals. The structure of a real catalyst, e.g. $Co - Mo - S$, is much more complex and will be considered next.

5.3.2 Nickelmolybdenum sulphide

In recent years it has been shown that Ni and Co promoter atoms decorate the edges of MoS_2 slabs and are located in the Mo-plane [106, 108, 109]. Bouwens *et al.* recently reported accurate geometrical data for the edges of $Ni-$ promoted MoS_2 obtained from EXAFS measurements, figure 5-5 [8]. Startsev has shown on the basis of the electroneutrality principle that the edge structure of $Co - Mo - S$ is very similar [100].

One of the most interesting features of the edge structure of $Ni - Mo - S$ as reported by Bouwens *et al.* is the five-fold coordination of the Ni atom. An apical sulphur atom in the $Mo - Ni$ plane (S_E) completes the square pyramidal coordination, but given the large uncertainty in the coordination number (5.3 +/- 1.0), the

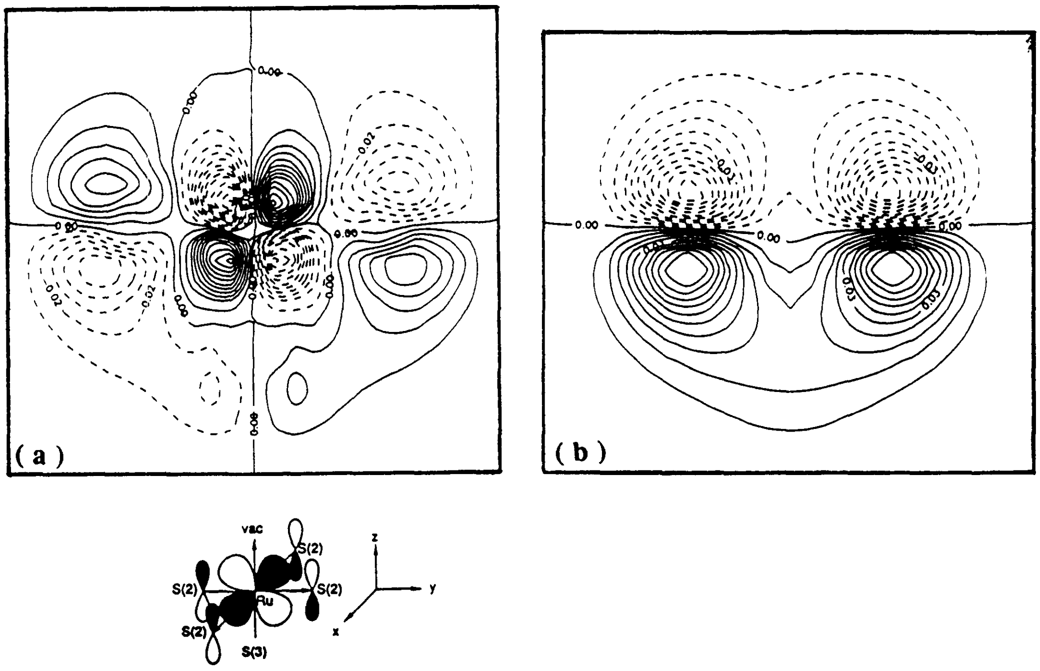


Figure 5-4: Contour plots for the 7e orbital of RuS_5^{-6}, see figure 5-1. In (a) the orbital is plotted in the yz-plane, in (b) the plane is spanned by the z-axis and by a line parallel to two neighbouring sulphur atoms (intersecting the axes at $x(y) = 5.45$ a.u.). Maximum contour values are 0.10 (a) and 0.05 (b). The contour interval is 0.01 for (a), 0.005 for (b). The metal d_{xz} contribution has been omitted for clarity in the schematic representation in (a).

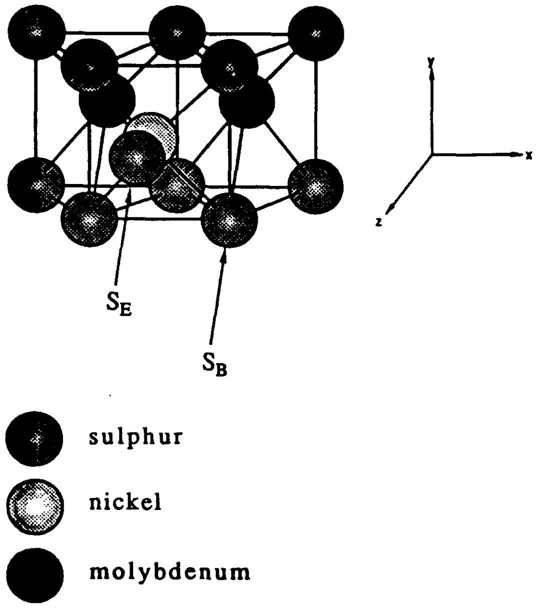
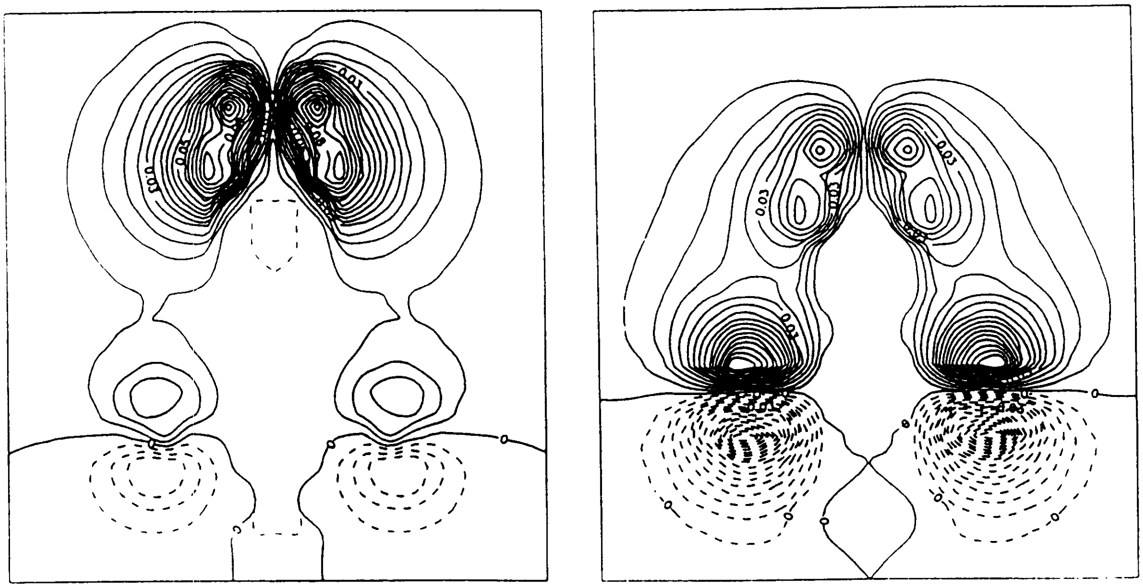


Figure 5-5: The edge structure of nickelmolybdenum sulphide, as reported by Bouwens *et al.* [8].

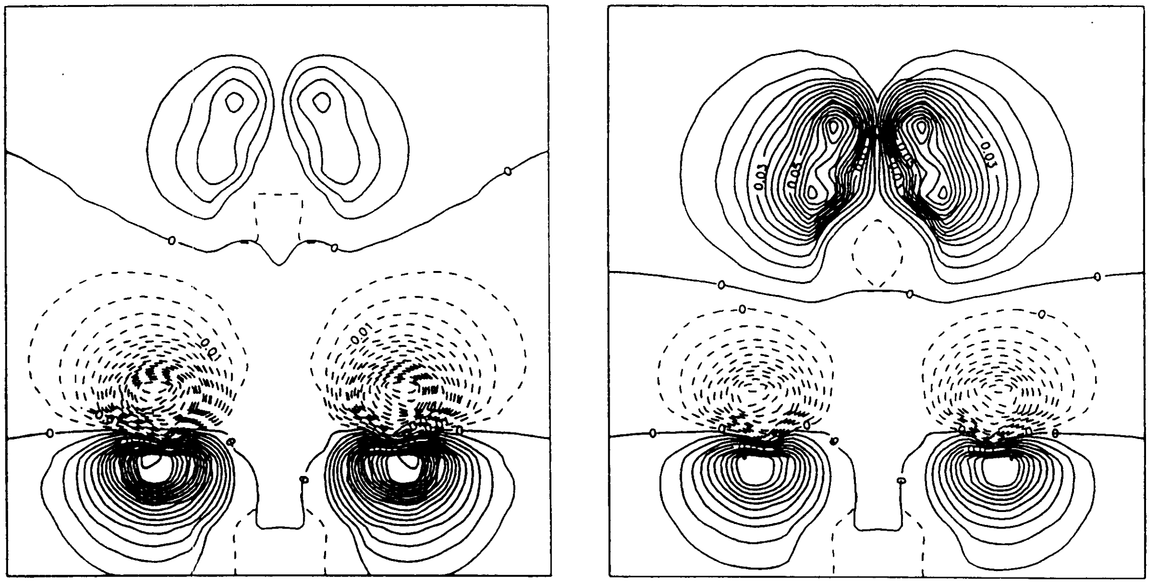
possiblity of four- or six-fold coordination can not be excluded. E.g. *six*-fold sulphur coordination of the promotor element has been observed for carbon-supported cobalt-molybdate [7] (but *five*-fold coordination when SiO_2 or Al_2O_3 is used as a support [9]). Similarly, Louwers *et al.* report a six-fold coordination for Ni in $Ni - W - S$ supported on carbon [62] (the structure of WS_2 is identical to that of MoS_2). The S_E atom is probably not very strongly bound to the catalyst: this site may be vacant and available for thiophene adsorption. The Ni atom is located slightly above the square formed by the terminal sulphur atoms above and below the $Mo - Ni$ plane (S_B), but the similarities between its local coordination and that of the Ru atom in the simple catalyst edge model, are immediately apparent. The electronic structure confirms this. The analogues for many of the RuS_5^{-6} (C_{4v}) orbitals can be readily identified. The symmetry analysis given above can now be extended to the nickel-molybdate edge structure. To compare the two cases, the thiophene molecule must be located in the $Mo - Ni$ plane (conveniently preserving the C_{2v} symmetry; it will later be shown that the effect of a rotation of the thiophene molecule about its two-fold axis is rather limited). The similarities between the electronic structure of the model and $Ni - MoS_2$ catalysts suggest similar orbital interactions for RuS_5^{-6}-thiophene and $Ni - MoS_2$-thiophene complexes. In the next section it will be shown that this is indeed the case: the simple model for the surface of a TMS catalyst captures the basic chemistry of the HDS process remarkably well.

In summary, orbital energies and topologies, in conjunction with symmetry restrictions, suggest that the adsorption process is dominated by the interaction between the out-of-plane sulphur lone pair of the thiophene molecule on the one hand, and catalyst $C_{4v} - e$ *(corresponding to* $C_{2v} - b_1 + b_2$*) orbitals near the Fermi level on the other.*



(a) (b)

Figure 5-6: The establishment of $p\pi$ bonding between the carbon atoms in the thiophene molecule and the sulphur atoms in the RuS_5^{-6} catalyst. In (a) the $Ru - S_T$ distance is 7.45 a.u., 5.45 a.u. in (b). The plane is spanned by the line $x = y$ and by the z-axis. Contour intervals are 0.005 in both (a) and (b).



(a) (b)

Figure 5-7: The establishment of $p\pi$ carbon-sulphur antibonding in the thiophene-RuS_5^{-6} adsorption complex. Specifications as in figure 5.6.

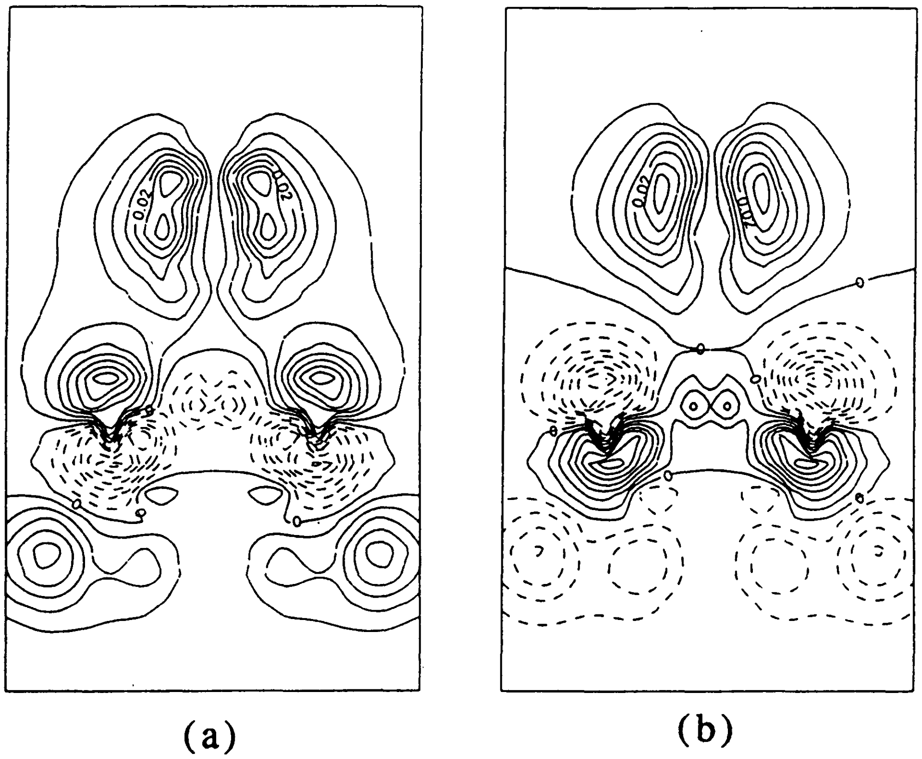


Figure 5-8: $P\pi$ carbon-sulphur bonding (a) and antibonding (b) orbitals for the $Ni - MoS_2$ catalyst-thiophene complex. The $Ni - S_T$ distance is 4.676 a.u. in (a), 5.176 a.u. in (b). Contour intervals are 0.004 for both (a) and (b). The plane is spanned by the line $x = y$ and the z-axis.

5.4 The adsorption of thiophene onto TMS catalysts

Electronic structure of thiophene-TMS complexes

Scattered-wave calculations have been carried out for the RuS_5^{-6} - thiophene complex shown in figure 5-3 and for the adsorption complex of thiophene on the $Ni - MoS_2$ structure reported by Bouwens *et al.*, figure 5-5, with the thiophene molecule located in the $Mo - Ni$ plane. For each of these two complexes the S_T-metal separation was systematically decreased in order to mimick the adsorption process. No relaxation of the thiophene molecule was incorporated into these calculations (geometry optimization can not be performed within the scattered-wave method). For RuS_5^{-6}-thiophene complexes the $S_T - Ru$ distance was reduced from 7.45 atomic units (a.u.) down to 4.45 a.u. (the metal-sulphur bond length in bulk RuS_2), in steps of 0.5 a.u.. For the $Ni - MoS_2$-thiophene complex, the $S_T - Ni$ separation was gradually decreased from 5.412 a.u to 3.912 a.u., also in steps of 0.5 a.u.. Additionally, calculations were carried out for a $S_T - Ni$ separation of 4.212 a.u..

Strong orbital interactions are identified by monitoring the changes in the character of individual orbitals. Charge redistribution is an appropriate measure of chemical reactivity as it portrays the establishment of chemical bonds and antibonds. Strong orbital mixing indicates strong interactions between the various components of a reaction complex. It does not necessarily imply strong bonding. A chemical bond between nuclei is the cumulative effect of all the orbitals in the system, bonding and antibonding (but the term (anti)bond is often used in reference to individual orbitals). The *total* bond strength can not be quantified in the scattered-wave method, but the strength of a specific bond can be estimated from the energy of that orbital (as compared to prior to the formation of that bond). An orbital's topology provides information on the nature of the bond. This series of calculations aims to identify the *basic* adsorption (i.e. reaction) mechanism. Despite its limitations, the scattered-wave method is adequate for this purpose, as the emphasis is on the topology of individual orbitals.

Many orbitals change character during adsorption, but only for two pairs of orbitals do strong orbital interactions occur at relatively large thiophene-catalyst distances. One member of each pair is originally one of the two highest occupied thiophene orbitals. The conjugates are catalyst orbitals belong to the manifold of sulphur $3p$ states.

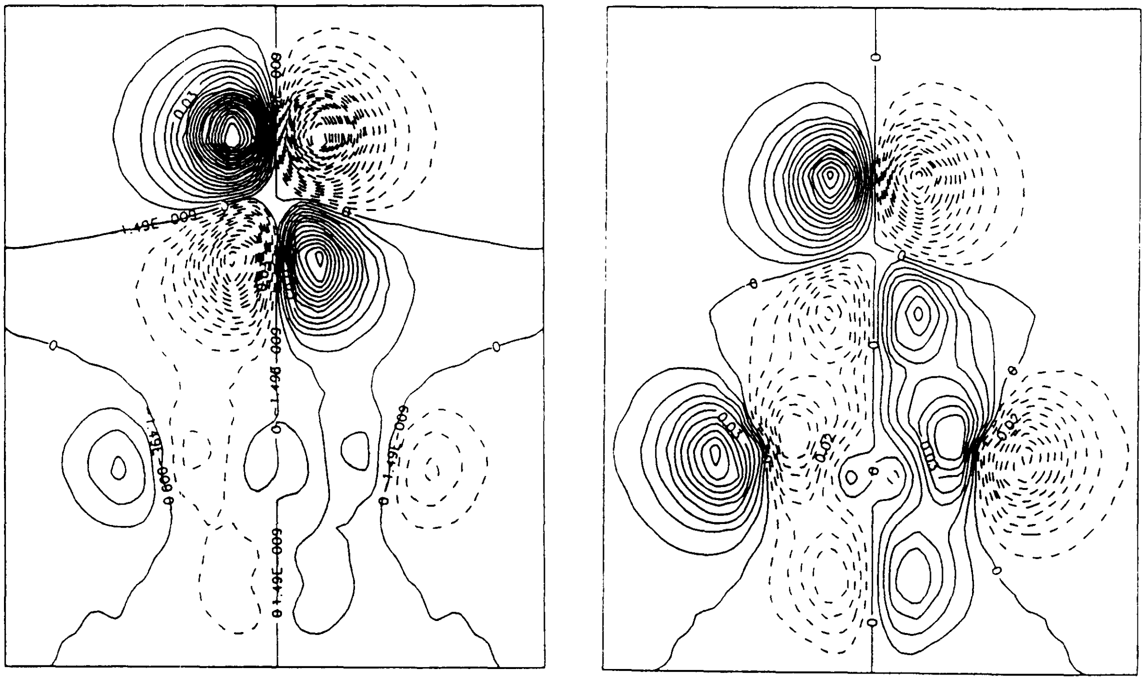
As the thiophene molecule approaches the surface of the catalyst, its HOMO evolves into a $p\pi$ bonding orbital between the carbon atoms and the sulphur atoms in the catalyst. The sulphur atom of the thiophene ring, S_T, and the metal atom in the model catalyst appear to have no part in this carbon-sulphur interaction at all, figure 5-6. A $p\pi$ antibonding orbital is also formed during adsorption, figure 5-7. The corresponding orbital pair for the $Ni - MoS_2$-thiophene system is shown in figure 5-8.

Figure 5-9 shows that $p\pi$ bonding is established between all the sulphur atoms in the RuS_5^{-6}-thiophene complex, resulting from the thiophene $2b_1$ orbital. The antibonding conjugate is shown in figure 5-10. Figure 5-11 gives the sulphur-sulphur orbital pair for the $Ni - MoS_2$-thiophene system.

One of the most striking features of the adsorption complex is the extent to which the thiophene molecule and the catalyst cluster have been preserved as subunits, except for the carbon-sulphur and sulphur-sulphur $p\pi$ interactions. For example, although the charge on S_T can not be accurately determined upon completion of the adsorption process, it is similar to that of free thiophene. The limited extent of orbital mixing is also demonstrated by the catalyst $7e$ orbital. Its character is almost unchanged from the isolated catalyst cluster (figure 5-4). Further evidence is provided by the number of sulphur $3p$ states for the adsorption complex. There are 10 such orbitals (not taking into account symmetry degeneracies). This number is characteristic of an MS_5^{-n} cluster, for MS_6^{-n} the number is 13.

How geometry affects orbital interactions

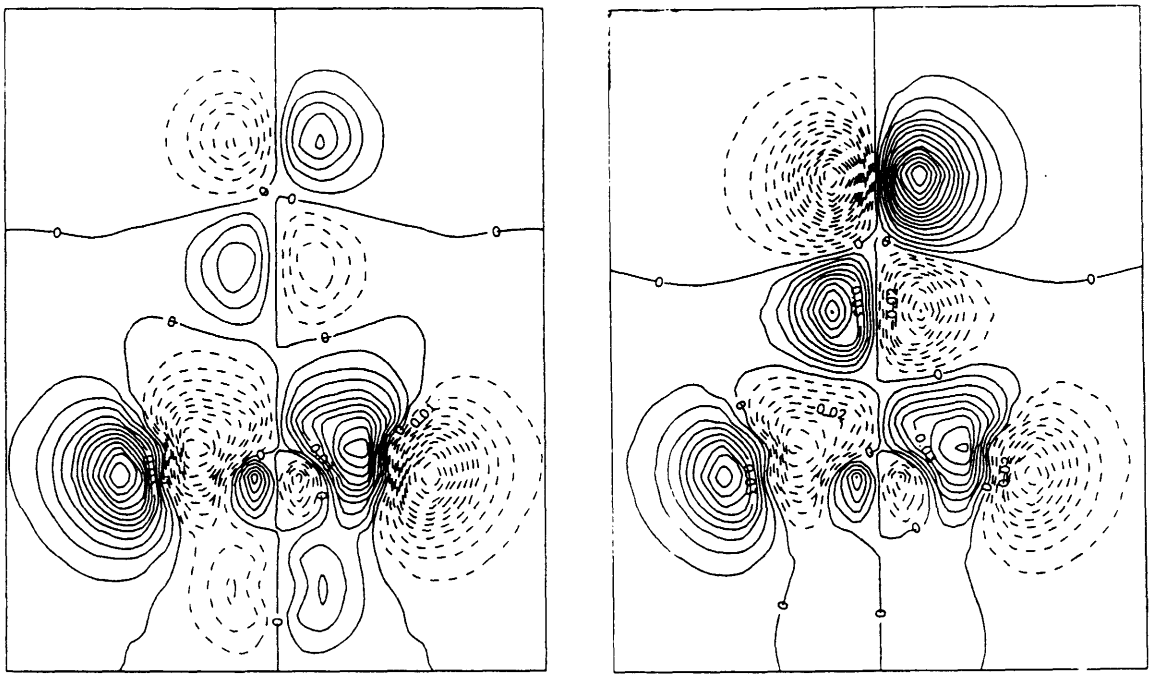
The symmetry analysis presented in section 5.3 shows that the carbon-sulphur $p\pi$ interactions, but not the sulphur-sulphur interactions, are a specific consequence of



(a)

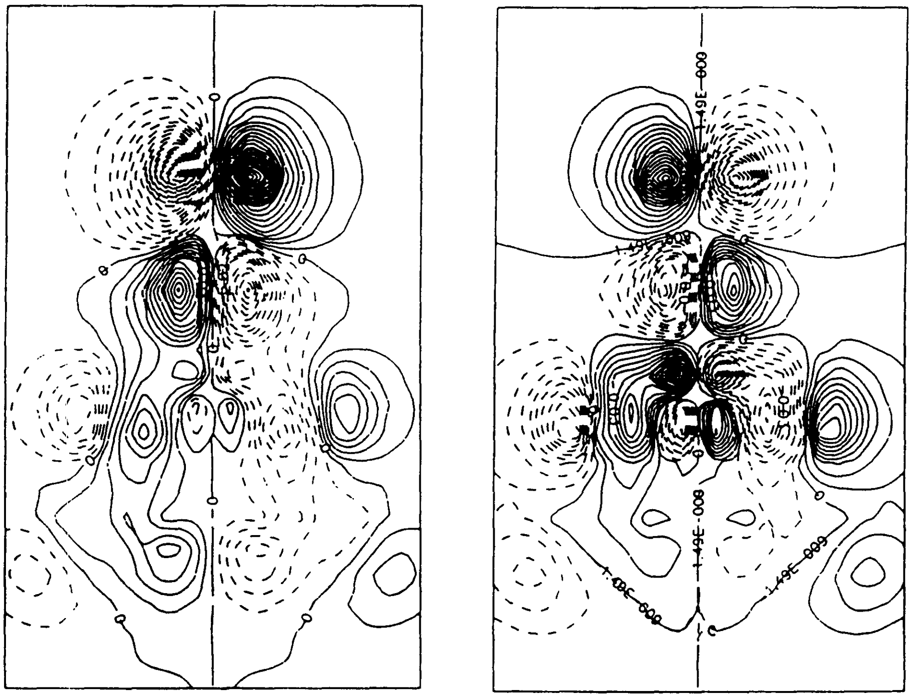
(b)

Figure 5-9: The establishment of $p\pi$ bonding between the sulphur atom in the thiophene molecule and the sulphur atoms in the RuS_5^{-6} catalyst. In (a) the $Ru - S_T$ distance is 7.45 a.u., 5.95 a.u. in (b). The plane is spanned by the line $x = y$ and the z-axis. Contour intervals are 0.005 in both (a) and (b).



(a) (b)

Figure 5-10: The establishment of $p\pi$ sulphur-sulphur antibonding for the RuS_5^{-6}-thiophene adsorption complex. Specifications as in figure 5.9.



(a) (b)

Figure 5-11: $P\pi$ sulphur-sulphur bonding (a) and antibonding (b) orbital for the $Ni - MoS_2$ catalyst-thiophene complex. The $Ni - S_T$ distance is 4.676 a.u. in both (a) and (b). Contour intervals are 0.005 for both (a) and (b). The plane is spnned by the line $x = y$ and the z-axis.

the geometry of the adsorption complex. These interactions would have been absent if the thiophene molecule had been rotated by 45^0 about its two-fold axis. Calculations on an MoS_5^{-6}-thiophene complex with this geometry confirm this. Rotation of the thiophene molecule by an arbitrary angle ϕ eliminates all symmetry, destroying the block-diagonal form of the secular determinant. *All* of the orbitals will now interact (in principle) but the strength of the interaction will depend on the value of ϕ (i.e., it will depend on the extent to which the various blocks of the determinant will mix). As ϕ is gradually increased to 45^0, the carbon-sulphur interaction strength slowly diminishes, but increases again upon further rotation to 90^0. Concerning the sulphur-sulphur interaction, the thiophene (C_{2v}) $2b_1$ orbital initially interacts with only catalyst b_1 orbitals (stemming from e orbitals in the simple catalyst model) , but as soon as the thiophene molecule is rotated, mixing with catalyst b_2 orbitals occurs. Rotation reduces the strength of the $b_1 - b_1$ interaction, but increases the strength of the $b_1 - b_2$ interaction, so that the *total* interaction strength does not depend strongly on the value of ϕ [2]. This is true not only for the model catalyst, but also for the $Ni - MoS_2$ system. The Ni atom is, to a first approximation, in a square planar sulphur environment: the conjugate of the out-of-plane sulphur lone pair (figure 5-2b) is a member of a *pair* of orbitals of b_1 and b_2 character, vey close in energy and similar in topology (this pair is the analogue of the $C_{4v} - e$ orbital). It is clear then, that the sulphur-sulphur interactions will be present regardless of the rotation angle, whereas the carbon-sulphur interactions are a result of the specific geometry for which calculations have been performed [3].

Figures 5-6-5-11 also demonstrate the similar chemistry for the model and real thiophene-catalyst complex. It is seen that the extremely simple model for the surface of a TMS catalyst accurately represents the basic chemistry of the HDS process. Throughout the remainder of this chapter I will focus on this edge model.

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[2] For arbitrary rotation angles ϕ, it is, strictly speaking, no longer possible to speak of irreducible representations b_1, b_2, etc.

[3] The same type of mixing arguments can also be applied to the case when the thiophene rotation axis is slightly off the z-axis.

Adsorption mechanism

No change in the orbital occupation numbers is observed during adsorption. Both bonding and antibonding orbitals are therefore fully occupied. This would suggest that the net effect of the interactions shown in figures 5-6-5-11 is antibonding, or at best weakly bonding. However, upon completion of the adsorption process, the sum of the orbital energies of each pair is substantially lower than the sum of the orbital energies of the original orbitals on the separate thiophene and catalyst clusters, due to an energy decrease of the thiophene (i.e. bonding) orbitals. From figure 5-1 it is evident that *all* the thiophene levels (including those whose topology has not changed significantly change during adsorption) have gone down in energy. A chemical shift has occurred, indicative of an electrostatic interaction with the catalyst. I previously argued that if an electrostatic interaction is operative, then it must result from the polarization of the sulphur lone pairs, particularly the out-of-plane $2b_1$ orbital which is least tied up with the π electron system of the aromatic ring. Given the limitations of the scattered-wave method and the use of a Watson sphere, it is impossible to conclusively determine whether the strong sulphur-sulphur $p\pi$ interactions are a manifestation of an electrostatic interaction between the thiophene molecule and the catalyst, or alternatively its primary cause, ultimately responsible for the deepening of all of the thiophene levels. Whatever the case may be, it is clear that the out-of-plane sulphur lone pair plays an important role in the adsorption process. I believe that strong sulphur-sulphur interactions lead to weak binding of the thiophene molecule to the catalyst. (Recall that the occurrence of carbon-sulphur interactions is a direct consequence of the geometry of the adsorption model.)

A topological argument provides further insight into the effect of the sulphur-sulphur interaction. The bonding orbital favours stretching of the $S_T - C_1$ bonds, but contraction of the $S_T - S_2$ bonds. The antibonding orbital on the other hand favours stretching of both bonds. The combined effect is a tendency to pull the S_T atom away from the thiophene molecule, towards the catalyst. Starting from an adsorbent-adsorbate separation of 6.45 a.u. and keeping all atomic positions except the S_T atom fixed, it was indeed found that the energy of the antibonding orbital is fairly independent of the position of the sulphur atom in thiophene, whereas the energy of the bonding orbital is significantly lowered for small downward displacements of the S_T atom. However, large displacements induce destabilization of the aromatic ring, so that, in effect, the *entire* thiophene molecule is pulled towards the catalyst by the sulphur-sulphur interaction.

It has been suggested that the strong delocalization of the $2b_1$ thiophene orbital *must* lead to the type of sulphur-sulphur interactions described above. However, the in-plane thiophene lone pair is similarly delocalized and should then be expected to also take part in strong thiophene-catalyst interactions when the thiophene molecule is still relatively far away from the surface of the catalyst. Formation of a σ metal-S_T bond is indeed observed, but only at small thiophene-catalyst separations, figure 5-12. The thiophene $1b_1$ orbital leads to metal-sulphur π bonding. The π bond is stronger for the $Ni - Mo - S$-thiophene complex than it is for the RuS_5^{-6}-thiophene complex, possibly due to the position of the Ni atom, roughly 0.8 a.u. above the square of the terminal sulphur atoms (see figure 5-5) and/or to the lower sulphur coordination of the metal atom. Even so, this bond is formed at small catalyst-thiophene separations. These calculations suggest that metal-sulphur interactions are operative only at relatively small thiophene-catalyst separations and as a direct consequence of the close proximity of the S_T atom to the exposed metal atom.

Perhaps the most remarkable feature of these results is not the presence of strong sulphur-sulphur interactions leading to weak binding, but the *absence* of strong metal-sulphur interactions. This is evident not only from the orbital topologies, but also from the heat of adsorption, the energy difference between the adsorption complex and the separate thiophene molecule and catalyst cluster. For η_1 adsorption of thiophene on the $Ni - MoS_2$ cluster, ΔH_{ads} is approximately 1.5 eV. This value agrees with the findings of Zonnevylle *et al.* for η_1-adsorption of thiophene onto an MoS_2 catalyst (2-3 eV) [120], the weak η_1 adsorption observed by Rong *et al.* [80], also for thiophene onto an MoS_2 catalyst, and with the one-vacancy cluster calculations of Joffre *et al.* [39, 40]. Joffre *et al.* also modeled two- and three-vacancy adsorption sites. Much higher values for ΔH_{ads} were found, presumably as a result of metal-sulphur bonds.

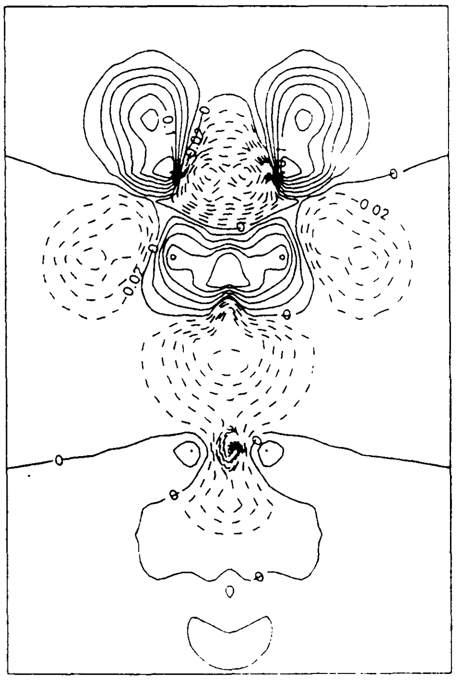

Figure 5-12: The σ metal-sulphur bonding orbital resulting from the thiophene $6a_1$ orbital, shown in the plane of the thiophene molecule for the RuS_5^{-6} cluster. The $Ru - S_T$ distance is 4.45 a.u..

It is informative to inquire what distinguishes RuS_2 from other TMS and from pure Ru. When a similar series of calculations is carried out for Ru-thiophene complexes, it is evident that the out-of-plane lone pair on S_T evolves into a strong metal-S_T π bond. This lone pair is least involved in the π electron system of the aromatic ring and thus available for bonding to the catalyst. If the catalyst is a pure metal, then *metal*-sulphur bonding is established, but for the sulphide, the out-of-plane lone pair is involved in *sulphur*-sulphur interactions. This has significant consequences for the activity and selectivity differences that exist between the sulphide and the pure metal, as will be discussed at a later point in this chapter.

The LUMO of thiophene is never occupied during adsorption. It does not play a significant role in η_1 adsorption, as was observed also by Zonnevylle *et al.* [120]. Hence, adsorption does not significantly weaken the carbon-sulphur bond in thiophene. This is consistent with infrared measurements of Qin *et al.* [74] for adsorbed thiophene, which show that the electronic configuration is practically identical to that of a free thiophene molecule. Since the calculations do not show a change in the orbital occupation numbers during adsorption, but only a change in the character of some orbitals, the Blyholder model is inappropriate for describing η_1 adsorption. Instead, complex Dewar-Chatt mechanisms are operative.

Adsorption in relation to periodic effects in TMS HDS catalysts

If the dependence of HDS activity on the position of the metal atom in the periodic table is an electronic effect, then the rate-limiting step must either directly or indirectly involve the metal atom of the catalyst. The catalyst orbital which takes part in the strong sulphur-sulphur interactions in the RuS_5^{-6}-thiophene complex belongs to the manifold of sulphur $3p$ states. The influence of the metal atom is extremely small. Combined with the absence of direct metal-sulphur bonding this suggests either that the electronic theory is invalid or that adsorption is not the rate-limiting step.

To verify the validity of this hypothesis, calculations have also been carried out on ZrS_5^{-6}- and MoS_5^{-6}-thiophene complexes. ZrS_2 is known to be a very poor catalyst. MoS_2 is also less active than RuS_2, but more active than ZrS_2 [70]. The metal-S_T distance was set at the metal-sulphur bond length in the bulk TMS (see table 7.1). In both cases, the out-of-plane sulphur lone pair on thiophene ($2b_1$) is seen to be involved in $p\pi$ sulphur-sulphur interactions. As was the case for the RuS_5^{-6}-thiophene complex, only weak metal-sulphur bonds are observed. Carbon-sulphur interactions are also weaker, particularly for ZrS_2. In general, the mixing between the catalyst and the thiophene molecule, and the strength of the metal-sulphur σ and π bonds, decreases in the order $Ru > Mo > Zr$, which is also the ranking for the experimental catalytic activities. The differences between the three cases are however small, particularly when compared to the differences between catalyst-dihydrothiophene complexes, which will be discussed in the next section. This may suggest *either* that periodic effects in HDS catalysts (the dependence of HDS activity on the position of the metal atom in the periodic table) are *not* an electronic effect determined by the quality of the active site, *or* that adsorption is not the rate-limiting step in the overall HDS process if the one-point end-on mechanism is operative. It is, however, particularly noteworthy that the strongest metal-S_T bonds are observed for the Ru-thiophene complex and for the $Ni - MoS_2$-thiophene complex (also the most active catalysts): although metal-sulphur bonds are weak for all three model sulphides considered, small differences are apparent, an indication of the role of metal-sulphur interactions in the later stages of the HDS process. Thus it is most likely that adsorption is not the rate-limiting step in the HDS process. This issue will be further addressed in the next section.

In summary, the out-of-plane sulphur lone pair on the thiophene molecule strongly interacts with the sulphur atoms in a TMS catalyst during adsorption, leading to weak binding of thiophene onto the catalyst. Metal-sulphur interactions are weak and operative at small thiophene-catalyst separations. The limited involvement of the metal atom in the adsorption process suggests that adsorption is not the rate-limiting step in the overall HDS process. ZrS_5^{-6}*-,* MoS_5^{-6}*- and* RuS_5^{-6}*-thiophene complexes yield very similar results, but small differences in metal-sulphur bonding are observed. This suggests that adsorption is not the rate-limiting step, but also that periodic variations are an electronic effect, dependent on the involvement of the metal atom in the later stages of the HDS process (interaction between the thiophene sulphur and metal atoms).*

5.5 The role of hydrogen

Hydrogenation of adsorbed thiophene: an introduction

After adsorption of thiophene into vacant sulphur sites, coadsorbed hydrogen assists in cleaving the carbon-sulphur bonds. There has been considerable debate over the question whether hydrogen attacks the sulphur atom of thiophene or the adjacent carbon atoms. Frontier orbital theory and the topology of the two highest occupied orbitals of thiophene do not rule out either possibility [25]. CNDO calculations by Ruette and Ludeña [82] show that a situation where the hydrogen atom is shared by neighbouring sulphur and carbon atoms is energetically more favourable than complete hydrogenation of the carbon atom, which in turn is favoured over hydrogenation of the S_T atom. In any case, C_1-hydrogenation is necessary at some point during the reaction, regardless of the possibility of a prior or simultaneous attack on the S_T atom. C_1-hydrogenation also leads to significant destabilization of the aromatic ring: Rong *et al.* [80] conclude from an elaborate bond order analysis of thiophene- and tetrahydrothiophene-catalyst complexes that thiophene is probably first hydrogenated and then desulphurized. The analysis of the hydrogenation process presented here is based on the validity of that assumption.

Lacroix *et al.* [54] recently reported two adsorption sites for hydrogen on an RuS_2 catalyst: (1) in the sulphur vacancies, in competition with thiophene, or (2) directly on top of adjacent sulphur atoms, forming $S - H$ groups. If hydrogen bonds to the metal atom, it blocks the adsorption pathway for thiophene (unless bonding to S_T occurs during adsorption, presumably as a result of interactions with the sulphur lone pairs). On the other hand, dissolution of the sulfhydryl groups, after η_1-adsorption of thiophene, makes hydrogen atoms available for hydrogenation of the carbon atoms of thiophene. That is the focus of this study. It is possible that this process (partially) determines the overall kinetics of the HDS reaction. A detailed study would require accurate full-potential quantum chemistry calculations on realistic catalytic structures; limited scattered-wave calculations on model clusters allow some general statements about the basic chemistry.

The formation of a dihydrothiophene-TMS complex and its relation to periodic effects in HDS catalysis

The effect of the sulfhydryl groups on the surface electronic structure of the catalyst is revealed by a $Ru(SH)_4S^{-6}$ cluster (a hydrogen atom has been placed on top of each sulphur atom on the TMS surface, adjacent to the exposed metal atom). Significant mixing between the metal-sulphur bonding orbitals and the sulphur $3p$ band is observed (see also figure 5-1, right column). These orbitals are all bonding with respect to hydrogen. The antibonding orbitals lie in the vicinity of the Fermi level. Mixing between the metal-sulphur antibonding orbitals and the sulphur $3p$ band is also evident, its extent depending on the exact position of the hydrogen atoms. The orbitals with the largest hydrogen content are essentially hydrogen s - sulphur p_z σ

antibonding, with relatively small metal contents. The energies of these orbitals depend strongly on the $S-H$ bond length and will go down as the bonds are stretched, yet always lie above the $1a_2$ level which delineates the sulphur $3p$ band (see figure 5-1, rightt column).

Periodic effects in HDS may arise from differences in the $S-H$ bond strength. Occupation of sulphur-hydrogen antibonding orbitals weakens the $S-H$ bonds and thus facilitates dissolution of the sulfhydryl group, affecting the rate of the hydrogenation process. The influence of the metal atom in the TMS is felt through the total d electron count and the energy gap between the (partially vacant) π and σ metal-sulphur antibonding orbitals and the sulphur $3p$ band. In this manner, the metal atom may indirectly determine the overall kinetics of the HDS process. A comparison of the electronic structures of ZrS_5^{-6} and RuS_5^{-6} shows that this hypothesis is inconsistent with the observed catalytic activities. The gap between the metal-sulphur π antibonding orbitals and the $1a_2$ sulphur non-bonding level is much larger for ZrS_2 than it is for RuS_2 (3 eV vs. 0.1 eV). However, for ZrS_5^{-6} the metal-sulphur antibonding levels are vacant; the extra electrons resulting from the addition of the four hydrogen atoms occupy sulphur-hydrogen antibonding levels. For RuS_2 on the other hand, some of the extra electrons can occupy the vacant metal-sulphur antibonding level ($2b_2$, figure 5-1, right column), thus depopulating a sulphur-hydrogen antibond. Hence, the $S-H$ bond is weakest for ZrS_2, so ZrS_2 would be expected to be the better catalyst. This is contrary to experiments [70]. [4]

It is alternatively possible that the attachment of hydrogen to carbon determines the kinetics, rather than the detachment of hydrogen from the surface. The formation of adsorbed dihydrothiophene has been modeled by varying the height of hydrogen atoms above the surface of the catalyst in a $Ru(SH)_2S_3^{-6}$-thiophene cluster (two hydrogen atoms have been added to the adsorption complex of figure 5-3, placed on diametrically opposite sulphur atoms) and, simultaneously, moving the H_1 atoms out of the plane of the thiophene molecule. The evolution of the electronic structure

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[4] This argument depends strongly on the total number of electrons in the cluster, as this affects the occupation of $S-H$ antibonding orbitals. It should therefore be noted that the $M(SH)_4S^{-6}$ contains hydrogen atoms, not protons. The alternative choice would not, however, affect the conclusion.

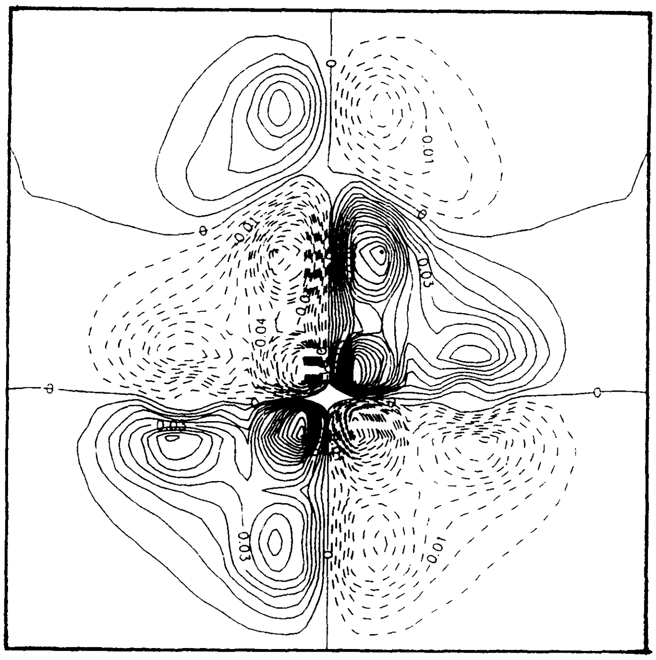

Figure 5-13: An example of a metal-sulphur π bond for a dihydrothiophene-RuS_5^{-6} complex. The plane is spanned by the line $x = y$ and the z-axis. The $Ru - S_T$ distance is 4.45 a.u..

is highly complex, and allows only general statements concerning the nature of this process. As the $S - H$ groups dissolve, the sulphur-hydrogen antibonding orbitals gradually become more strongly antibonding with respect to the S_T atom, but bonding with respect to carbon. Consequently, the hydrogen atoms are pushed away from the S_T atom and pulled towards the carbon atoms. This suggests that hydrogen attacks the carbon atoms, rather than the sulphur atom of thiophene, but arguments based on the occupation of these orbitals fail to explain activity differences across the periodic table.

Despite the obvious shortcomings and limitations of these calculations, it might be inferred that hydrogenation is not the rate-limiting step in the overall HDS process. The most that can be said is that during hydrogenation and the formation of dihydrothiophene, the mixing of catalyst and (dihydro)thiophene orbitals increases, particularly the *metal-*S_T bond strength. This is evident most clearly when dihydrothiophene-catalyst complexes are considered.

Dihydrothiophene-TMS complexes

When the hydrogenation process is completed, dihydrothiophene is adsorbed on the surface of the TMS. In dihydrothiophene, the net charge on the S_T atom is slightly more negative than it is in thiophene. More important, however, is the difference in the sulphur lone pairs. For thiophene, their character was given in table 5.1. In dihydrothiophene the resemblance to true lone pairs is much greater, as is evident from the sulphur content, approximately 50 percent for both the in-plane and out-of plane lone pair. The difference between thiophene and dihydrothiophene is greatest for the out-of-plane lone pair, which was shown to play a major role in the adsorption process. In short, the S_T atom is much less involved in the electron system of the aromatic ring in dihydrothiophene than it is in thiophene.

The significance of this result is evident from a dihydrothiophene-RuS_5^{-6} complex. Strong metal-S_T π bonding, resulting from the out-of-plane sulphur lone pair, is observed (figure 5-13). The in-plane lone pair leads to metal-S_T σ bonding, which appears to be much weaker. Consequently, the S_T atom is now effectively shared by the aromatic ring and the catalyst. The distinction between a dihydrothiophene and catalyst subunit is much more ambiguous than it is for the thiophene-RuS_5^{-6} complex. Hydrogenation of the carbon atoms adjacent to S_T has clearly resulted in a stronger $Ru - S_T$ bond. (See also Choi *et al.* [14], who found that S-coordination of dihydrothiophene to transition metal centers promotes the liberation of butadiene).

There is also a striking difference in the π metal-S_T bond for ZrS_5^{-6}-, MoS_5^{-6}- and RuS_5^{-6}-dihydrothiophene complexes, as table 5.2 demonstrates. The $Ru - S_T$ bond is stronger than the $Mo - S_T$ bond, which, in turn, is stronger than the $Zr - S_T$ bond. This is also the observed order for the catalytic activities. The differences in the σ metal-S_T bonds are small by comparison. Harris and Chianelli [29, 30] have argued that it is the ability of the metal atom to bond covalently to sulphur which determines the catalytic activity of the TMS. These results for ZrS_5^{-6}-, MoS_5^{-6}- and RuS_5^{-6}-dihydrothiophene complexes are therefore rather satisfying, as they show that

TMS	*Energy (-eV)*	*Charge*	*Character*			*Charge*	*Character*		
			%s	%p	%d		%s	%p	%d
ZrS_5^{-6}	9.0	3% C_1	0	100	0	5% C_2	0	100	0
		46% S_T	0	100	0	4% H_1	100	0	0
		0% H_2	0	0	0	9% S_2	1	99	0
		2% S_3	0	100	0	6% Zr	0	4	96
		27% int	0	0	0	0% out	0	17	10
MoS_5^{-6}	9.4	3% C_1	0	100	0	3% C_2	0	100	0
		28% S_T	0	100	0	3% H_1	100	0	0
		0% H_2	0	0	0	16% S_2	0	100	0
		7% S_3	0	100	0	15% Mo	0	0	100
		26% int	0	0	0	0% out	0	10	16
RuS_5^{-6}	9.7	2% C_1	0	100	0	2% C_2	0	100	0
		18% S_T	0	100	0	2% H_1	100	0	0
		0% H_2	0	0	0	17% S_2	0	100	0
		8% S_3	0	100	0	27% Ru	0	0	100
		23% int	0	0	0	0% out	0	10	18

Table 5.2: Orbital characteristics for the remnants of the out-of-plane sulphur lone pair for ZrS_5^{-6}-, MoS_5^{-6}-, and RuS_5^{-6}-dihydrothiophene complexes. Nomenclature for the atoms corresponds to figure 5-3. Specifications as in table 5.1.

the strongest metal-S_T bonds are formed for the most covalent TMS [5].

Implications for the overall HDS process

Not only has hydrogenation of thiophene induced the formation of strong metal-S_T bonds, it has also weakened the carbon-sulphur bonds. E.g. the $1b_1$ orbital of thiophene has a large sulphur p_z component and is bonding between sulphur and carbon (see table 5.1). In dihydrothiophene on the other hand, it is essentially a $C_1 - H_1$ bonding orbital (38 percent C_1, 36 percent H_1). The sulphur component has been reduced significantly to only 10 percent (from 38 percent in thiophene). The sulphur atom contributes much less to the π electron system of the aromatic ring for dihydrothiophene than for thiophene. Before hydrogenation, S_T is very much part of the thiophene molecule in the adsorption complex. After hydrogenation, the metal atom in the catalyst and the aromatic ring compete for S_T. It may be concluded that hydrogenation must take place before, or in conjunction with, desulphurization. Whether desulphurization or desorption of the dihydrothiophene molecule occurs following hydrogenation depends on the activation mechanism for the carbon-sulphur bonds (not included in this study) and on the strength of the metal-sulphur bond. It is nonetheless clear from table 5.2 that periodic effects in HDS catalysis are an electronic effect: the strength of the metal-sulphur interaction determines the catalytic activity of the TMS. The attractive force between the sulphur atom in thiophene and the exposed metal atom results primarily from covalent π metal-S_T bonds but will be partially cancelled by metal-sulphur antibonding orbitals near the Fermi level. The effect of the occupation and character of these orbitals will be demonstrated in chapter 7, where periodic effects in TMS are considered in detail. If desulphurization of dihydrothiophene and desorption of butadiene take place, the sulphur atom probably

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[5] More important than the *bond* strength is the *interaction* strength, i.e. the extent of mixing between metal d and sulphur $3p$ electrons. In chapter 7, a parameter I will be defined which is a measure of the strength of that interaction and which correlates directly to HDS activity. Bond strength and interaction strength are distinct concepts. While I will argue that metal-sulphur bond strength in bulk TMS does not correlate to HDS activity, it *is* useful to focus on the bond strength between the exposed metal atom in the catalyst and the sulphur atom of the thiophene molecule. See also the discussion in chapter 8.

remains on the surface of the catalyst, since it is the ability of S_T to bond to the catalyst which so clearly influences the activity of the catalyst.

The fact that hydrogenation induces metal-S_T bond formation points to an essential difference between pure transition metals and TMS. Pure TM are more active, but less selective than TMS: more surface sulphur and carbon fragments and gaseous dihydrogen are formed, but fewer useful hydrocarbons. The undesirable byproducts result from strong adsorbent-adsorbate interactions. Strong $Ru - S_T$ bonds are formed during adsorption of thiophene onto a single Ru atom: significant lowering of the energy can be achieved through the interaction of the sulphur $3p$ band with the metal d band. However, carbon $2p$ states interacting with the metal d band also result in energy gains, hence binding of the thiophene molecule onto the pure TM surface. The formation of metal-sulphur and possibly metal-carbon σ and π bonds significantly destabilizes the aromatic ring and essentially pulls apart the thiophene molecule. Thus there are two reasons why pure transition metals are more *active* but less *selective* catalysts than TMS. (1) The requirements for binding of thiophene onto a TMS are more specific than the requirements for binding to a pure transition metal and (2) hydrogenation must occur before, or in conjunction with, desulphurization for TMS but not necessarily for pure transition metals. Incidentally, this also shows that, in order to understand the HDS chemistry of TMS, it is insufficient to model the TMS as a single metal atom [18] or as a single protonic center [118].

In summary, hydrogenation itself is not the rate-limiting step in the overall HDS process, induces the formation of strong metal-sulphur bonds, weakens the $C - S_T$ bonds and must take place before, or in conjunction with, desulphurization. Desulphurization is the rate-limiting step in HDS; the periodic variation in HDS activity is an electronic effect, dependent on the strength of the metal-sulphur interactions.

5.6 Discussion

Harris and Chianelli [29, 30] have shown that it is the ability of the metal atom to bond covalently to the sulphur atom in thiophene which determines the activity of the catalyst. Their analysis is often taken to imply that adsorption is the rate-limiting step in the overall HDS process, and furthermore that a one-point end-on mechanism is operative. However, the authors themselves note that η_1-binding is *not inconsistent* with the observed correlation between theory and experiment. Calculations were carried out only for octahedral TMS clusters, the thiophene molecule was not included. Hence they provide evidence only for the fact that the rate-limiting step in the overall HDS process must involve metal-sulphur bonding, not that this step should be adsorption.

A priori, the formation of metal-S_T bonds during adsorption is most likely for perpendicular, rather than parallel, binding. The results presented in this chapter show that even for η_1 binding, strong metal-sulphur bonds are *not* formed during adsorption. In general therefore, regardless of whether η_1, η_2 or η_5-binding is operative, adsorption is not governed by metal-sulphur interactions and not the rate-limiting step in the overall HDS process. Strong sulphur-sulphur and/or electrostatic interactions lead to weak binding of the thiophene molecule to the catalyst in η_1 adsorption. *Weak* metal-sulphur bonding is observed upon completion of the adsorption process. The most likely reason for the absence of strong metal-sulphur bonds is the strong involvement of the S_T electrons in the electron system of the aromatic ring (the S_T atom has positive character).

Hydrogenation involves the dissolution of sulfhydryl groups, whose presence has been experimentally determined, and transfer of hydrogen to the C sites. Again, the involvement of the metal atom in this process is expected to be less for η_5-binding than it is for η_1 binding. But even for η_1-binding, the metal atom can only be involved *indirectly*, influencing the strength of the $S-H$ bond through the availability of empty metal-sulphur antibonding orbitals near the Fermi level. This fails to explain the variation in catalytic activity across the periodic table. This indicates that hydrogenation is not the rate-limiting step in the overall HDS process, regardless of the details of the specific binding mode. It furthermore shows that hydrogenation must occur *before*, or in conjunction with, opening of the aromatic ring, i.e. desulphurization.

Strong metal-sulphur bonds and interactions are observed when dihydrothiophene is adsorbed perpendicularly onto the catalyst surface. Hydrogenation of the carbon atoms adjacent to S_T lessens the involvement of S_T in the aromatic ring electron system, thus inducing the formation of metal-sulphur bonds.

A comparison of ZrS_5^{-6}-, MoS_5^{-6}-, and RuS_5^{-6}-dihydrothiophene complexes shows that it is the ability of the metal atom to interact with the S_T atom which determines the activity of the catalyst, in agreement with the findings of Harris and Chianelli. Metal-sulphur bonding is seen to be important, indicating that the relative catalytic activities of various TMS are essentially determined by the rate of the final desulphurization step. Although the chemistry taking place prior to this does not appear to determine the overall *activity*, it will affect the *selectivity* of the catalyst. I have shown that activity and selectivity differences between pure metals and TMS can be explained qualitatively on the basis that strong metal-sulphur bonds are absent during adsorption of thiophene onto TMS, but not for adsorption onto pure metal surfaces. Similarly, the specifics of the binding mechanism are also likely to affect selectivity. For example, it is to be expected that temperature effects will affect catalyst selectivity. This issue has not been further investigated, nor has the precise mechanism through which $C - S_T$ cleavage occurs been studied. Throughout these studies, the emphasis has been on electronic properties which determine the quality of the catalyst, in an attempt to aid experimentalists in the rational design of new catalysts.

5.7 Conclusions

1. The absence of strong metal-S_T bonds during the adsorption of thiophene onto a TMS catalyst forms the basis for understanding the entire HDS process. Metal-sulphur interactions are weak compared to sulphur-sulphur and/or electrostatic interactions. Strong sulphur-sulphur interactions lead to weak binding of thiophene onto the TMS catalyst. Adsorption is not the rate-limiting step in the overall HDS process. This suggests that sulphur vacancies need not be present on the surface of the catalyst for the adsorption of thiophene. Other adsorption

mechanisms may be operative, as will be discussed in the next chapter.

2. Hydrogen adsorbed on the surface of the catalyst probably attacks not the sulphur atom of thiophene, but the adjacent carbon atoms. Hydrogenation reduces the involvement of the S_T atom in the electron system of the aromatic ring and induces the formation of (primarily π) metal-S_T bonds. Hydrogenation must take place *before* or in conjunction with desulphurization, thus explaining activity and selectivity differences between pure transition metals and the transition metal sulphides. Hydrogenation itself is not the rate-limiting step in the overall HDS process.

3. The strongest catalyst-thiophene interactions and the strongest metal-S_T interactions in catalyst-dihydrothiophene complexes are observed for the most active TMS. This suggests that the periodic variation of HDS activity is an electronic effect, dependent upon the rate of the final desulphurization step in the HDS process. Activity differences between various TMS can be explained on the basis of the strength of metal d - sulphur $3p$ interactions, as will be shown in the chapter 7.

Chapter 6

The Importance of Sulphur-Sulphur Bonding in the HDS Process: an Alternative Adsorption Mechanism

6.1 Introduction

The calculations on the one-point end-on mechanism described in the previous chapter show that $p\pi$ interactions between the sulphur atom in the thiophene molecule and the sulphur atoms in the catalyst are responsible for weak thiophene-catalyst binding during adsorption of thiophene onto the catalyst, rather than the establishment of metal d - S_T p bonds, as was widely believed. The absence of metal-sulphur bonding during adsorption suggests that exposed metal atoms may not be necessary for the adsorption of thiophene onto the catalyst. Salmeron *et al.* observed that thiophene can adsorb onto the basal plane of MoS_2, consisting entirely of sulphur atoms [84]. The heat of adsorption is small for basal plane adsorption, indicating that only weak substrate-adsorbate bonds are formed. Subsequent desulphurization does not occur, for it is well-known that only the edges of MoS_2 sheets, where metal atoms are exposed, are catalytically active [84, 21]. It is likely that strong substrate-S_T bonds are necessary for desulphurization; the results presented in the previous chapter suggest that these must be metal-sulphur bonds. Since these bonds are not formed even if thiophene adsorbs into a sulphur vacancy, alternative *adsorption* mechanisms, which do not require sulphur surface vacancies, may be operative. As long as such a mechanism allows for the subsequent formation of metal-sulphur bonds, it can be part of the overall HDS reaction.

The object of this chapter is to investigate the possibility of adsorption of thiophene along the edges of MoS_2 sheets through a mechanism based on sulphur-sulphur interactions alone. Specifically, the results of scattered-wave calculations of the adsorption process of thiophene on the $Ni - MoS_2$ edge structure of figure 5-5 are reported. In the calculations reported in the previous chapter, it was assumed that the edge sulphur site which lies in the $Mo - Ni$ plane is vacant, such that a standard one-point end-on mechanism can be operative. In the calculations reported in this chapter, this edge sulphur atom, S_E, is present in the cluster. Combined with an analysis of the electronic structure of thiophene, I suggest the possibility of a new reaction mechanism for the HDS process, not requiring sulphur vacancies on the surface of the catalyst, but based on sulphur-sulphur bonding.

This new *adsorption* mechanism, which will be referred to as the sulphur-sulphur mechanism, has been studied by performing a series of calculations on catalyst-thiophene complexes. By varying the distance between the thiophene molecule and the catalyst, the important orbital interactions can be identified and studied. The results indicate that strong interactions between S_T and the catalyst sulphur atom located in the Mo-Ni plane occur, resulting in weak-to-moderate bonding (as indicated by the heat of adsorption), of similar strength as was observed for the standard end-on mechanism. The implications of this result for the entire HDS process will be discussed.

6.2 Ni-promoted MoS_2 catalysts

(Electronic) Structure

Scattered-wave calculations were carried out for the $Ni - Mo - S$ structure shown in figure 5-5, point group symmetry C_{2v}. A Watson sphere was used in the calculations; all atoms were given the charge according to their formal oxidation state (-2, +4 and +2 for S, Mo and Ni respectively; in the calculations reported in this paper, the possible reduction of Mo by Ni [29, 100] has not been taken into account). Two orbitals close to the Fermi level (irreducible representations b_1 and b_2) show a very large $S_E - p$ content: 42(40) percent $S_E - p$ vs. 16(15) percent $Ni - d$ and 10(11) percent $S_B - p$. Much lower in energy lies an a_1 orbital which is almost exclusively $S_E - s$ in character (87 percent).

Implications for the adsorption of thiophene

The electronic structure of the $Ni - Mo - S$ catalyst, particularly the presence of the $S_E - p$ dominated orbitals close to the Fermi level, in combination with the $S_T - p$ dominated thiophene b_1 orbital (the out-of-plane lone pair, figure 5-2), suggests the possibility of the formation of S_T-S_E $p\pi$ bonds if thiophene adsorbs *directly onto the* S_E *atom.* This is the basis for the hypothesis that the thiophene molecule can bind to the sulphur atom located in the $Mo - Ni$ plane through $p\pi$ sulphur-sulphur interactions (it will later be shown that $S_T - S_E$ σ bonds are also formed). In this adsorption mechanism, sulphur-sulphur interactions must be responsible for binding the thiophene molecule to the catalyst, since the metal atom is shielded by the apical sulphur atom (S_E). A sulphur vacancy need not be present on the surface of the catalyst for the adsorption of thiophene.

Once a thiophene-catalyst adsorption complex has been formed, subsequent desulphurization must involve cleavage of the $C - S_T$ bonds. Hydrogenation of the thiophene molecule significantly weakens these bonds and probably precedes desulphurization, see previous chapter and ref. [80]. Regardless of the details of the hydrogenation

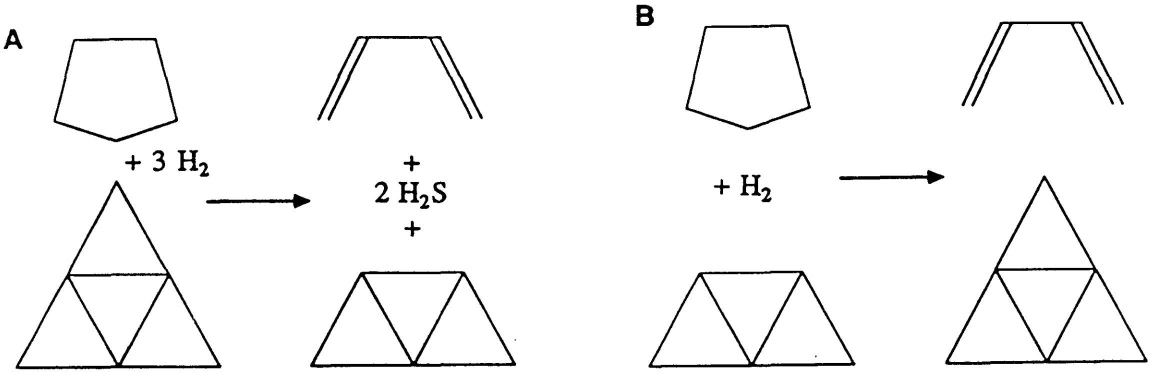


Figure 6-1: Schematic representation of the HDS reaction mechanism. The catalyst structures in A and B are top views of the nickelmolybdenum-sulphide structures of figure 5-5, with and without atom S_E. Metal atoms are not included. In (A), thiophene binds to the catalyst through $S_T - S_E$ bonding, resulting in the formation of butadiene, H_2S and a vacancy on the surface of the catalyst. This is the sulphur-sulphur mechanism. In (B) the well-known one-point end-on mechanism is depicted. See text for further details.

and desulphurization mechanisms, it is clear that the S_T atom of thiophene can form an S_2 unit with the apical sulphur atom (S_E) on the edge of the catalyst during these stages of the HDS process. This may lead to a sixfold coordination of the Ni atom. E.g. the $S_T - S_E$ unit may lie in the $Mo - Ni$ plane, in which case there will be an electrostatic attraction between Ni and the electron cloud between the two sulphur atoms on the edge, in addition to direct orbital interactions. This is consistent with experimental findings [7, 62] and supported by full-potential density-functional calculations [60].

This S_2 unit will most likely be unstable in the H_2/H_2S environment in which the HDS process takes place. Attack by hydrogen will result in the formation of H_2S and either regenerate the original edge structure (with a *five*-fold coordinated Ni atom), or lead to an exposed Ni atom (*four*-fold coordination), as shown in figure 6-1A. I emphasize that in the proposed sulphur-sulphur mechanism, a sulphur vacancy is not required for the adsorption of thiophene onto the catalyst. The proposed reaction mechanism is not inconsistent with the presence of elemental sulphur and other sulphur species on the surface of the transition metal sulphide catalyst, an issue which is open to strong debate. Recently the existence of these sulphur phases on the surface of pyrite was reported by de Donato *et al.* [16]. It may furthermore offer an explanation for the large uncertainty in the Ni coordination number reported by Bouwens and co-workers, and is consistent with the variety of different edge structures previously discussed [6, 7, 8, 9, 61, 62].

Figure 6-1B is the standard end-on mechanism, based on vacant sulphur sites. In this model, the vacancies are supposed to have been created through the prior combination of hydrogen with sulphur forming H_2S (recall that the HDS process takes place in an H_2/H_2S environment). I do not dispute the validity of this process (although to my knowledge no accurate electronic structure calculations of this vacancy creation mechanism have yet been reported), but merely hypothesize that the process shown in figure 6-1A, may be operative simultaneously. This mechanism has not previously been reported, perhaps because of the emphasis on metal d - sulphur p interactions, rather than sulphur - sulphur $p\pi$ interactions.

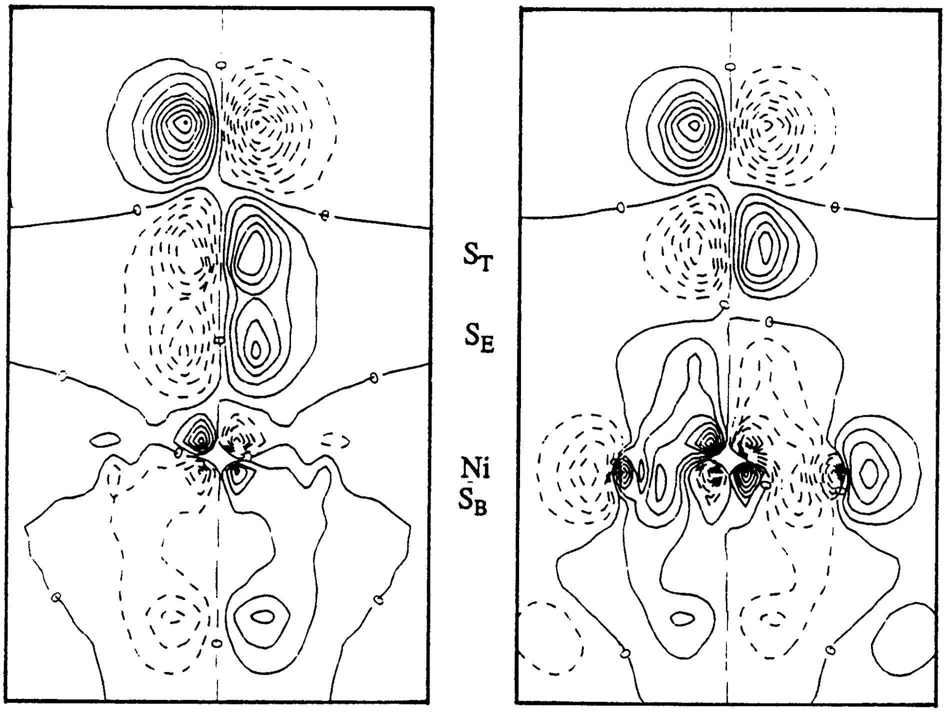
The remainder of this chapter will be devoted to the adsorption of thiophene. Only a brief discussion of the other steps in the HDS process will be given. The goal is to show that the proposed sulphur-sulphur mechanism is indeed possible and that it can be an integral part of the overall HDS process.

6.3 Adsorption of thiophene on Ni-promoted MoS_2 catalysts through sulphur-sulphur bonding

Scattered-wave calculations have been carried out for thiophene approaching the edge of a nickelmolybdate catalyst, figure 5-5 (i.e. including the S_E atom). The thiophene molecule lies in the $Mo - Ni$ plane, its rotation axis coinciding with the z-axis. The resulting point group symmetry for the complex is C_{2v}. The distance between the S_T and S_E atom was varied from 5.412 atomic units (a.u.) down to 3.912 a.u., in steps of 0.5 a.u.. Additional calculations were carried out for an $S_T - S_E$ separation of 4.212 a.u.. No relaxation of the catalyst or thiophene coordinates was incorporated in the calculations. In this manner it was possible to examine the evolution of the orbitals and in particular to identify specific interactions between catalyst and thiophene orbitals (taking into account symmetry restrictions).

In principle, all orbitals which transform according to the same irreducible representation, interact with one another. However, in most cases it is possible to identify pairs of interacting orbitals, sometimes more orbitals participate. In figure 6-2a, a contour plot is given for what was originally the thiophene b_1 orbital shown in figure 5-2. As the thiophene molecule approaches the catalyst surface, $p\pi$ $S_T - S_E$ *bonding* is established. This orbital is antibonding between the pair of sulphur atoms in the $Mo-Ni$ plane (S_T and S_E) on the one hand, and the butadiene part of the thiophene molecule on the other, and also between the sulphur pair and the remainder of the catalyst structure. The conjugate of this orbital is also shown (figure 6-2b). This orbital is originally located on the catalyst, but becomes $p\pi$ $S_T - S_E$ *antibonding* as the thiophene-catalyst separation is reduced. The net effect of the strong interaction (strong orbital mixing) between these two orbitals is weak-to-moderate bonding, as is evident from the decrease in the sum of the orbital energies as a function of thiophene-catalyst separation (figure 6-3). Although contour plots for the $S_T - S_E$ bonding and antibonding orbitals are shown for only one of the five separate $S_T - S_E$ distances for which calculations have been carried out, it should be noted that even for the maximum thiophene-catalyst separation for which calculations have been performed, the orbitals are far from exclusively centered on either the thiophene molecule or the catalyst cluster. This indicates that this particular $p\pi$ interaction is operative at relatively large thiophene-catalyst separations, i.e. in the very early stages of the adsorption process. For larger thiophene-catalyst separations, the limitations of the scattered-wave method become clearly apparent, in particular the effect of the large interstitial region on the value of the potential (for details of the scattered-wave method, see ref. [41]).

In addition to $p\pi$ $S_T - S_E$ bonding, $s\sigma$ $S_T - S_E$ bonding is also established during the adsorption process. A bonding-antibonding pair of interacting orbitals can again be identified easily (figure 6-4). One of these orbitals was originally located almost



(a) (b)

Figure 6-2: Sulphur-sulphur ($S_T - S_E$) $p\pi$ bonding and antibonding orbital pair for the sulphur-sulphur mechanism. The distance between S_T and S_E is 4.412 a.u.. Both contour plots are for the plane spanned by the line $x = y$ and the z-axis (as defined in figure 5-5). Positions along the z-axis are indicated for relevant atoms. In (a) the π bond between the S_T and S_E atoms is clearly visible. Below this bond there is a small $Ni - d$ contribution; above the π bond the carbon p contributions are significant. The S_E atom is π-bonded to the Ni and S_B atoms through d and p contributions respectively. In (b) $S_T - S_E$ antibonding is evident. Also note the p contributions from the S_B atoms. The bonding orbital is originally (i.e. for infinite thiophene-catalyst separations) based exclusively on the thiophene molecule. The conjugate antibonding orbital is originally a catalyst-based orbital.

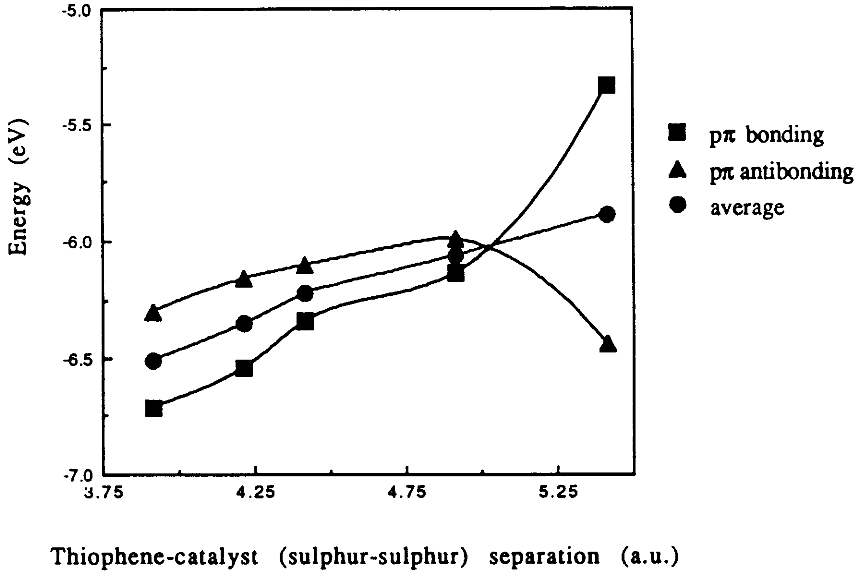
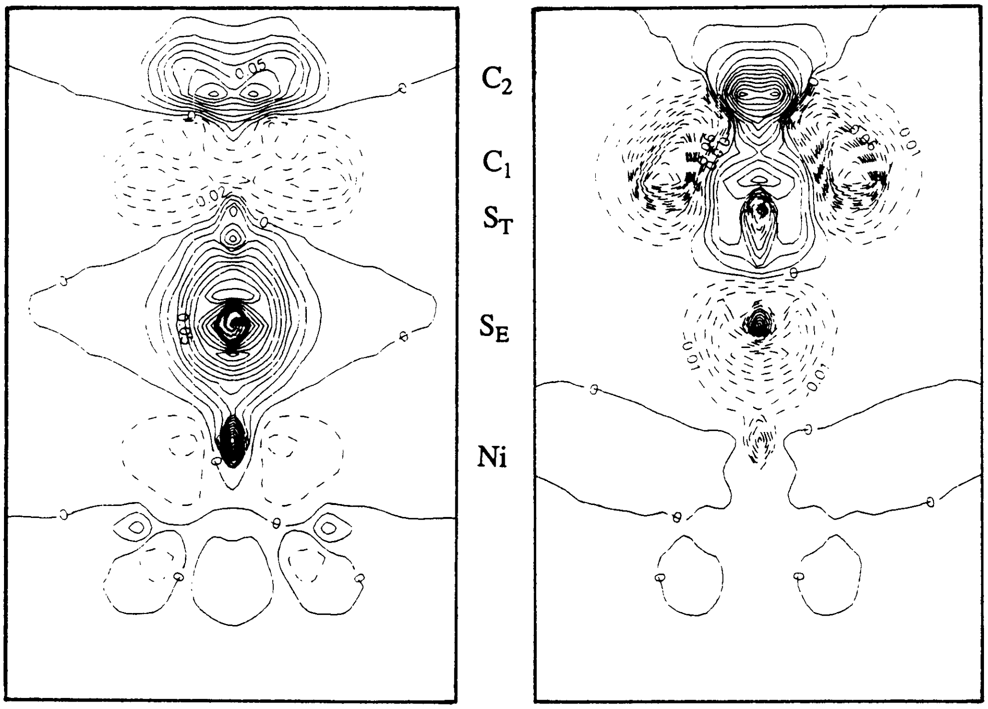


Figure 6-3: The energies of the $p\pi$ $S_T - S_E$ bonding (figure 6-2a) and antibonding (figure 6. 6-2b) orbital as a function of $S_T - S_E$ separation. The net effect of the interaction is bonding.



(a)

(b)

Figure 6-4: $S\sigma$ bonding and antibonding orbital pair. The orbitals are plotted in the xz-plane (as defined in figure 5-5) for an $S_T - S_E$ separation of 4.412 a.u.. Since this is the plane of the thiophene molecule, its geometry can easily be recognized. As in the case of the $p\pi$ interactions in figure 6-2, the bonding orbital is originally a thiophene orbital, the antibonding orbital is initially based on the catalyst.

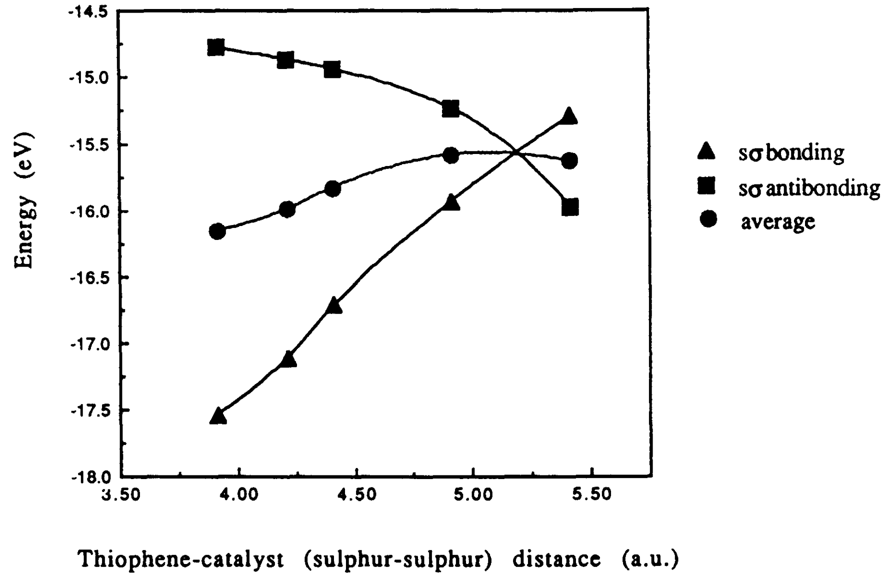


Figure 6-5: The energies of the $s\sigma$ $S_T - S_E$ bonding and antibonding orbitals of figure 6-4 as a function of $S_T - S_E$ separation. The net effect of the interaction is bonding.

exclusively on the S_E atom (s-character), the other on the thiophene molecule. The orbital energies are given in figure 6-5 as a function of thiophene-catalyst separation. Again, the net effect of this interaction is bonding.

These are of course not the only orbital interactions which occur when the thiophene molecule is lowered onto the catalyst. These particular orbitals are highlighted because significant changes in orbital character take place when the thiophene molecule is still relatively far removed from the catalyst surface. The results clearly show that $S_T - S_E$ bonding can indeed occur, as I hypothesized on the basis of specific orbital topologies for the thiophene molecule and the catalyst separately. This is also evident from the heat of adsorption (the energy difference between the adsorption complex and the separate thiophene molecule and catalyst cluster), approximately 1.7 eV. The substrate-thiophene interaction is attractive, but rather weak. This value is very close to the heat of adsorption for the one-point end-on mechanism, reported in the previous chapter (1.5 eV). The important aspect of this result is not the exact value of ΔH_{ads}, but rather the similar magnitude (see also the discussion in next section) of the two values. Since *only* sulphur-sulphur interactions can be responsible for the binding of thiophene in the sulphur-sulphur mechanism, this further indicates that sulphur-sulphur interactions are also responsible for thiophene-catalyst binding in the one-point end-on mechanism. It must be emphasized that these calculations only concern the first step of the HDS process, i.e. the adsorption of thiophene on the surface of the catalyst. I believe that the results presented here provide sufficient evidence for the acceptance of the sulphur-sulphur *adsorption* mechanism, given in figure 6-1A.

6.4 Discussion

In this section some of the limitations associated with (1) the scattered-wave formalism, and (2) the choice of geometry, will be discussed. A brief discussion of the main findings and their implications will also be given.

Despite its succesful application to many problems in chemistry and materials science, the scattered-wave model, and in particular its use of muffin-tin averaged potentials, has received much attention/criticism over the years. The inability to calculate accurate total energy figures with this method is well-known. Consequently, the values reported for the heat of adsorption are only approximate, but nonetheless consistent with earlier reports [39, 40, 80, 120]. The conclusions are based not on total energy differences but instead on specific orbital interactions. For example, the topologies of specific orbitals pointed to a particular reaction mechanism. I believe that the scattered-wave method is very well suited for this approach. Nonetheless, for thiophene-catalyst separations larger than the ones for which results are reported in this paper, difficulties in doing the calculations have been encountered. The likely cause is the inaccurate representation of the potential in the (large) interstitial region. These problems can be circumvented by partitioning the thiophene-catalyst complex into subclusters, each of which has its own interstitial region and potential [57]. Alternatively, a full-potential quantum chemistry method may be used [60].

Secondly, the geometry of the adsorption models for which calculations have been performed, warrants further discussion. From the start, the investigations have been limited to an end-on reaction model, i.e. the axis of symmetry of the thiophene molecule coincides with the symmetry-axis of the catalyst cluster. By having the thiophene molecule lie in the $Mo - Ni$ plane, the model has the same point group symmetry as the components from which it has been built, i.e. C_{2v}. This greatly influences the speed of the calculations: any rotation of the thiophene molecule about the z-axis other than by 90 degrees, would destroy all symmetry, hence destroy the block-diagonal form of the secular determinant. However, specific orbital topologies form the basis for the novel reaction mechanism proposed in this paper, so one may question the effect of rotating the thiophene molecule. Its effect on the standard end-on mechanism was investigated in the previous chapter. Here the sulphur-sulphur mechanism is considered.

The $s\sigma$ interaction, shown in figures 6-4 and 6-5, is independent of the rotation angle, but the $p\pi$ interaction of figures 6-2 and 6-3 is not. There are two catalyst orbitals close to the Fermi level with strong $S_E - p_x/p_y$ character respectively. When thiophene lies in the $xz-$ or $yz-$ plane, the out-of-plane sulphur lone pair on thiophene can interact with only one of these orbitals (one or the other). Any other choice would imply that this thiophene orbital interacts with both these orbitals, the strength of the interaction with each of them depending on the rotation angle. The interaction mechanism would remain unchanged, and is independent of the choice of geometry. The basic chemistry does not change when the thiophene molecule is rotated about the $z-$axis.

It is concluded that adsorption of thiophene on TMS catalysts is possible through a mechanism based solely on sulphur-sulphur bonding. If adsorption occurs on the edges of promoted MoS_2 catalysts, a slight reconstruction of the edge enables the formation of additional metal-sulphur bonds. These bonds appear to be necessary for the latter stages of the HDS process. Hence, sulphur-sulphur adsorption can be an integral part of the HDS process, if it occurs along the edges of MoS_2. In contrast, basal plane adsorption, albeit possible, does not allow for the formation of metal-sulphur bonds in the subsequent stages of the HDS process, since all the metal atoms are shielded by sulphur. As a result, the basal planes of MoS_2 are catalytically inactive.

6.5 Conclusions

Adsorption of thiophene onto a TMS catalyst does not require sulphur vacancies on the surface of the catalyst but can occur through a mechanism based exclusively on sulphur-sulphur bonding. If sulphur-sulphur adsorption occurs along the edges of (promoted) MoS_2 catalysts, this mechanism can be an integral part of the overall HDS process and may lead to the formation of anion surface vacancies.

Chapter 7

A Unified Theory of Periodic and Promotion Effects in Transition Metal Sulphide HDS Catalysts

7.1 Introduction

The previous two chapters, which both dealt with the fundamental HDS reaction mechanism, have provided the basis for understanding periodic and promotion effects in HDS catalysis. The results of chapter 5 (section 5.5) suggest that the nature of periodic effects is probably electronic. Differences in the rate of the final desulphurization step may ultimately be responsible for activity differences between different TMS. The discussion in chapter 3 illustrates that proposal of a new theory for periodic effects or endorsement of an existing theory implies rejection of alternatives. Thus the purpose of this chapter is threefold: (1) To review two competing theories for the dependence of HDS activity of monometallic TMS on the position of the transition metal in the periodic table, (2) To present a new theory based on the strength of the interaction between metal *d* and sulphur $3p$ electrons, and (3) To demonstrate how this theory explains promotion effects in mixed sulphides, particularly cobalt- and nickelmolybdenum-sulphides.

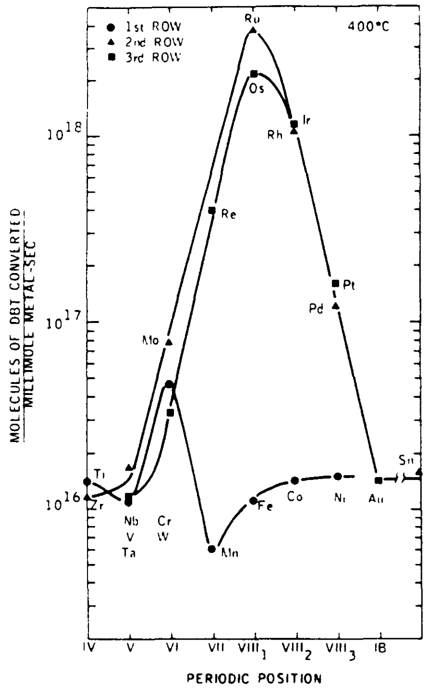


Figure 7-1: The activity of monometallic TMS for desulphurization of dibenzothiophene (ref. [70]).

7.2 The periodic variation of HDS activity in monometallic sulphides: a critical review of two competing theories

A systematic investigation of the dependence of HDS activity of unsupported monometallic TMS on the position of the transition metal in the periodic table was first carried out by Pecoraro and Chianelli [70]. Previously, it had been observed that HDS activities do not, in general, correlate to BET surface area [105]. Normalised on a per mole metal basis, it is seen that the first row TMS are generally less active than second and third row TMS, figure 7-1. A distinct minimum occurs for MnS. Maxima in HDS activity occur for Ru and Os for second and third row TMS respectively. Similar trends were later observed by Vissers *et al.* for carbon-supported TMS [111] and by Ledoux *et al.*, also for carbon-supported TMS [56].

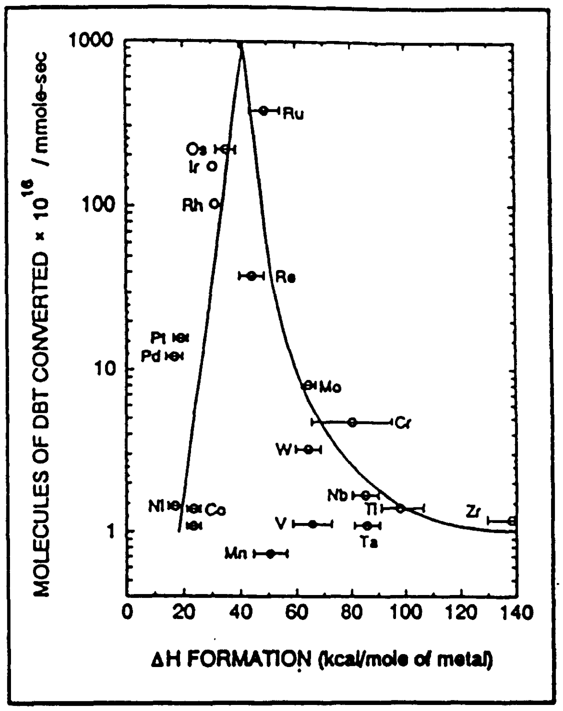


Figure 7-2: HDS activity (for dibenzothiophene) plotted against the heat of formation per mole metal atoms, ΔH_f, for monometallic TMS. From ref. [107].

It is generally agreed that the catalytic activity takes place at anion vacancies on the surface/edges of the catalyst, where exposed metal atoms can interact with the thiophenic species [84]. It follows that the *number* of vacancies directly relates to the activity of the catalyst. The rate of the rate-limiting step in the overall HDS process may however be determined by the *quality* of the active site. As yet there is no general agreement whether the activity differences between different TMS are due to differences in the number of active sites, or alternatively due to the quality of such sites (or both).

When the HDS activity is plotted against the heat of formation of the TMS (on a per mole metal basis), ΔH_f, a Balandin- or volcano-curve appears [12], typical for many catalytic processes. According to Sabatier's principle [83], the metal-sulphur bond should be neither too weak nor too strong for maximum catalytic activity. Effective catalysts must easily form and regenerate surface vacancies, yet have the ability to adsorb the thiophenic species onto the vacancy. However, $\Delta H_{f,MnS}$ falls in the optimum range, but the activity of MnS is extremely low. V_2S_3 also poses a problem. Scattered-wave $X\alpha$ calculations on octahedral MS_6^{-n} clusters (where M denotes the transition metal atom and n is the total charge of the cluster if all the elements are in the formal oxidation state representative of the TMS) led Harris and Chianelli [29, 30] to propose that it is the ability of the metal atom to bond covalently to sulphur, which determines the activity of the catalyst. The low activity of MnS and other first row TMS is explained by the ionicity of the metal-sulphur bond, which is not adequately reflected in the value of ΔH_f. A theoretical activity parameter was constructed, based on the covalency of the metal-sulphur bond and the number of electrons in the highest occupied molecular orbital (HOMO). This parameter correlated well with the experimental HDS activities. One is thus led to believe that the quality of the active site governs the catalytic activity. Harris and Chianelli pointed out that this is not inconsistent with a one-point end-on mechanism whereby the thiophene molecule binds into a surface vacancy through its sulphur atom. I emphasize that it does not follow that adsorption must be the rate-limiting step in the overall HDS process (experiments indicate that it is not); the observed correlation merely indicates that the rate-limiting step must involve metal-sulphur bonding. I will return to the analysis of Harris and Chianelli shortly.

Topsøe and co-workers [68, 107] point out that a volcano relationship is not observed if the HDS activty is plotted against the heat of formation of the TMS on a per mole *sulphur* basis. Rather, a monotonic decline in activity is observed with increasing ΔH_f, but the scatter in the data points is very large. Topsøe argues that it is easy to create sulphur surface vacancies if ΔH_f is small and concludes that most of the variations between various TMS can be explained through variations in the number of surface vacancies, although the catalytic activity may also, to a limited extent, depend on the rate of the rate-limiting step. Sulphur binding energies are obtained from augmented-spherical-wave calculations on $4d$ TMS having the $CsCl$ structure [23]. Values for $3d$ and $5d$ TMS are based on an approximate model [68]. This approach has, in my opinion, several severe limitations. For example: (1) None of the TMS have the $CsCl$ structure, in which each metal atom has 8 sulphur near-

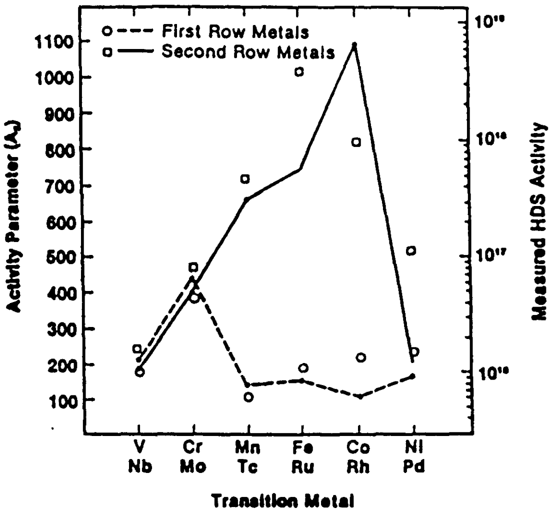


Figure 7-3: The theoretical activity parameter of Harris and Chianelli and the experimental HDS activities of the monometallic TMS for HDS of dibenzothiophene. From ref. [29].

est neighbours. Most TMS have octahedral (e.g. RuS_2) or trigonal prismatic (e.g. MoS_2) symmetry, in which there are 6 nearest neighbour sulphur atoms. Exceptions are PdS and PtS where the metal atom is in a square planar environment (4 nearest neighbours). The important aspect of this discussion is not the detailed structure of all the TMS, but the fact that the stoichiometry, structure and symmetry of the TMS affect the oxidation state of the metal atom. This is not taken into account in the $CsCl$-structure calculations, nor in the approximate model based on those calculations. (2) Many catalysts, e.g. MoS_2 and WS_2, form sheets, stacked on top of each other with weak Van der Waals bonding between them. The catalytic activity takes place at the edges of these sheets, where metal atoms are exposed, not on the basal planes, where they are not. The Topsøe values for the sulphur binding energies apply to the bulk catalyst, i.e. to the basal planes!

To settle the issue whether the periodic variation in activity results from different numbers of active sites or alternatively from the difference in the quality of those sites one needs the *intrinsic* activity for a number of different catalysts. Oxygen titration experiments provide information on the number of sites, the total catalytic activity

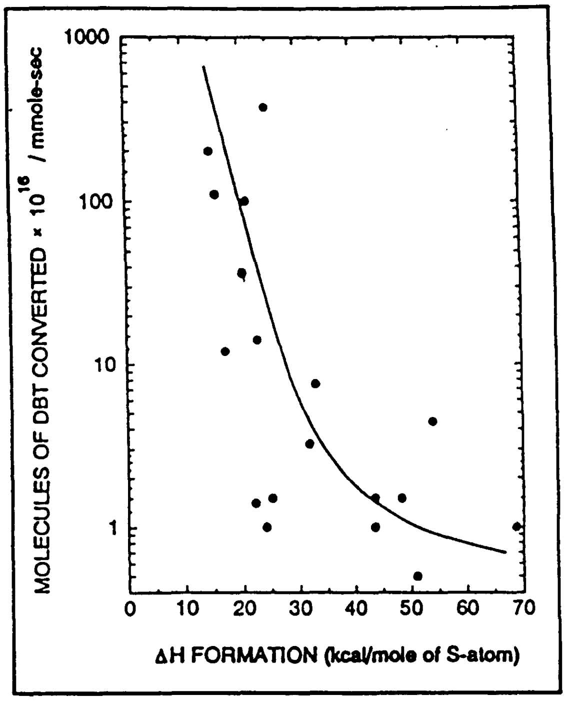


Figure 7-4: The HDS activity (for dibenzothiophene) against the heat of formation of monometallic TMS on a per mole sulphur atoms basis. From ref. [107].

can be measured in the usual way. Thus, Carvill and Thompson [10] report that the intrinsic activity of MoS_2 is roughly 40-50 times higher than for FeS, and CoS and 3-4 times lower than for $CoMoS$, etc.. Arnoldy *et al.* [2] show that *Re* is 2-20 times more active than Mo. This unambiguously demonstrates that the variation in activities is an electronic effect, explained by the quality of the active sites. This is not to say that the number of sites is not important for the overall activity. Obviously, more sites will mean a higher activity, regardless of the rate of the rate-limiting step. Small, finely dispersed particles are likely to have relatively many surface vacancies: the analysis of Kasztelan [48, 49] remains valid even if the periodic variation is an electronic effect.

I return to the analysis of Harris and Chianelli. Prins *et al.* [73] have noted that it remains unclear why the linear combination of the particular electronic parameters identified (number of electrons in the HOMO of an octahedral MS_6^{-n} cluster, n, and the covalency of the metal-sulphur bond) would correlate so well to HDS activity. Furthermore, the analysis contains several unsatisfying features: (1) Spinned calculations were carried out for the first row TMS, but not for second and third row TMS. As a result, the maximum value of n, hence also of the activity, is twice as low for first row TMS as it is for second and third row TMS. While the effect of spin is without question significant for first row TMS, n as such does not have any physical/chemical meaning, I will show that one should instead focus on the absolute and relative numbers of π and σ metal d-sulphur $3p$ antibonding electrons. (2) The HOMO is a π metal d - sulphur $3p$ antibonding orbital for all the second and third row TMS, except for Pd and Pt, where it is a σ antibonding orbital. The occupation of this orbital is forced by the total d-electron count. Again, n does not have any physical/chemical meaning, for it does not take into account the character of the orbital to which it applies. While I agree with Harris and Chianelli that the dependence of activity on the position of the metal atom in the periodic table is an electronic effect, and that it is the ability of the metal atom to bond covalently to sulphur which determines the activity of the catalyst, the above issues must be addressed. In the following a chemical basis/understanding for the observed correlation between theory and experiment will be provided. The analysis fundamentally differs from that of Harris and Chianelli in that it takes into account the absolute and relative numbers of σ and π electrons and the character of the orbitals. This leads to a completely different interpretation of the promotion effect in mixed TMS.

7.3 An alternative explanation of the periodic variation of HDS activities based on the metal d - sulphur $3p$ interaction strength

In chapter 5 I reported calculations on thiophene-catalyst complexes which indicate that interactions between the sulphur atom in thiophene and the sulphur atoms in the catalyst dominate the adsorption process [95, 98, 99]. Metal-sulphur interactions are weak at this stage in the HDS process. In contrast, dihydrothiophene-catalyst complexes display significant interactions between the sulphur "lone pairs" in the

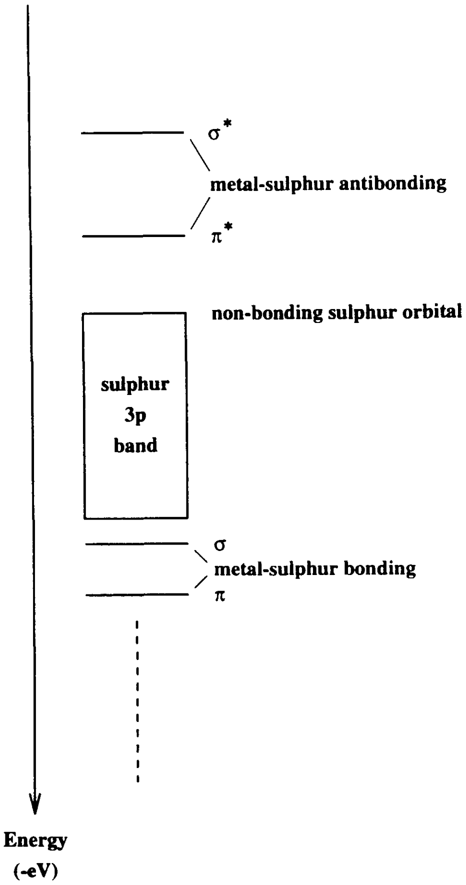


Figure 7-5: A schematic representation of the electronic structure of an octahedral TMS MS_6^{-n} cluster. See text for details.

thiophene molecule and the metal *d* orbitals. This suggests that adsorption is not the rate-limiting step in the overall HDS process and that hydrogenation must take place before, or in conjunction with, desulphurization. Furthermore, the strength of the metal *d*-sulphur 3*p* interaction is a function of the transition metal: weak for *Zr* but strong for *Ru*. This suggests that the rate of the rate-limiting step is determined by the quality of the site and prompts a new look at the octahedral TMS clusters examined by Harris and Chianelli.

A schematic representation of a molecular orbital diagram is given in figure 7-5 for the non-magnetic second and third row TMS, starting from metal *d* -sulphur 3*p* σ and π bonding orbitals. Going up in energy, one first finds a manifold of states dominated by sulphur 3*p* contributions (with some metal *s* character mixed in). A non-bonding sulphur level delineates this sulphur "band" for all the TMS clusters and has been used as a reference state in the calculations reported here. Next there are π and σ metal d - sulphur $3p$ antibonding levels, in that order. Different transition metals will have different numbers of d-electrons. This, in conjunction with the oxidation state of the transition metal, *directly* affects the occupation number of the antibonding orbitals. However, many aspects of the electronic structure are *indirectly* affected. E.g. the metal contribution to the bonding orbitals (generally increasing when going from left to right in the periodic table), the sulphur contribution to the antibonding orbitals (also increasing from left to right), the orbital energies of the antibonding levels (decreasing), the energies of the bonding levels (decreasing), the width of the sulphur band (increasing) all depend on the position of the transition metal in the periodic table. The goal is to define a parameter, I, which takes into account all these manifestations of the character of the transition metal *and* accurately represents the strength of the metal d -sulphur $3p$ interaction. This can be achieved by multiplying the orbital occupation numbers by the energy of that orbital relative to the non-bonding sulphur reference state, and summing over all the orbitals depicted in figure 7-5. E.g. if the σ orbital, occupied by 4 electrons, lies 2.5 eV below the reference state, it contributes 10 units to this parameter. Similarly, antibonding orbitals, lying above the reference state, lower the value of I.

It follows that the σ antibonding level, if occupied, has a much larger effect on I than the π antibonding orbitals, for this orbital lies relatively high in energy. When the topologies of these orbitals are considered, figure 7-6, it is immediately clear that this indeed should be the case. A σ antibonding electron strongly contributes to the repulsion between one sulphur atom and the remainder of the cluster, MS_5^{-n}, for it is unambigously antibonding between the metal and the sulphur atom, figure 7-6a. A π antibonding level on the other hand is antibonding between the metal and sulphur atoms, but bonding between the sulphur atoms, figure 7-6b. Furthermore, the π levels with the largest sulphur contents (strongest sulphur-sulphur attraction), e.g. RuS_2, lie lowest in energy. This is consistent with the definition of I. Turning to the experimental activity curve, figure 7-1, it is striking that a significant decrease

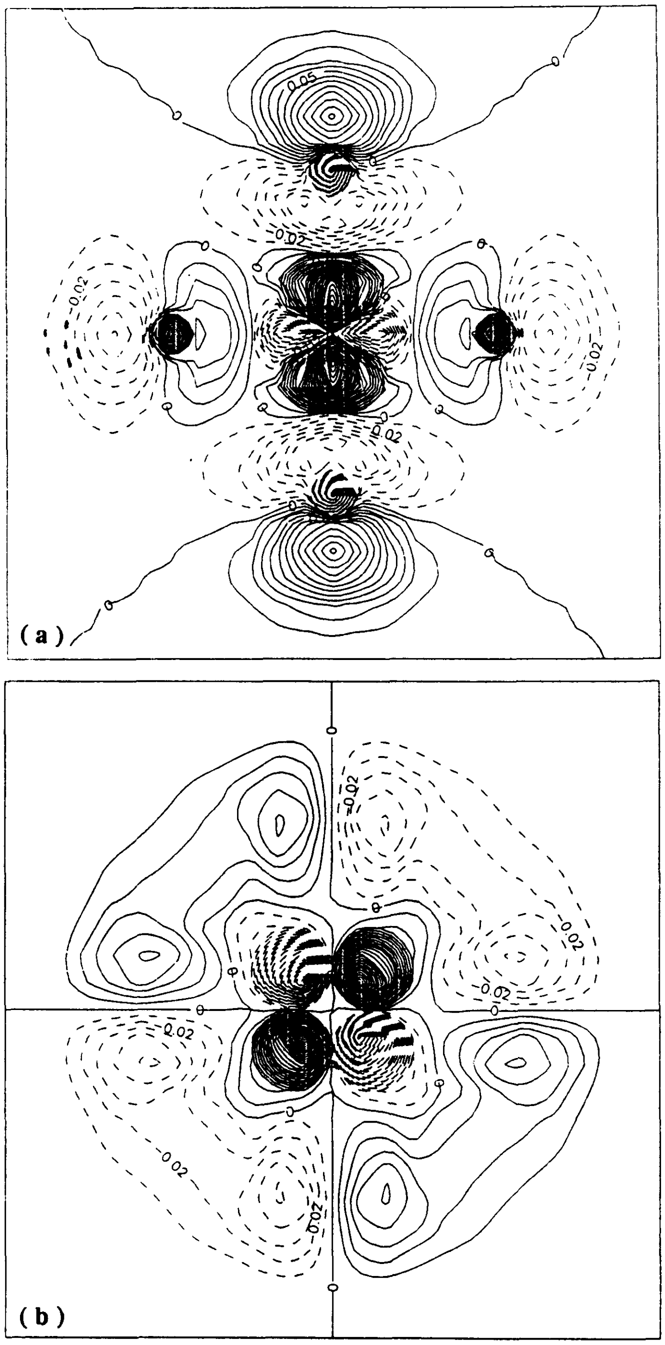


Figure 7-6: The metal-sulphur σ^* (a) and π^* (b) antibonding orbital for an octahedral RhS_6^{-9} cluster.

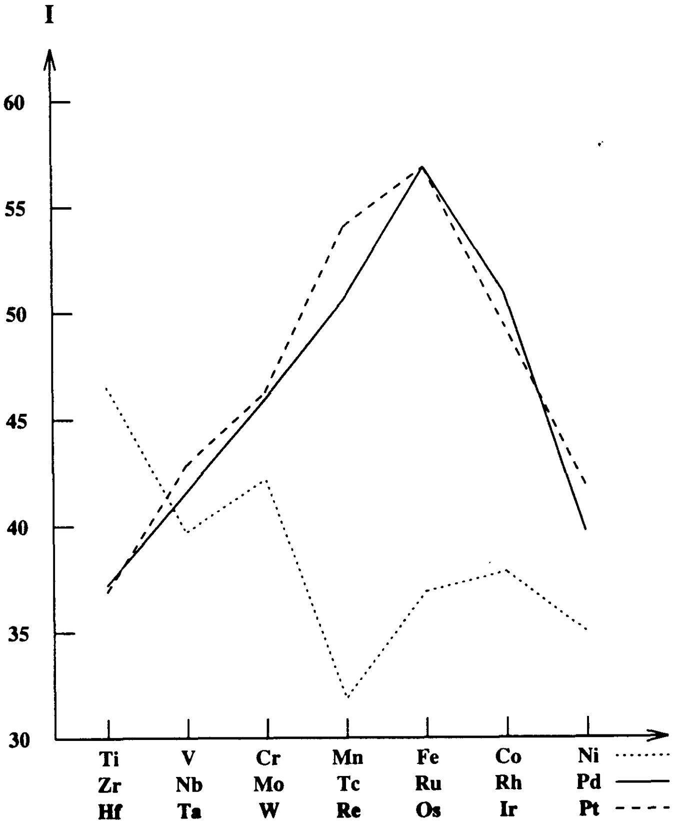


Figure 7-7: The metal d - sulphur $3p$ interaction strength, I, plotted against the position of the transition metal in the periodic table. See text for details.

in activity is observed precisely when the σ antibonding level is first occupied. For first row TMS, this occurs at MnS, due to the importance of spin. For the non-magnetic second and third TMS, the σ antibonding level is first occupied for Pd and Pt. This goes to show that I takes into account both the number of d electrons and the absolute and relative number of σ and π electrons, as well as the character of these orbitals.

Scattered-wave density-functional calculations on octahedral TMS clusters have been carried out on all the first, second and third row TMS for which Pecoraro and Chianelli report experimental HDS activities. The exchange-correlation potential of Hedin and Lundqvist [34] was used for the second and third row TMS. Spin was included for the first row TMS, for which Ceperley and Alder's [11] exchange-correlation

TMS	*metal ion oxidation state*	*metal-sulphur bond length (a.u.)*	*number of σ^* electrons*	*number of π^* electrons*
TiS_2	+4	4.57	-	0
V_2S_3	+3	4.48	-	1
Cr_2S_3	+3	4.57	-	3
MnS	+2	4.89	2	3
FeS	+2	4.27	-	6
Co_9S_8	+2	4.38	1	6
Ni_3S_2	+2	4.54	2	6
ZrS_2	+4	4.84	-	0
NbS_2	+4	4.67	-	1
MoS_2	+4	4.57	-	2
TcS_2	+4	4.50	-	3
RuS_2	+4	4.45	-	4
Rh_2S_3	+3	4.48	-	6
PdS	+2	4.76	2	6
HfS_2	+4	4.84	-	0
TaS_2	+4	4.61	-	1
WS_2	+4	4.55	-	2
ReS_2	+4	4.38	-	3
OsS_2	+4	4.42	-	4
IrS_2	+3	4.48	-	6
PtS	+2	4.53	2	6

Table 7.1: The oxidation state of the metal atom and the metal-sulphur bond length in octahedral MS_6^{-n} clusters, which were used to calculate I (figure 7-7). Also given is the number of σ^* and π^* electrons in these clusters.

potential was used. Note that the inclusion of spin does not lead to an inconsistency since *all* d electrons are incorporated in I. I does not depend on the number of electrons in any specific orbital. Figures 7-1 and 7-7 demonstrates that I correlates well with the experimental HDS activities.

Two factors in the present analysis critically affect the value of I: (1) the oxidation state of the transition metal, affecting the number of electrons that contribute to I (hence my objection to the $CsCl$-structure calculations of Topsøe and coworkers), and (2) the metal-sulphur bond length, affecting the energy of the levels that contribute to I. I have chosen the oxidation state based on the stoichiometry of the TMS, see table 7.1 (except for Ir). For example, $Ru(IV)$ has been used rather than $Ru(II)$.

The alternative choice would not, in first order, significantly affect I. It corresponds to the addition of two π antibonding electrons to the cluster, which for RuS_2 lie very close in energy to the sulphur reference state. This is an indication of the covalency of the metal-sulphur interaction. Furthermore, the choice for $Ru(II)$ would be based on the application of Pauling's rules to the pyrite structure, not appropriate for covalent compounds. The metal-sulphur bond length, table 7.1, corresponds to the observed bond length in the TMS, except for PdS and PtS. Only for the latter two compounds is the metal atom in a four-fold sulphur environment. Hence for these sulphides the bond length has been estimated from the Shannon ionic radii [88].

This simple model does not take into account the detailed surface structure of the catalyst, yet I correlates rather well with experimental activities. This analysis is aimed at identifying the *basic chemistry* that is involved in the rate-limiting step of the overall HDS process. I consider such information essential for the rational design of new catalysts. From the observed correlation it appears that the interaction between the sulphur $3p$ lone pairs on the thiophene molecule with the metal d orbitals (but also with the sulphur atoms in the catalyst) greatly influences the activity of the catalyst. Keeping this in mind, the relatively high I-value for TiS_2 is unsatisfactory, but no cause for great concern since Ti^{4+} lacks d electrons alltogether.

Before addressing promotion effects, I note an interesting observation by Carvill and Thompson [10], consistent with the theory presented. The average state of reduction of molybdenum in MoS is much higher than it is in MoS_2, but the intrinsic catalytic activity is significantly higher for MoS_2.

7.4 Promotion effects

Cobalt- and nickelmolybdenum sulphides are the most commonly used industrial HDS catalysts. The activity of these catalysts is higher than that of CoS (NiS) and MoS_2 separately. The nature of this synergistic promotion effect has not been conclusively determined [72]. It may be electronic (meaning that Mo and $Co(Ni)$ may act together to create especially active HDS sites) and/or structural (meaning that the dispersion of the catalyst is improved, thus increasing the number of sites). A related question is whether the promotor element is merely a promotor element, as the name suggests, or itself the active site.

In the theory presented in the previous section, the oxidation state of the metal atom plays a very significant role. Harris and Chianelli have shown that only Co and Ni, and possibly Fe, have the ability to donate electrons to Mo in the mixed sulphides, thus altering the *d*-electron density on these atoms [31]. These are precisely the elements for which promotion effects have been observed [10, 31]. Magnetic susceptibility measurements by Topsøe and co-workers indicate that extensive electron delocalization occurs in $Co - Mo - S$ and $Ni - Mo - S$ [110]. XPS data of Shepelin *et al.* [89] show that partial transfer of electron density from nickel to tungsten (molybdenum) occurs through the formation of mixed surface sulphides: the oxidation state of Ni is higher in the mixed sulphide than it is in the monometallic sulphide [89, 100]. In the interpretation of Harris and Chianelli [31], the increase in catalytic activity in $Co(Ni) - MoS_2$ (compared to MoS_2) is due to the increased *d*-electron density on the Mo atoms. However, the value of I is lower for an $Mo(II)S_6^{-10}$ cluster than it is for $Mo(IV)S_6^{-8}$ since two π antibonding electrons have been added to the cluster. On the other hand, the reduction of Mo corresponds to the removal of σ antibonding electrons from $Co(Ni)$. This significantly increases the value of I. If I indeed represents the intrinsic HDS activity accurately, then this crude first-order analysis (no change in the metal-sulphur bond length has been incorporated) shows that the activity of the Mo atoms has gone down, but also that the activity of the $Co(Ni)$ atoms has increased sharply! In other words, the theory predicts that Co and Ni are in fact the active sites in $Co(Ni) - Mo - S$. Although there is still no consensus on the exact structure of the $Co - Mo - S$ and $Ni - Mo - S$ phase, there are many reports that Co and Ni decorate the edges of MoS_2 sheets, covering the Mo atoms. This essentially means that MoS_2 acts as a support for highly active $Co(Ni)$ atoms [100]. This offers interesting possibilities for designing new catalysts. Doping the support with appropriate elements may alter the *d*-electron density on the catalytically active sites. If this does not sacrifice the dispersion of the catalyst on the support, a significant increase in catalytic activity may thus be achieved.

The role of the support has received much interest over the years. E.g. Arnoldy *et al.* [2] found that the activity of rhenium sulphides depended slightly on the support used (in the order $SiO_2 < Al_2O_3 <$ carbon), but the effect on MoS_2 is much more pronounced. Ramirez *et al.* [76] observed a higher intrinsic activity for TiO_2- than for Al_2O_3-supported $Mo - S$ and $Co - Mo - S$ catalysts. Since they do not observe a significant shift in XPS binding energies, an electronic basis for this phenomenon is ruled out. However, it must be noted that the presence of some Mo^{+6} was detected for the sulphided catalysts supported on TiO_2, but not if Al_2O_3 was used as a support. This is consistent with the theory presented, for the removal of two π antibonding electrons from the MoS_2 cluster leads to an increase in the value of I. Similarly, doping of a TiO_2 support with fluorine (a very electronegative element) has a strong promoting effect, as shown by Ramirez *et al.* [75].

Experimental verification of the theory presented (or any other theory of promotion effects for that matter) is a challenging task, since electronic and structural promotion effects often occur simultaneously. Yet it should be possible to determine/estimate the oxidation state of Ni and Co decorating the edges of $Co(Ni) - MoS_2$, using e.g. XPS (as was done by Shepelin *et al.* [89]) or EXAFS. Further research in this area of HDS catalysis is clearly needed.

7.5 Conclusions

1. The dependence of the HDS activity of monometallic TMS on the position of the metal atom in the periodic table is above all an electronic effect. The quality of the active site determines the rate of the rate-limiting step.

2. The strength of the interaction between the sulphur $3p$ and metal d electrons, I, correlates well with the experimental HDS activities. The main factors determining the value of I are the oxidation state of the transition metal atom and the metal-sulphur bond length.

3. In $Co(Ni) - Mo - S$, cobalt and nickel donate electrons to molybdenum. The removal of σ antibonding electrons greatly enhances the intrinsic activity of these elements. It follows that MoS_2 acts as a support for highly active $Co(Ni)$.

4. The catalytic support not only influences the dispersion of the catalyst, but may also interact electronically with the active phase by influencing the d electron density on the transition metal atom.

Chapter 8

Discussion

Obtaining a full understanding of a complex chemical process requires detailed knowledge of the separate phases of that process. Often not all the information needed is available, e.g. because experimental techniques are not sufficiently advanced or because it is not a priori clear which measurements can lead to the achievement of this goal. Quantum chemistry avoids some of the limits that are imposed by laboratory equipment and thus circumvents many problems that are encountered in experimental research. Even so, the conduct of scientific research remains a tedious (and sometimes frustrating) exercise. Frequently new approaches and ideas have to be abandoned if they prove inconsistent with experimental data. Occasionally several paths converge, integrating seemingly separate phenomena and measurements into one theory. In the end, if one is fortunate, a theory emerges that is consistent with all the experimental data available, but this is by no means guaranteed at the start.

Quantum calculations on the separate stages of the HDS process themselves provide little information, but much uncertainty, about the underlying chemistry. *Combined* a clear picture emerges of how an HDS catalyst functions, of the basic HDS reaction mechanism, and of the factors that determine the quality (activity and selectivity) of the TMS catalyst. Validation/falsification of the theory presented requires new experimental measurements. Although not anticipated, modifications to the theory may subsequently be required.

The parameter I is a measure of the interaction strength between sulphur $3p$ and metal d electrons; it does not represent the metal-sulphur bond strength. The latter represents the energy changes which occur during the formation of metal-sulphur bonds and antibonds when metal and sulphur combine to form the sulphide, i.e. the bond strength is a measure of the heat of formation and vice versa. Net binding results if the energy gains due to the bonding orbitals outweigh the energy losses due to the antibonding orbitals. Generally, this means that more electrons occupy the bonding orbitals than the antibonding orbitals. When going from left to right in the periodic table, the extra d electrons occupy antibonding orbitals (see figure 7-5), the net binding effect monotonically decreases and so does ΔH_f.

A key feature of the formation of the sulphide is the change in the oxidation states of the metal and sulphur atoms. No such change is observed for the perpendicular adsorption of thiophene onto MS_5^{-n}. I measures the ability of an MS_5^{-n} cluster to "capture" an extra sulphur atom into its vacancy, giving MS_6^{-n-2}, i.e. in the context of HDS catalysis it represents the ability of the catalyst to capture the sulphur atom of thiophene during the desulphurization step. For lack of a better term, I has been called an interaction strength; it is not the metal-sulphur bond strength in bulk TMS. If it represents a bond strength at all, then it refers specifically to the metal-S_T bond.

The calculations on thiophene- and dihydrothiophene-catalyst complexes, described in chapter 5, have thus served an important purpose, for they illustrate when and how the S_T atom interacts with the catalyst. It was shown that in thiophene-catalyst complexes, the complex can be divided into 2 clearly distinguishable subunits: both the thiophene molecule and the catalyst have retained their individual character. The strong involvement of the sulphur atom of thiophene in the electron system of the aromatic ring is responsible for the lack of metal-S_T interactions for perpendicularly adsorbed thiophene. When thiophene is hydrogenated, the involvement of S_T in the aromatic ring is reduced: strong metal-S_T interactions are now observed.

Hence it is the strong basicity of the sulphur atom in thiophene which lies at the basis of understanding the HDS mechanism. Hydrogenation of thiophene must take place before desulphurization is possible (or the processes must occur simultaneously). When this happens, it is the interaction of S_T with the catalyst, i.e. I, which then determines the activity of the catalyst. Thus in order to explain periodic effects, the issue whether thiophene adsorbs through η_1, η_2 or η_5 binding is largely irrelevant, for adsorption takes place prior to and is clearly distinguishable from the rate-limiting step in the overall HDS process. All three adsorption mechanisms may occur [1]. In fact, chapter 6 shows that an entirely different adsorption mechanism, not based on sulphur vacancies on the surface of the catalyst, may also be operative. The only necessary requirement is that metal-S_T interactions are possible at some point along the HDS reaction path, either through the prior existence of a sulphur vacancy (as in η_1, η_2 and η_5 adsorption), or through reconstruction of the surface/edge of the catalyst (as in the sulphur-sulphur mechanism).

Certain aspects of the theory presented may be counterintuitive and warrant a brief explanation/discussion.

A more positive metal atom is less likely to act as an electron (charge) donor for the sulphur atom in thiophene, yet the theory predicts that a higher oxidation state for the metal atom in the TMS will correspond to a catalyst with a higher intrinsic catalytic activity. There is no inconsistency here, for the strong basicity of the sulphur atom is neutralized not through charge transfer form the metal atom (changing its oxidation state), but through hydrogenation of the adjacent carbon atoms. Recall that adsorption must be described in terms of complex Dewar-Chatt mechanisms, not through the Blyholder model.

Furthermore, while a higher oxidation state for the transition metal implies a higher intrinsic activity, pure transition metals (oxidation state 0) tend to be more active than the corresponding sulphides. Again, there is no inconsistency here: the theory applies to transition metal *sulphides*, not to pure transition metals or to the formation os transition metal sulphides. When HDS occurs on a pure transition metal, significant energy gains can be achieved through the establishment of metal-sulphur bonds. This immediately leads to the formation of the sulphide. That is the reason

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[1] It is worth emphasizing again that calculations on perpendicularly adsorbed thiophene allow for the most general conclusions, since metal-S_T interactions are most likely for this adsorption mode.

why e.g. Joffre *et al.* [40, 39] calculate high values for the heat of adsorption on two- and three-vacancy sites on the surface of a TMS. The question is whether such sites are in fact available in real TMS. I emphasize again that I does not represent the metal-sulphur bond strength in bulk TMS.

Catalysis lends itself particularly well to close cooperation between theoreticians and experimentalists. It has been shown that quantum chemistry and the multiple-scattered-wave method are powerful *predicitive* as well as *explanatory* tools in catalysis. The implications of the theory that has been developed for the design of new catalysts have been emphasized throughout this thesis. For example, doping the catalytic support appears to be a promising way to improve catalytic performance. It is now up to the experimentalists to fully explore these possibilities. The methods employed in this research may also be applied to other catalysts and catalytic processes. That will be the topic of chapter 10

Chapter 9

Summary and Conclusions

HDS Mechanism

1. **Adsorption**

   - Adsorption is not the rate-limiting step in the overall HDS process. Even if thiophene adsorbs perpendicularly into a single sulphur vacancy on the surface of a TMS catalyst, the formation of strong bonds between the exposed metal atom and the sulphur atom in thiophene is not observed. Strong sulphur-sulphur interactions lead to weak binding of the thiophene molecule to the catalyst.
   - Alternative adsorption modes based on sulphur vacancies, such as η_2- and η_5-binding, may be operative. The involvement of the metal atom is expected to be even less than for η_1-binding. Thus the conclusions concerning η_1-binding may be extended to cover all adsorption modes.
   - Adsorption is also possible through a mechanism based solely on sulphur sulphur bonding. This mechanism does not require sulphur vacancies on the surface of the catalyst, but can only be an integral part of the overall HDS process if it allows for the formation of metal-sulphur bonds in the later stages of the HDS process. Hence along the edges of nickel(cobalt)molybdenum sulphide catalysts, this mechanism may be operative in conjunction with the standard end-on mechanism.

2. **The Role of Hydrogen**

   Hydrogenation is not the rate-limiting step in the overall HDS process. Hydrogenation of adsorbed thiophene (leading to adsorbed dihydrothiophene) lessens the involvement of the sulphur atom in the electron system of the aromatic ring and induces the formation of metal-sulphur bonds. Consequently, hydrogenation must take place before, or in conjunction with, desulphurization.

3. **Desulphurization**

   Desulphurization is the rate-limiting step in the overall HDS process. Its rate is determined by the ability of the sulphur atom in thiophene to interact covalently with the metal and sulphur atoms in the TMS catalyst.

Periodic and Promotion Effects

4. **Periodic Effects**

   - The dependence of the HDS activity of monometallic TMS on the position of the metal atom in the periodic table is above all an electronic effect. The quality of the active site determines the rate of the rate-limiting desulphurization step.
   - The strength of the interaction between the sulphur $3p$ and metal d electrons, I, correlates well with the experimental HDS activities. The main factors determining the value of I are the oxidation state of the transition metal and the metal-sulphur bond length.

5. **Promotion Effects**

   In cobalt(nickel)molybdenum sulphide, cobalt and nickel donate electrons to molybdenum. The removal of σ antibonding electrons greatly enhances the intrinsic activity of these elements. It follows that MoS_2 acts as a support for highly active $Co(Ni)$.

Miscellaneous

6. The Influence of the Catalytic Support

The catalytic support not only influences the dispersion of the catalyst, but may also interact electronically with the active phase by influencing the *d*-electron density on the transition metal atom.

7. TMS vs. Pure Transition Metals

Activity and selectivity differences between TMS and pure transition metals as HDS catalyst can be explained on the basis of metal-sulphur (S_T) bonds. For pure transition metals, such bonds are formed immediately during adsorption of the thiophene molecule (in addition to carbon-metal bonds, etc.). For TMS, the formation of these bonds requires hydrogenation of the thiophene molecule. Since metal-sulphur bonds are required for desulphurization, the pure transition metals are more active HDS catalysts, but the TMS are more selective.

Chapter 10

Suggestions for Further Research

Further research need not be focused on improving TMS HDS catalysts. Other catalysts and catalytic processes should also be explored. Many systems can be studied with the methods used in this thesis. Two examples, directly related to HDS, are given below.

1. **Hydrodenitrogenation (HDN)**

   In addition to sulphur, nitrogen must be removed from fuel feestocks in order to obtain "clean" oil products, see chapter 1. Hydrodenitrogenation of pyridine, quinoline and related compounds is completely analogous to the HDS of thiophenic species. TMS are also used as HDN catalysts, but nickelmolybdenum sulphide is the preferred catalyst for HDN, rather than cobaltmolybdenum sulphide. The nitrogen-containing molecule adsorbs perpendicularly into a sulphur vacancy on the surface of the TMS, followed by hydrogenation. [1] In general, HDN is more difficult to achieve than HDS. The reason may lie in the electron configuration of the N atom in the aromatic ring: there is no nitrogen out-of-plane lone pair, facilitating the formation of metal-nitrogen bonds during hydrogenation.

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[1] In thiophene HDS there is some ambiguity whether hydrogenation precedes desulphurization or not. In pyridine HDN experiments indicate that hydrogenation precedes denitrogenation [87].

Periodic effects are also observed for HDN by monometallic TMS [19, 55, 101]. Contrary to HDS catalysis, in HDN the third row TMS are considerably more active than the second row TMS. In analogy with HDS catalysis, it is to be expected that interactions between the nitrogen 2*p* electrons, metal *d* electrons and sulphur 3*p* electrons determine the rate of the rate-limiting denitrogenation step. Preliminary calculations on MS_5N^{-n} clusters indicate that this is indeed the case, but have not yet been able to explain activity differences between second and third row TMS [96]. More research is needed. This area represents a logical and promising extension to the research presented in this thesis and moreover offers the possibility of unifying the fields of HDS and HDN catalysis.

2. Transition Metal Carbides and Nitrides

Currently there is much interest in transition metal carbides and nitrides for HDS and other catalytic reactions. Fewer experimental data are available for these systems, but the nature of these catalysts for HDS may very well be similar to HDS through TMS. Employment of the same methods used in this thesis for the study of carbides and nitrides is strongly recommended.

Biographical Note

Timotheus Servaas Smit, born April 26, 1968 (Assen, The Netherlands), completed his pre-university education at the *United World College of the Atlantic* (Llantwit Major, Wales), where he obtained the "International Baccalaureate" diploma in May 1986. He began his studies for the degree of "Technisch Natuurkundig Ingenieur" (Master of Science, Applied Physics) at *Delft University of Technology* (Technische Universiteit Delft) in the Netherlands in September 1986. His thesis, entitled "Monte Carlo Renormalization of the 3D Ising Model: The Analyticity of Block Spin Transformations." was completed under the supervision of Dr. H.W.J. Blöte and Dr. J.R. Heringa in November 1990. He was hired by Akzo Corporate Research America Inc. (Dobbs Ferry, New York) and assigned to a joint Akzo-MIT project in computational chemistry at the *Massachusetts Institute of Technology* in January 1991. The results of his research as a Ph.D. student in the Department of Materials Science and Engineering, under the supervision of Professor K.H. Johnson, are described in this thesis.

Scientific Output

Delft University of Technology

1. H.W.J. Blöte, A. Compagner, J.H. Croockewit, Y.T.J.C. Fonk, J.R. Heringa, A. Hoogland, T.S. Smit and A.L. van Willigen, *Monte Carlo Renormalization of the Three-Dimensional Ising Model*, Physica A 161, pp.1-22 (1989)

2. T.S. Smit, J.R. Heringa, H.W.J. Blöte, A. Compagner, Y.T.J.C. Fonk and A. Hoogland, *Monte Carlo Renormalization of the 3-D Ising Model and the Analyticity of Block-Spin Transformations*, Proceedings of the CP90 Europhysics Conference on Computational Physics (Amsterdam, September 1990), pp. 487-490, World Scientific 1991, A. Tenner (editor)

Massachusetts Institute of Technology

3. T.S. Smit and K.H. Johnson, *Hydrodesulphurization of Thiophene: a Molecular Orbital Topology Study*, Chemical Physics Letters 212, pp. 525-533 (1993)

4. T.S. Smit and K.H. Johnson, *The Importance of Sulphur-Sulphur Bonding in the Hydrodesulphurization of Thiophene, using Transition Metal Sulphide Catalysts*, poster presentation at the American Conference for Theoretical Chemistry, Rochester (NY), June 1993

5. T.S. Smit, *Hydrodesulphurization of Thiophene using Transition Metal Sulphides*, invited oral presentation at Akzo Workshop on Hydrotreating Catalysts, Amsterdam, October 1993

6. T.S. Smit and K.H. Johnson, *The Importance of Sulphur-Sulphur Bonding in the Hydrodesulphurization of Thiophene, using Transition Metal Sulphide Catalysts*, Journal of Molecular Catalysis, accepted for publication, November 1993

7. T.S. Smit and K.H.Johnson, *A Unified Theory of Periodic and Promotion Effects in Transition Metal Sulphide Hydrodesulphurization Catalysts*, submitted to Catalysis Letters

8. T.S. Smit and K.H. Johnson, *Hydrodesulphurization of Thiophene by Transition Metal Sulphides: The Electronic Basis for Catalytic Activity*, oral presentation at the Materials Research Society Spring Meeting, San Fransisco, April 1994. Also submitted for proceedings.

In Preparation

10. T.S. Smit and K.H. Johnson, in preparation for the Journal of the American Chemical Society

11. T.S. Smit and K.H. Johnson, in preparation for the Journal of Computer-Aided Materials Design

12. T.S. Smit and K.H. Johnson, invited oral presentation for the 210th meeting of the American Chemical Society, Washington D.C., August 1994

Bibliography

[1] P. W. Anderson. *Concepts in Solids.* Frontiers in Physics. Addison-Wesley Publishing Company, 1963.

[2] P. Arnoldy, E. M. van Oers, V. H. J. de Beer, J. A. Moulijn, and R. Prins. *Appl. Catal.*, 48:241, 1989.

[3] M. R. Blake, M. Eyre, R. B. Moyes, and P. B. Wells. In T. Seiyama and K. Tanabe, editors, *Proceedings of the 7th International Congress on Catalysis (Tokyo, 1980)*, page 591. Elsevier, 1981.

[4] G. Blyholder. *J. Phys. Chem.*, 68:2772, 1964.

[5] M. Born and J. R. Oppenheimer. *Ann. Phys.*, 84:457, 1927.

[6] S. M. A. M. Bouwens, R. Prins, V. H. J. de Beer, and D. C. Koningsberger. *J. Phys. Chem.*, 94:3711, 1990.

[7] S. M. A. M. Bouwens, J. A. R. van Veen, D. C. Koningsberger, V. H. J. de Beer, and R. Prins. *J. Phys. Chem.*, 95:123, 1991.

[8] S.M.A.M. Bouwens, D.C. Koningsberger, V.H.J. de Beer, S.P.A. Louwers, and R. Prins. *Catal. Lett.*, 5:273, 1990.

[9] S.M.A.M. Bouwens, F.B.M. van Zon, A.M. van der Kraan, J.A.R. van Veen, V.H.J. de Beer, and D.C. Koningsberger. *J. Catal.*, accepted for publication.

[10] B. T. Carvill and L. T. Thompson. *Appl. Catal.*, 75:249, 1991.

[11] D.M. Ceperley and B.J. Alder. *Phys. Rev. Lett.*, 45:566, 1980.

[12] R. R. Chianelli, T. A. Pecoraro, T. R. Halbert, W. H. Pan, and E. I. Stiefel. *J. Catal.*, 86:226, 1984.

[13] R.R. Chianelli. In H. Heinemann and G.A. Somorjai, editors, *Catalysis and Surface Science.* Dekker, New York, 1985. Also published in Catal. Rev. -Sci Eng. 26(3,4), 1985.

[14] Moon-Gun Choi, L. M. Daniels, and R. J. Angelici. *Inorg. Chem.*, 30:3647, 1991.

[15] J. B. Danese and J. W. D. Connelly. *J. Chem. Phys.*, 61:3063, 1974.

[16] Ph. de Donato, C. Mustin, R. Benoit, and R. Erre. *Appl. Surf. Sci.*, 68:81, 1993.

[17] J. B. Diamond. *Chem. Phys. Lett.*, 20:63, 1973.

[18] A. J. Duben. *J. Phys. Chem.*, 82:348, 1978.

[19] S. Eijsbouts, V.H.J. de Beer, and R. Prins. *J. Catal.*, 109:217, 1988.

[20] S. Eijsbouts, J.J.L. Heinerman, and H.J.W. Eizerman. In *Akzo Catalyst Symposium: Hydroprocessing*, page 201. Akzo Chemie b.v., 1991.

[21] M.H. Farias, A.J. Gellman, G.A. Somorjai, R.R. Chianelli, and K.S. Liang. *Surf. Sci,*, 140:181, 1984.

[22] K. Fukui. *Top. Curr. Chem.*, 15:1, 1970.

[23] C. D. Gelatt Jr., A. R. Williams, and V. L. Moruzzi. *Phys. Rev. B*, 27:2005, 1983.

[24] U. Gelius, C.J. Allan, G. Johansson, H. Siegbahn, D.A. Allison, and K. Siegbahn. *Physica Scripta*, 3:237, 1971.

[25] U. Gelius, B. Roos, and P. Siegbahn. *Theoret. Chim. Acta (Berl.)*, 27:171, 1972.

[26] R. Gleiter and J. Spanget-Larsen. *Topics in Current Chemistry*, 86:139, 1979.

[27] O. Gunnarsson, M. Jonson, and B. I. Lundqvist. *Phys. Rev. B*, 20:3136, 1979.

[28] B. Harris, R.J.W. Le Fevre, and E.P.A. Sullivan. *J.Chem.Soc.*, page 1622, 1953.

[29] S. Harris and R.R. Chianelli. *J. Catal.*, 98:17, 1983.

[30] S. Harris and R.R. Chianelli. *Chem. Phys. Lett.*, 101:603, 1983.

[31] S. Harris and R.R. Chianelli. *J. Catal.*, 86:400, 1984.

[32] S. Harris and R.R. Chianelli. In J.B. Moffat, editor, *Theoretical Aspects of Heterogeneous Catalysis*, page 206. Van Nostrand Reinhold, New York, 1990.

[33] H. D. Hartough. *Thiophene and its Derivatives.* Interscience Publishers, 1952.

[34] L. Hedin and B.I. Lundqvist. *J. Phys. C*, 4:2064, 1971.

[35] A. Henriksson-Enflo. In S. Gronowitz, editor, *Thiophene and its Derivatives, part one.* John Wiley, 1985. The Chemistry of Heterocyclic Compounds, Vol. 44.

[36] Frank Herman, Arthur R. Williams, and Keith H. Johnson. *J. Chem. Phys.*, 61:3508, 1974.

[37] P. Hohenberg and W. Kohn. *Phys. Rev.*, 136:B 864, 1964.

[38] J. P. Huke, I. W. Parsons, and S. J. Till. *J. Chem. Phys.*, 93:1814, 1990.

[39] J. Joffre, P. Geneste, and D.A. Lerner. *J. Catal.*, 97:543, 1986.

[40] J. Joffre, D. A. Lerner, and P. Geneste. *Bull. Soc. Chim. Belg.*, 93:831, 1983.

[41] K. H. Johnson. *Advan. Quantum Chem.*, 7:143, 1972.

[42] K. H. Johnson. *Chimia*, 31(10), 1977.

[43] K. H. Johnson. In J. P. Dahl and J. Avery, editors, *Local Density Approximations in Quantum Chemistry and Solid State Physics*, page 487. Plenum, 1984.

[44] K. H. Johnson and R. P. Messmer. *J. Vac. Sci. Technol.*, 11:236, 1974.

[45] K. H. Johnson and R. P. Messmer. *Int. J. Quantum Chem.*, 10:147, 1976.

[46] K. H. Johnson and F. C. Smith. *Phys. Rev. Lett.*, 24:139, 1970.

[47] K. H. Johnson and F. C. Smith. In P. M. Marcus, J. F. Janak, and A. R. Williams, editors, *Computational Methods in Band Theory*, page 377. Plenum Press, 1971.

[48] S. Kasztelan, H. Toulhoat, J. Grimblot, and J. P. Bonnelle. *Bull. Soc. Chem. Belg.*, 89:807, 1984.

[49] S. Kasztelan, H. Toulhoat, J. Grimblot, and J. P. Bonnelle. *Appl. Catal.*, 13:127, 1984.

[50] W. Kohn. In R. M. Dreizler and J. da Provincia, editors, *Density Functional Methods in Physics*, page 1. NATO ASI Series, series B: Physics Vol. 123, Plenum, 1985.

[51] W. Kohn and L. J. Sham. *Phys. Rev.*, 140:A 1133, 1965.

[52] T. Koopmans. *Physica*, 1:104, 1934.

[53] Yeong-Jen Kuo and B. J. Tatarchuk. *J. Catal.*, 112:229, 1988.

[54] M. Lacroix, C. Mirodatos, M. Breysse, T. Decamp, and S. Yuan. In *Studies in Surface Science and Catalysis, Volume 75A: New Frontiers in Catalysis*, page 597. Proceedings of the 10th International Conference on Catalysis (July 1992, Budapest, Hungary), Elsevier Science Publishers B.V., 1993.

[55] M.J. Ledoux and B. Djellouili. *J. Catal.*, 115:580, 1989.

[56] M.J. Ledoux, O. Michaux, and G. Agostini. *J. Catal.*, 102:275, 1986.

[57] F.A. Leon. *Molecular Partitioning and Approximate Coupling Techniques in Multiple Scattering Theory.* PhD thesis, Massachusetts Institute of Technology, 1984.

[58] J. G. Lipsch and C. G. A. Schuit. *J. Catal.*, 15:174, 1969.

[59] J. G. Lipsch and G. C. A. Schuit. *J. Catal.*, 15:163, 1969.

[60] J. N. Louwen, E.T.C. Vogt, and S. Eijsbouts. To be published.

[61] S. P. A. Louwers and R. Prins. *J. Catal.*, 133:94, 1992.

[62] S. P. A. Louwers and R. Prins. *J. Catal.*, 139:525, 1993.

[63] K. Lu, Y.-J. Kuo, and B. J. Tatarchuk. *J. Catal.*, 116:373, 1989.

[64] M. C. McHenry, R. C. O'Handley, and K. H. Johnson. *Phys. Rev. B*, 35:3555, 1987.

[65] R. P. Messmer and K. H. Johnson. In *Electrolysis on Non-Metallic Surfaces*, page 67. National Bureau of Standards, 1976.

[66] R. B. Moyes. In Zoltán Paál and P. G. Menon, editors, *Hydrogen Effects in Catalysis (Chemical Industries, v. 31)*, chapter 22, page 583. Marcel Dekker, Inc., 1988.

[67] J. G. Norman. *J. Chem. Phys.*, 61:4630, 1974.

[68] J. K. Nørskov, B. S. Clausen, and H. Topsøe. *Catal. Lett.*, 13:1, 1992.

[69] P. G. Parr and W. Yang. *Density Functional Theory of Atoms and Molecules*, volume 16 of *The International Series of Monographs on Chemistry.* Oxford University Press, 1989.

[70] T. A. Pecoraro and R. R. Chianelli. *J. Catal.*, 67:430, 1981.

[71] J. P. Perdew and A. Zunger. *Phys. Rev. B*, 23:5048, 1981.

[72] R. Prins. In M. Graziani and C.N.R. Rao, editors, *Advances in Catalyst Design*, page 42. World Scientific, Singapore, 1991.

[73] R. Prins, V.H.J. de Beer, and G.A. Somorjai. *Catal. Rev. Sci. Eng.*, 31:1, 1989.

[74] Xin Qin et al. To be submitted.

[75] J. Ramirez, R. Cuevas, L. Gasque, M. Vrinat, and M. Breysse. *Appl. Catal.*, 71:351, 1991.

[76] J. Ramirez, S. Fuentes, Díaz, M. Vrinat, M. Breysse, and M. Lacroix. *Appl. Catal.*, 52:211, 1989.

[77] J.T. Roberts and C. M. Friend. *Surf. Sci.*, 186:201, 1986.

[78] J.W. Robinson, editor. *Handbook of Spectroscopy, vol. I.* CRC Press, Cleveland, 1974.

[79] C. Rong and X. Qin. In L. Guczi, F. Solymosi, and P. Tétényi, editors, *Studies in Surface Science and Catalysis, Volume 75 C: New Frontiers in Catalysis*, page 1919. Proceedings of the 10th International Congress on Catalysis (July 1992, Budapest, Hungary), Elsevier Science Publishers B.V., 1993.

[80] Chen Rong and Xin Qin. *J. Mol. Catal.*, 64:321, 1991.

[81] Chen Rong, Xin Qin, and Hu Jinglong. *J. Mol. Catal.*, 75:253, 1992.

[82] F. Ruette and E. V. Ludeña. *J. Catal.*, 67:266, 1981.

[83] P. Sabatier. *Ber. Deutsche Chem. Ges.*, 44:2001, 1911.

[84] M. Salmeron, G. A. Somorjai, A. Wold, R. R. Chianelli, and K. S. Liang. *Chem. Phys. Lett.*, 90:105, 1982.

[85] C.N. Satterfield. *Heterogeneous Catalysis in Industrial Practice.* McGraw-Hill, Inc., 2 edition, 1991.

[86] C.N. Satterfield and G.W. Roberts. *AIChE J.*, 14:159, 1968.

[87] C.N. Satterfield and S.H. Yang. *Ind. Eng. Chem., Process. Des. Dev.*, 23:11, 1984.

[88] R.D. Shannon. *Acta Cryst.*, A 32:751, 1976.

[89] A. P. Shepelin, P. H. Zhdan, V. A. Burmistrov, A. N. Startsev, and Yu I. Yermakov. *Appl. Catal.*, 11:29, 1984.

[90] J. C. Slater. *Phys. Rev.*, 81:385, 1951.

[91] J. C. Slater. *Adv. Quantum Chem.*, 6:1, 1972.

[92] J. C. Slater. *The Self-Consistent Field for Molecules and Solids*, volume 4 of *Quantum Theory of Molecules and Solids.* McGraw-Hill, 1974.

[93] J. C. Slater and K. H. Johnson. *Phys. Rev. B*, 5:844, 1972.

[94] J. C. Slater and K. H. Johnson. *Physics Today*, page 34, October 1974.

[95] T. S. Smit and K. H. Johnson. *Catal. Lett.*, submitted.

[96] T.S. Smit. Unpublished.

[97] T.S. Smit and K.H. Johnson. *J. Am. Chem. Soc.*, in preparation.

[98] T.S. Smit and K.H. Johnson. *J. Mol. Catal.*, accepted for publication.

[99] T.S. Smit and K.H. Johnson. *Chem. Phys. Lett.*, 212:525, 1993.

[100] A. N. Startsev. In L. Guczi, F. Solymosi, and P. Tétényi, editors, *Studies in Surface Science and Catlysis, Volume 75 C: New Frontiers in Catalysis*, page 1911. Proceedings of the 10th International Congress on Catalysis (July 1992, Budapest, Hungary), Elsevier Science Publishers B.V., 1993.

[101] C. Sudhakar, S. Eijsbouts, V.H.J. de Beer, and R. Prins. *Bull. Soc. Chim. Belg.*, 96:885, 1987.

[102] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry.* McGraw-Hill Publishing Company, 1982.

[103] Y. Takai, M. M. Donovan, K. H. Johnson, and G. Kalonji. *Chem. Phys. Lett.*, 159:376, 1989.

[104] Y. Takai and K. H. Johnson. To be published in *Chem. Phys. Lett.*

[105] S. J. Tauster, T. A. Pecoraro, and R. R. Chianelli. *J. Catal.*, 63:515, 1980.

[106] H. Topsøe, B. S. Clausen, R. Candia, C. Wivel, and B. Mørup. *Bull. Soc. Chem. Belg.*, 90:1189, 1981.

[107] H. Topsøe, B. S. Clausen, N. Y. Topsøe, J. Hyldtoft, and J. K. Nørskov. In *Symposium on the Mechanism of HDS/HDN Reactions*, page 683, Chicago, IL, August 1993. Division of Petroleum Chemistry, Inc., American Chemical Society.

[108] H. Topsøe and B.S. Clausen. *Catal. Rev.-Sci. Eng.*, 26:395, 1984.

[109] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, and S. Mørup. *J. Catal.*, 68:433, 1981.

[110] H. Topsøe, N. Y. Topsøe, S. Sørensen, R. Candia, B. S. Clausen, S. Kallesøe, E. Pedersen, and R. Nevald. In R. K. Grasselli and J. F. Brazdil, editors, *Solid State Chemistry in Catalysis)*, page 235, Washington, D.C., August 1983. Division of Petroleum Chemistry, Inc., American Chemical Society.

[111] J. P. R. Vissers, C. K. Groot, E. M. van Oers, V. H. J. de Beer, and R. Prins. *Bull. Soc. Chim. Belg.*, 93:813, 1984.

[112] R. J. H. Voorhoeve and J. C. M. Stuiver. *J. Catal.*, 23:228, 1971.

[113] M.L. Vrinat. *Appl. Catal.*, 6:137, 1983.

[114] R. E. Watson. *Phys. Rev.*, 111:1108, 1958.

[115] A. R. Williams and R. A. de Groot. *J. Chem. Phys.*, 63:628, 1975.

[116] C. Wivel, R. Candia, B.S. Clausen, S. Mørup, and H. Topsøe. *J. Catal.*, 68:453, 1981.

[117] Han Xu and C. M. Friend. *J. Phys. Chem*, 97:3584, 1993.

[118] M. Zdražil. *Appl. Catal.*, 4:107, 1982.

[119] M. Zdražil and J. Sedláček. *Collection Czechoslov. Chem. Commun.*, 42:3133, 1977.

[120] M. C. Zonnevylle, R. Hoffmann, and S. Harris. *Surf. Sci.*, 199:320, 1988.