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Molecular Orbital Calculations of the Hydrodesulfurization of Thiophene over a Mo–Co Catalyst

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We report molecular orbital calculations (CNDO) of the desulfurization reaction of thiophene over a molybdena catalyst. In particular, we have studied the relative stabilities of several molybdenum oxide structures ranging from MoO to a linear chain Mo_3O_{10}. The processes of hydrogenation and sulfidation of Mo_3O_{10} leading to vacancy formation were investigated. It was found that the formation of a partially sulfided active catalyst structure with a vacancy over the Mo atom was energetically allowed. Concerning the adsorption of thiophene on this catalyst model, our calculations show, however, that the C–S bond cleavage need not occur prior to ring hydrogenation and that a concurrent hydrogenation of the β carbons may also occur quite readily. Finally, the role of cobalt as a vacancy stabilizer is also discussed.

1. INTRODUCTION

There have been, over the years, numerous studies of hydrodesulfurization reaction (HDS) of thiophene and related compounds over different types of catalysts and, in particular, over cobalt–molybdenum catalysts supported on alumina. This work is reviewed in Refs. (*1–6*). The kinetics of the HDS of thiophene has been studied by several authors (*7–13*), and also recently, much work has been devoted to the characterization of molybdena catalysts and their active sites (*14–34*), as well as to the understanding of the role of supports and promoters (*35–44*). These studies have often lead to contradictory results which, as pointed out by Massoth (*6*), usually arise due to the differences in catalyst preparation.

In spite of the progress achieved in elucidating the details of this important reaction, there are still several unanswered, or partially answered, questions which have to do with the nature of the catalyst, the effect of hydrogen and sulfur in the formation of vacancies, the effect of cobalt in stabilizing these vacancies and in promoting the reaction, etc. Furthermore, with regard to the particular case of thiophene, there are questions concerning the way in which it is adsorbed, the type of hydrogenation and ring cleavage, and also the nature of the intermediates.

The first mechanism for thiophene HDS was proposed by Griffith, *et al.* (*45*), who assumed a two-point adsorption of thiophene on adjacent molybdenum sites. Other early work postulated a hydrogenation of thiophene to tetrahydrothiophene as a step which precedes the cleavage of the C–S bond (*46*). In the work of Owens and Amberg (*8, 9*), Kolboe and Amberg (*47*), and Desikan and Amberg (*48, 49*), evidence was advanced in support of the cleavage of the C–S bond as the initial step of a single-site adsorption mechanism. In their view, the formation of butadiene is a necessary step; a subsequent hydrogenation of this molecule and isomerization of the butenes is assumed in order to explain the appearance of 1-butene, *cis*- and *trans*-2-butene, butane, and hydrogen sulfide as the primary products.

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In the model of Lipsch and Schuit (*17*) a description of the catalyst is given in terms of a two-dimensional monolayer. Vacancies are formed by reduction by H_2/H_2S; these vacancies, consisting of Mo(IV), are the active sites for thiophene adsorption. The reaction proceeds via a hydrogenation of the α carbon, a cleavage of the C–S bond, and the formation of butadiene as an intermediate. Hydrogenation of the sulfur initially attached to the vacancy frees H_2S and regenerates the catalyst. According to this model, the active catalyst is a molybdenum oxysulfide, where the ratio S/Mo tends to 1. Addition of more sulfur leads to a breakup of the monolayer configuration.

Massoth (*20, 50*) has proposed the monolayer model proper by modifying the model of Lipsch and Schuit. The oxidic catalyst is assumed to be made up of one-dimensional molybdena chains attached to the alumina support. This model allows for a ratio S/Mo higher than 1, a fact which is in closer agreement with experiment. It also introduces refinements in mechanistic details such as, for example, allowing for the presence of Mo(V). According to Massoth, when the catalyst is sulfided it retains its monolayer structure. This idea differs from that advocated in the intercalation model of de Beer *et al.* (*24*), where, upon sulfidation, the monolayer structure is broken up and crystallites of MoS_2 are formed. These crystallites are then the active catalysts in the HDS reaction.

Still another model has been recently advanced by Delmon (*51*), where catalytic activity is explained by postulating a "contact synergism" between phases of MoS_2 and Co_9S_8.

The actual catalyst is probably a highly complicated system and since a number of variables in the preparation process are neither well controlled nor well understood, there might be in fact a multiplicity of catalysts. The results of HDS studies reflect, therefore, particular characteristics of these catalysts; for this reason, it becomes rather difficult to assess the particular effect of a given catalyst structure upon the HDS process. In the actual catalyst several structures might coexist simultaneously and at different conditions their preponderance might change.

Bearing in mind the existence of this plurality of models and interpretations arising from a large body of experimental data and also the difficulty in obtaining unequivocal data, for the reasons discussed above, we have considered that a theoretical study of very simple but well-defined systems by means of the molecular orbital method, could be of some use.

In the present work we report CNDO calculations for the reaction of thiophene over a molybdena catalyst. We have studied four main aspects of this reaction: (a) the relative stabilities of several possible structures of molybdenum oxide ranging from MoO to Mo_3O_{10}; (b) the process of hydrogenation and sulfiding leading to vacancy formation; (c) the adsorption of thiophene over a model oxysulfide catalyst, devoting particular attention to the interaction of the liable hydrogen with the C–S bond of thiophene; and (d) the possible role of cobalt with respect to the stabilization of the model catalyst.

Recently, two other applications of molecular orbital methods to the HDS reaction have been reported (*54, 55*). The present work differs both in scope and intention from these previous studies in that we have considered the determination of a workable model of the catalyst to be of crucial importance and have devoted, therefore, some effort to the calculation of several of its possible structures. In particular, we have studied the process of vacancy formation produced by hydrogenation and sulfiding on a model catalyst, as this process has been postulated in various models as preliminary to thiophene adsorption. In addition, since we have made no a priori assumptions concerning the cleavage or formation of bonds, we have examined in this work the effect of the liable hydrogen (belonging to the catalyst) on the carbon and sulfur atoms in thiophene.

In Section II we discuss briefly the modified version of the CNDO program which we have developed for the purpose of handling calculations of catalytic systems. In Section III we report some pertinent details of the calculations dealing with the four main aspects listed above and also discuss some of the relevant results.

II. METHODS

The usual molecular quantum chemistry methods employed in the description of catalytic processes are the Extended Hückel (EH) method, the Complete Neglect of Differential Overlap (CNDO) method with its many modifications, and the Self-Consistent χ-α scattering theory and ab initio methods. Recent reviews of these methods are given in articles by Messmer and Salahub (*52a*), Blyholder (*52b*), and Baetzold (*53*).

In the present work, some preliminary calculations were performed using the EH method. The results were unsatisfactory with regard to convergence and stability criteria, notwithstanding the introduction of corrections on the ionic character (*56*) and the repulsive energies of atoms (*57*). Although the EH method seems to work well for adsorption on pure metal surfaces it is not adequate when the catalyst is composed of a collection of different atoms, as it tends to build up unrealistic charges. For this reason, the use of a more stable method, such as the CNDO, was preferred in this work.

We have developed, based on the Beveridge and Pople version (*58*) of the CNDO, a versatile program which can handle any atom with *s*, *p*, and *d* valence orbitals, regardless of their principal quantum numbers. This was necessary since we are interested in calculating molecules containing second-row transition atoms such as Mo. In addition, the program may deal with different radial exponents for *s*, *p*, and *d* orbitals belonging to the same shell. This individual treatment of individual orbitals has proven to be quite useful (*52b*).

In order to circumvent the convergence difficulties which are frequently encountered in the applications of the CNDO method to clusters, we have adopted the convergence criterion advanced by Baetzold (*59*) and Blyholder (*60*), which basically involves small modifications of the density matrix from one iteration to the next. Also, in order to accelerate convergence for very large systems, we have resorted to the strategy of subdividing a complicated molecule into molecular fragments (adsorbed molecule and catalyst, for example) which are calculated and brought to convergence separately. These results serve then as input for the calculation of the combined system, where the initial Hamiltonian matrix is constructed as follows:

$$\begin{bmatrix} A & AB \\ BA & B \end{bmatrix}.$$

The blocks A and B are the Hamiltonian matrices of the fragments (previously brought to convergence); the interaction blocks AB and BA are computed for the initial iteration by the formula

$$H_{ij}{}^{AB} = \tfrac{1}{2} S_{ij}{}^{AB} \left(H_{ii}{}^{A} + H_{jj}{}^{B}\right).$$

For the subsequent iterations the total matrix is constructed in the usual way.

III. COMPUTATIONS AND RESULTS

A. Choice of Parameters

For atoms other than Mo, we have used the ionization potentials, electron affinities, and β's reported in the literature (*58, 64, 65*). For Mo, the only reported values for valence state ionization potentials are those estimated by Lohr and Lipscomb (*63*). As these values are only rough approximations (the same values $Is = 8.0$ eV, $Ip = 7.0$ eV, and $Id = 9.0$ eV are used by these authors for Cr, Mo, and W), we have recalculated these quantities using spectroscopic data (*61*). The incompleteness of the spectra prevented us, however, from obtaining definitive values for these quantities and at best we can only claim to have made educated guesses. Whenever possible, the missing lines for Mo were assigned by linear interpolation using the spectrum of Cr (*62*) as reference. Our estimated values are: $Is = 6.86$ eV, $Ip = 2.14$ eV, and $Id = 8.35$ eV. These values for Is and Id are in good agreement with those of Lohr and Lipscomb and also with the one-electron SCF energies $\epsilon_{5s} = 6.04$ eV and $\epsilon_{4d} = 9.71$ eV calculated by Clementi and Roetti (*77*) for the $5s^2 4d^6$ (^7S) atomic configuration for Mo. Unfortunately there is no available ϵ_{5p} value for comparison. The value of $I_p = 2.14$ eV, was estimated by assigning the 796 missing lines (out of 1512 possible ones) in the spectrum of the $4d^5 5p$ configuration of Mo, a value half-way between the average value for the 716 known lines and the ionization potential for this configuration. In this sense, our estimated value may be considered as a lower bound to Ip.

For the electron affinity As of Mo, we adopted the experimental value $As = 1.0$ eV (*66*). The values of Ap and Ad were estimated in the usual way (*58*) using a linear extrapolation for Tc^0, Ru^+, and Rh^{2+}. The average values of electron affinities and ionization potentials are given in Table 1. The screening parameters for the atomic functions were determined by Slater's rules.

It is well known that in a semiempirical method, such as the CNDO, the choice of parameters is of crucial importance and that the validity of the results is highly dependent upon the type of parametrization used. In the present calculations we have searched for the optimal value of the parameter β for Mo so that at the average experimental distance (1.67 Å) for the MoO bond (*67*), the experimental bond energy (*68*) of 145 kcal/mole (0.23 a.u.) is reproduced. This optimal value for β is -5.85. In order to have an independent check, we have also calculated MoO using Lohr and Lipscomb's parameters. For a $\beta = -3.00$, we obtained the same dissociation energy (0.23 a.u.) and although there was a small shift in the orbital energies, their relative ordering remained unchanged and the differences between the levels were almost the same. For example, the difference between the HOMO and the LUMO for Lohr and Lipscomb parameters was 0.362 a.u., as compared to 0.366 for our parameters.

TABLE 1

Values of $(Im + Am)/2$ (in eV)

	H	C	O	S	Co	Mo
s	7.176	14.051	25.390	17.650	4.170	3.93
p		5.572	9.111	6.989	1.160	0.71
d				0.713	5.839	4.53

It has been determined experimentally (*68*) that in Mo compounds containing several oxygen atoms, the energy of each MoO bond remains fairly constant and has approximately the same value as for an isolated MoO molecule. In the present calculations, we observe (see Table 2) a constancy in this bond energy at approximately 0.12 a.u. when we go from MoO_4 to Mo_2O_7 and to Mo_3O_{10}. Although this value differs from that of the isolated MoO, the constancy of the bond energies is assumed as significant in validating the present method of calculation, particularly since we are only interested in relative energies when these oxidic structures undergo reactions with H_2, H_2S, and thiophene.

B. Molecular Coordinates

The chain structure (*69*) of bulk molybdenum oxide is described in Fig. 1; the distances and angles are also given. Only the angles of the four nearest oxygens (for tetrahedral symmetry) are indicated. In Fig. 2, the molecules $Mo_3O_{10}H_3$ and $Mo_3O_7S_3H_6C_4$ are shown. The numbers are used for indexing the atoms and are referred to throughout this paper. In Fig. 3, schematic drawings of the intervening structures are presented. Only the atoms

TABLE 2

Charge Densities and Energies per Bond of Molybdenum Oxide Model Catalyst Molecules

	MoO	MoO_2	MoO_3	MoO_4	Mo_2O_7	Mo_3O_{10}
O(1)	−0.32	+0.04	−0.19	−0.05	−0.09	−0.10
Mo(2)	+0.32	+0.14	+0.87	+0.60	+0.60	+0.66
O(3)		−0.18	−0.49	−0.37	−0.30	−0.36
O(4)				−0.13	−0.15	−0.16
O(5)			−0.19	−0.05	−0.13	−0.16
Mo(6)					+0.60	+0.86
O(7)					−0.30	−0.43
O(8)					−0.15	−0.18
O(9)					−0.09	−0.16
Mo(10)						+0.66
O(11)						−0.36
O(12)						−0.16
O(13)						−0.10
Energy per Bond (a.u.)	−0.23	−0.16	−0.14	−0.11	−0.12	−0.12

above the molybdenum layer are shown and the lower part of the molecule is just indicated by a horizontal line. In all these calculations, whenever possible, the coordinates were obtained from experimentally determined bond distances and angles (*70–73*).

C. The Molybdenum Oxide Precatalyst

In this section we calculate some of the possible Mo_nO_m compounds which may be considered as precursors to the active catalyst. There seems to be agreement (*6*) on the fact that the active oxidic catalyst on

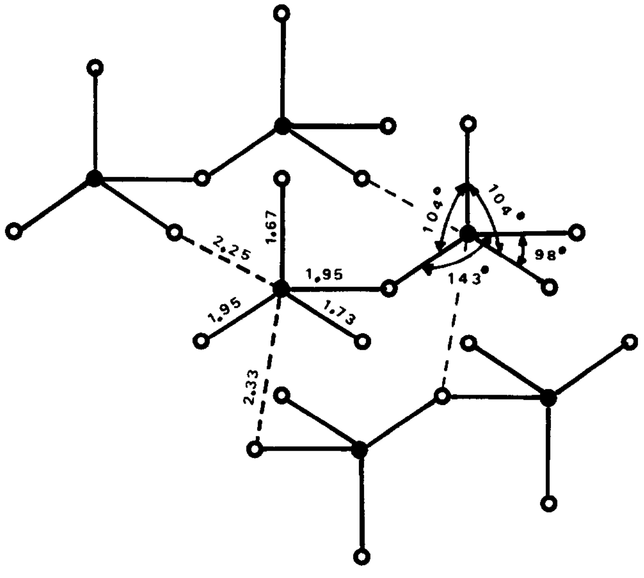

FIG. 1. Chain structure of molybdenum oxide.

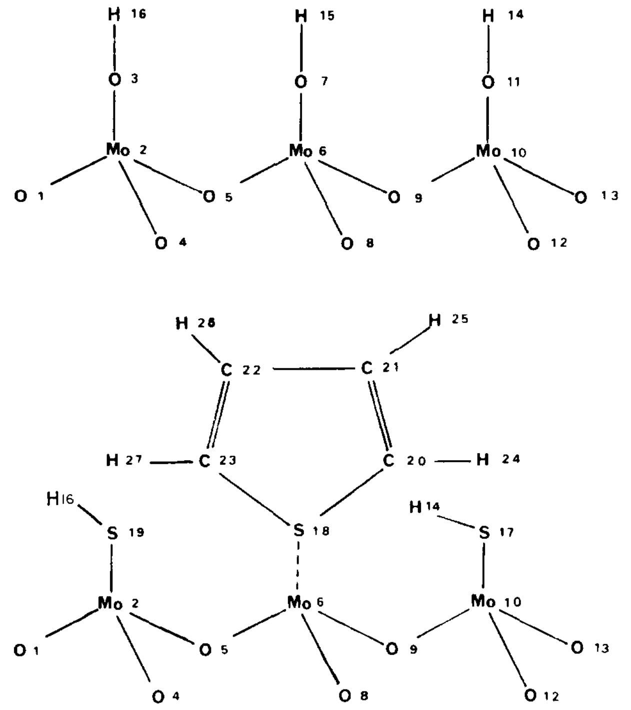

FIG. 2. Labeling of atoms in some characteristic structures.

the alumina surface is neither bulk MoO_4, nor $Al_2(MoO_4)_3$; there is strong evidence that it occurs as a monolayer. Although Lipsch and Schuit (*17*) and Schuit and Gates (*5*) have proposed a two-dimensional monolayer model, a number of authors have proposed instead a one-dimensional model. Thus, Ratnasamy *et al.* (*23, 33*) suggest that a significant portion of the molybdena occurs as one-dimensional chains. Medena *et al.* (*34*) have found MoO_4 tetrahedra at low coverages and suggest the presence of polymeric molybdate structures (almost tetrahedral) at higher coverages. Also, in Massoth's model (*20, 50*), the catalyst is in the form of a one-dimensional monolayer, where the individual units are molybdena tetrahedra.

Bulk molybdenum may be viewed as a collection of interacting parallel polymer chains (*69*), where the Mo atoms are found in a transitional state between octahedral and tetrahedral coordination. For the reasons discussed above, we have considered the oxidic precatalyst to be formed by one of these chains, which effectively, due to the absence of neighboring oxygen atoms from other chains (see Fig. 1), gives a tetrahedral coordination to the molybdenum atoms. We have calculated the following molecules with one, two, and three molybdenum atoms: MoO, MoO_2, MoO_3, MoO_4, Mo_2O_7, and Mo_3O_{10}. Both for Mo_2O_7 and Mo_3O_{10} we have considered bridged structures of the type Mo–O–Mo with terminal Mo=O bonds; evidence for the existence of these structures has been advanced by Brown, *et al.* (*29*). The angles and bond lengths have been taken to be those of the polymeric chains in bulk MoO_3 (Fig. 1).

We have not taken into account the effect of the support as there is evidence that its main action consists in providing the framework for the formation of the monolayer (*6*). Besides, including the support will unduly increase the size of the catalyst model.

The energies, bond orders, and charge

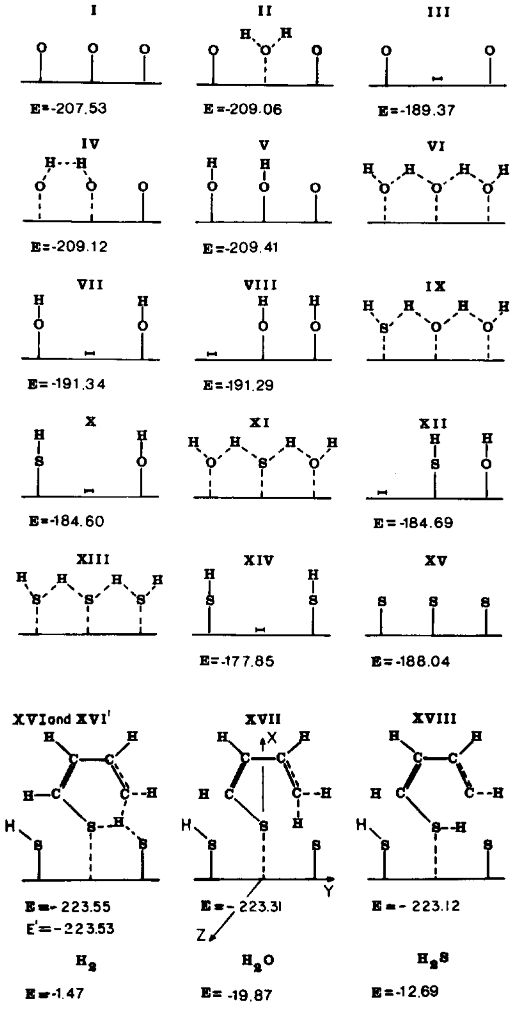

FIG. 3. Schematic representation and CNDO energies (in a.u.) of participating structures.

densities for the catalyst model molecules MoO_4, Mo_2O_7, and Mo_3O_{10} are given in Tables 2 and 3. Although MoO, MoO_2, and MoO_3 do not possess the appropriate tetrahedral symmetry, for the sake of completeness, their corresponding values are also listed.

From these results we observe, first of all, that the average energies per bond remain almost constant when we go from MoO_4 to Mo_3O_{10}. There are, however, important changes in the net charges of the Mo atoms and in the bond orders of the Mo–O bonds. The positive charge in Mo increases from $+0.60$ in MoO_4 and Mo_2O_7 to $+0.66$ for the lateral Mo in Mo_3O_{10} and to $+0.86$ for the central Mo. The negative charge buildup on the oxygens above the chain is also greatest for Mo_3O_{10}, which has a value of -0.43 for O(7) as opposed to -0.30 for O(7) and O(3) in Mo_2O_7 and -0.37 for O(3) in MoO_4. Furthermore, in Mo_3O_{10}, the bond orders Mo(6)–O(7) and Mo(6)–O(8) are the smallest; hence these bonds may be easily broken and as a consequence the most liable oxygen atoms are O(7) and O(8). The charge on O(8) is -0.18; this charge is considerably smaller than the charge on O(7)(-0.43). One may infer, therefore, that O(7) is the most likely position for an electrophilic attack in order to produce a rupture of the Mo–O bond. In Mo_2O_7, on the other hand, the smallest bond orders correspond to the bridged oxygen O(5); this implies that the weakest bonds are those of the Mo–O–Mo bridge. Presumably, a hydrogenation reaction could fraction this molecule at one of these bonds. The molecule NoO_4 shows a low bond order for Mo(2)–O(4).

In this work we have adopted Mo_3O_{10} as a convenient and simple model for the oxidic precatalyst (structure (I) in Fig. 3). This is also the minimal chain structure compatible with the mechanism for thiophene adsorption, such as that proposed, for example, by Lipsch and Schuit (*17*). We would like to stress the fact that this work is merely a preliminary attempt to understand certain aspects of the HDS reaction from a theoretical standpoint. There are, obviously, a number of other oxidic precatalysts compatible with the formation of, for example, MoS_2 crystallites, which in turn, as pointed out by a considerable body of experimental evidence, are quite likely to be the active species for HDS. Also, the examination of other model catalysts made up by linear chains of molybdena tetrahedra anchored on the alumina surface (*20*) was not carried out in the present work. As the alumina support would have to be included, such a model is beyond the scope of

TABLE 3

Bond Orders for Molybdenum Oxide Model Catalyst Molecules

	MoO	MoO_2	MoO_3	MoO_4	Mo_2O_7	Mo_3O_{10}
Mo(2)–O(1)	4.77	5.55	4.77	4.57	4.64	4.71
Mo(2)–O(3)		5.13	4.74	4.86	5.16	5.12
Mo(2)–O(4)				4.40	4.79	4.75
Mo(2)–O(5)			4.77	4.57	4.57	4.92
Mo(6)–O(5)					4.57	5.01
Mo(6)–O(7)					5.16	4.60
Mo(6)–O(8)					4.79	4.49
Mo(6)–O(9)					4.64	5.01
Mo(10)–O(9)						4.92
Mo(10)–O(11)						5.12
Mo(10)–O(12)						4.75
Mo(10)–O(13)						4.71

our present calculations, which are restricted to rather simple and well-defined systems.

D. Hydrogenation and Vacancy Formation

In what follows we consider the hydrogenation of Mo_3O_{10} (structure (I) in Fig. 3). A vacancy formation over a Mo atom is a prerequisite in the monolayer model (*6*) for the HDS reaction to take place. This process of vacancy formation may occur in two different ways. In the first, there could be a direct attack of the hydrogen molecule on the most electronegative oxygen, O(7) in (I), with a subsequent elimination of H_2O. This would proceed according to the reaction

$$(\text{I}) + H_2 \rightarrow (\text{II}) \rightarrow (\text{III}) + H_2O, \quad \Delta E = -0.24 \text{ a.u.} \quad (1)$$

The value of ΔE was obtained by subtracting the computed energies of the reactants (I) and H_2 from those of the products (III) and H_2O. Structure (II) (see Fig. 3) corresponds to a transition state. In the second, the hydrogen molecule might attack two adjacent oxygen atoms giving rise to an intermediate structure (IV) which in turn becomes (V):

$$(\text{I}) + H_2 \rightarrow (\text{IV}) \rightarrow (\text{V}), \quad \Delta E = -0.41 \text{ a.u.} \quad (2)$$

From purely energetic considerations, it seems that hydrogenation would proceed more readily according to reaction (2). Actually, we could have two types of vacancies; one which occurs on the central Mo atom and which implies a reaction

$$(\text{V}) + H_2 \rightarrow (\text{VI}) \rightarrow (\text{VII}) + H_2O, \quad \Delta E = -0.74 \text{ a.u.}, \quad (3)$$

and a second one on a lateral Mo,

$$(\text{V}) + H_2 \rightarrow (\text{VI}) \rightarrow (\text{VIII}) + H_2O, \quad \Delta E = -0.69 \text{ a.u.} \quad (4)$$

We observe that both reactions would proceed through essentially the same transition state. From the ΔE values we may conclude that structure (VII) with the central vacancy is slightly more stable than structure (VIII), with the lateral vacancy. The energy difference between structures (VII) and (VIII) is sufficiently small so that the vacancy could easily be shifted between lateral and central sites. This implies that in a real catalyst one could expect some degree of mobility among the vacancy sites.

E. Sulfidation

When bulk MoO_3 is sulfided with a mixture of H_2/H_2S, there occurs a rapid conversion of MoO_3 to MoO_2 which in turn is slowly transformed into MoS_2 (*74*). The presence of molybdenum oxysulfide phases has not been detected in this case.

When the oxidic catalyst is sulfided, the situation is, however, not so simple. In the first place, the sulfur level is dependent upon the sulfidation temperature. In the second place, there seems to be some disagreement as to whether the sulfiding is complete or not with respect to MoS_2 formation, or to Co_9S_8, also, when cobalt is present (*6*). According to de Beer *et al.*, the sulfiding is complete and the apparent lower sulfiding value is the result of contamination by air. On the other hand, Massoth (*6*) has reexamined this question and suggests that the evidence advanced by de Beer *et al.* may be explained by the presence of residual adsorbed H_2S and that the high sulfur values reported by these authors (*24*) might not accurately represent the actual sulfide content of the catalyst. In Massoth's opinion (*6*), "the sulfided catalyst either consists of a mixed surface oxysulfide species or some bulk MoS_2 and another oxysulfide species."

The formation of molecular MoS_2 as the active form of the sulfided catalyst has been proposed by several authors (*14, 19, 24*) and the presence of small MoS_2 crystals has been advocated by others (*18, 25, 26*). Although XPS data (*31*) may be used in support of the contention that a separate MoS_2 phase is formed, it has been pointed out that this interpretation may not be sufficiently clear cut to rule out the presence of molybdenum oxysulfides (*28*).

In the present work we have considered the sulfidation of the oxidic precatalyst molecule Mo_3O_{10} leading to an oxysulfide. We believe that in view of all the experimental difficulties which arise in the elucidation of the nature of the catalyst, the study of this simple molecule might be enlightening. This represents, however, only one of the many sulfidation processes which one may consider. Another interesting process is, for example, the sulfidation of Massoth's monolayer catalyst. But as mentioned in the previous section, such a calculation would require the simulation of the alumina support and of the alumina tetrahedra anchored on its surface.

In order for sulfidation of the Mo_3O_{10} molecule to take place, a vacancy formation should have occurred already in the hydrogenated molybdenum oxide precatalyst. We can consider the process of sulfidation as proceeding through the reactions

$$(\mathrm{VIII}) + H_2S \rightarrow (\mathrm{IX}) \rightarrow (\mathrm{X}) + H_2O, \quad \Delta E = -0.49 \text{ a.u.}, \quad (5)$$

and

$$(\mathrm{VII}) + H_2S \rightarrow (\mathrm{XI}) \rightarrow (\mathrm{XII}) + H_2O, \quad \Delta E = -0.53 \text{ a.u.} \quad (6)$$

The difference in energy between these two reactions is extremely small and it reflects the fact that the vacancies in these precursors can be shifted easily. The species (X) and (XII) can undergo further sulfidation. For example, adding two H_2S molecules to structure (X) we obtain

$$(\mathrm{X}) + 2H_2S \rightarrow (\mathrm{XIII}) + H_2O. \quad (7)$$

The intermediate species (XIII) can lead by elimination of an H_2S molecule to the formation of a sulfided catalyst with either a lateral or a central vacancy. The interconvertibility between these two structures allows us to select, because of steric reasons, the central vacancy structure (XIV) as the active form of the catalyst for thiophene adsorption. Hence, we can write the sulfuration reaction as

$$(\mathrm{X}) + 2H_2S \rightarrow (\mathrm{XIV}) + H_2S + H_2O, \quad \Delta E = -0.28 \text{ a.u.}, \quad (8)$$

and

$$(\mathrm{XII}) + 2H_2S \rightarrow (\mathrm{XIV}) + H_2S + H_2O, \quad \Delta E = -0.19 \text{ a.u.} \quad (9)$$

The discussion, given above, for hydrogenation, vacancy formation, and sulfuration starts from an assumed Mo_3O_{10} molecule. One could consider, however, other possibilities such as an oxide which has been partially sulfided. For example, a precatalyst molecule (**XV**) might undergo hydrogenation in order to form an active catalyst (**XIV**), according to the reaction

$$(\mathbf{XV}) + 2H_2 \rightarrow (\mathbf{XIV}) + H_2S, \quad \Delta E = +0.44 \text{ a.u.} \quad (10)$$

The energy difference is positive and this endothermic reaction would probably not be favored.

In conclusion, the present calculations show that the sulfidation of a vacancy holding oxidic catalyst is allowed energetically. Hence, a possible oxysulfide species in the active catalyst is structure (**XIV**).

F. Reaction of Thiophene on the Active Catalyst

In this section we consider the adsorption of thiophene over the vacancy on the central Mo atom of structure (**XIV**). This is the crucial step of the hydrodesulfurization reaction and its complete theoretical analysis would require a number of lengthy calculations to study the nature of the transition states and of the ensuing products. Due to the large size of the thiophene–catalyst complex, this type of study is computationally prohibitive, even at the CNDO level. Furthermore, because of the very nature of the molecular orbital approximation, these results would not be conclusive.

There are, however, several important questions, related for example to the model of Lipsch and Schuit, which may be answered by a limited number of calculations. The first has to do with whether there is a cleavage of the C–S bond of thiophene upon hydrogenation of the adsorbed thiophene by the liable hydrogens of the catalyst. The cleavage of both C–S bonds is assumed in this model, so that butadiene appears as an intermediate product. A second question deals with whether the liable hydrogen attacks the S or the C atom in thiophene. After the hydrogenation by the first liable hydrogen has occurred, one may ask which is the most likely site for a second hydrogenation and whether this reaction proceeds by the reaction of the remaining liable hydrogen or not. According to the model of Lipsch and Schuit, the second liable hydrogen attacks the α carbon atom in thiophene. This reaction leads to the cleavage of the second C–S bond; it forms butadiene and leaves a sulfided catalyst from which the active catalyst is regenerated by further hydrogenation and elimination of H_2S.

In the present calculations we endeavor to answer these specific questions concerning the plausibility of the mechamistic scheme of the model of Lipsch and Schuit.

In order to study the adsorption process we have performed calculations for four structures. The first two (**XVI**) and (**XVI′**) represent the simultaneous interaction of H(14) with both S(18) and C(20). The third (**XVII**) represents the breaking of the S(18)–C(20) bond caused by an attack of H(14) on the C(20) carbon atom of thiophene. The last (**XVIII**) represents the breaking of the S(18)–C(20) bond through the interaction of H(14) with the sulfur atom S(18) of thiophene. Starting from a basic configuration with the thiophene molecule on the x–y plane placed above the catalyst at a distance $R(S(18)\text{–}Mo(6)) = 2.5$ Å (*75*) and the H(14) also located on the x–y plane symmetrical to H(24) (with respect to the axis that goes through C(21) and C(20)), the four structures are generated by means of rotations about the C(22)–C(21) axis, where only the atoms H(25), C(20), H(24), and H(14) are moved. Thus, structure (**XVI**) is obtained by a rotation of 27.3°. At this angle, the distance $R(S(18)\text{–}H(14)) = 1.334$ Å. Hence, in structure (**XVI**), the hydrogen H(14) is placed at 1.334 Å from S(18) and at 1.078 Å from C(20); these distances correspond precisely to those of a S–H bond in H_2S and of a C–H bond in thiophene. The angle Mo(6)–S(18)–H(14) is 111°. Structure (**XVI′**) is generated by a rotation of 42.05°. At this angle, the distance R(S(18)–H(14)) = 1.834 Å and corresponds to an increment of 0.5 Å with respect to the S–H distance in H_2S, whereas the distance R(C(20)–H(14)) remains that of the C–H bond in thiophene. As can be seen in Table 4, both structures (XVI) and (XVI′) have almost the same energy: −223.55 and −223.53 a.u., respectively. Although R(S(18)–H(14)) in (XVI′) is elongated with respect to (XVI), the bond order (1.15) is still too large to assume that this structure corresponds to a cleavage of the S(18)–C(20) bond with the concomitant migration of H(14) attached to C(20). Structure (XVI′) may be regarded also as an intermediate case where H(14) is interacting strongly with both S(18) and C(20).

In structure (XVII), which is generated by a rotation of 56.6°, the distance R(S(18)–H(14)) = 2.334 Å. The H(14) is in this case sufficiently removed from the thiophene sulfur atom. The bond order for S(18)–H(14) diminishes to 0.76, and at the same time the bond order for S(18)–Mo(6) increases to 5.67. Clearly, for this structure (XVII), there has occurred a cleavage for the S(18)–C(20) bond; the bond order is, in this case, 3.48 as compared to 4.88 and 4.62 for (XVI) and (XVI′), respectively. The total energy for structure (XVII) is −223.31 a.u. This value is 0.22 a.u. above that of (XVI′) and 0.24 a.u. above that of (XVI). Energetically, therefore, structure (XVII) is less stable than both (XVI) and (XVI′).

Finally, structure (XVIII) is obtained from structure (XVI) by an additional rotation of 40.0° which displaces only the atoms H(25), C(20), and H(24), leaving H(14) attached to S(18); at this point, the distance R(H(14)–C(20)) increases by 0.5 Å and becomes 1.578 Å. In structure (XVIII), the distance R(S(18)–H(14)) is the same as R_{SH} in H_2S. In Table 4 we see that in structure (XVIII) the bond order for C(20)–H(14) has decreased to 0.68; also, the bond order for S(18)–C(20) has gone down to 3.62. Clearly then, this structure represents the cleavage of the S–C bond caused by the attack of H(14) on the sulfur atom of thiophene. The energy for this structure is −223.12 a.u. This is by far the most unstable situation as it lies 0.43 a.u. above structure (XVI).

TABLE 4

Results for the Thiophene-Catalyst Adsorption Complexes

Bond order	XVI	XVI′	XVII	XVIII
S(18)–H(14)	1.54	1.15	0.76	2.04
C(20)–H(14)	1.40	1.63	1.75	0.68
C(20)–H(24)	1.33	1.37	1.41	1.40
S(18)–Mo(6)	4.94	5.34	5.67	4.84
S(18)–C(20)	4.88	4.62	3.48	3.62
Energy (a.u.)	−223.55	−223.53	−223.31	−223.12
B.E. (a.u.)	−10.86	−10.84	−10.63	−10.44

TABLE 5

LUMO Coefficients and Net Charges For Structure (XVI)

Atom	S(18)	C(20)	C(21)	C(22)	C(23)
p_z	0.1555	0.2671	0.1528	0.2712	0.1683
Net charge	−1.31	+0.17	+0.10	+0.16	+0.19

We may conclude from these calculations that the initial attack of the labile hydrogen H(14) on the adsorbed thiophene molecule does not lead to the breaking of the S–C bond with the hydrogen atom being transferred either to the C or S atoms but, rather, that it proceeds through intermediate structures, where the hydrogen is shared by both atoms.

In order to determine the most plausible site for the subsequent hydrogenation of structure (XVI) we have made use of Fukui's frontier electron theory (*76*). According to Fukui, the reactivity indexes for a nucleophilic reaction are determined by the size of the LUMO coefficients. In Table 5 we list the values of the p_z coefficients on the thiophene ring for structure (XVI) along with the net charges on the atoms. As we can see from this table, only the carbon atoms have a net positive charge, and are therefore likely sites for a nucleophilic attack. In addition, the largest coefficient

(0.2712) corresponds to C(22), although the next largest coefficient (0.2671) is that of C(20). This implies that after the initial attack of H(14) on the S(18)–C(20) bond, the reaction may proceed via the hydrogenation of atoms C(20) and C(22), in which case, a partial saturation of the olefin could occur before the dissociation actually takes place. Such a reaction would lead to partially saturated olefins and it would rule out the production of butadiene. In conclusion, the present calculations suggest that the reaction mechanism is much more complicated than what is proposed in the model of Lipsch and Schuit.

In the present work we have assumed that the thiophene approaches the catalyst on the x–y plane and that the adsorption involves the interaction of the sulfur atom with the Mo vacancy. There is the possibility that the thiophene might not interact with the vacancy through its sulfur atom but rather through the whole ring via its π orbital. In fact, the possibility of such an attack has been studied theoretically in a recent calculation (*54*), where the catalyst was simulated by a simple electron acceptor center. It is shown, for this case, that the interaction takes place primarily through the S atom.

We did not investigate the possibility of π ring interaction using our more realistic model for the catalyst because it seems more likely, from electrostatic and energetic considerations, that the sulfur atom would be directly joined to the Mo vacancy. The reason is that the charge on the sulfur atom in an isolated thiophene is −0.98 (Table 6). This is the only negative charge; all other atoms show a small positive charge. At the same time, the positive charge buildup on the Mo vacancy for the active catalyst (**XIV**) is +0.76 (Table 6). This is again, by far, the largest positive charge on the catalyst. This electrostatic view is strengthened by the fact that the HOMO of thiophene is almost entirely made up by the $p_z(0.85)$ and $d_{xz}(0.13)$ orbitals of sulfur. Since the adsorption may be viewed as a charge transfer from the HOMO of thiophene to the LUMO of the catalyst, it then follows that most of the charge would have to come from the sulfur atom and not from the ring π orbital.

G. Effect of Cobalt

One of the most challenging questions concerning the HDS reaction is the role of cobalt as a promoter. It is well known that the addition of small amounts of Co to the MoO_3–Al_2O_3 catalyst has a marked effect on the HDS efficiency. As yet there is no unequivocal explanation, although several theories have been proposed (*6*). The difficulty stems from the fact that the catalyst is not well known and, therefore, only conjectures can be made regarding its interaction with cobalt.

Basically, the role of cobalt has been explained either by assuming that the active catalyst is MoS_2 and that Co forms an intercalation compound (*24*), by postulating a synergetic action between the active catalyst and Co^0 and Co^{2+}.
monolayer model (*23*) by assuming that there is some interaction between the catalyst and Co° and Co^{2+}.

It is clear that compounds such as $CoMoO_4$ are not responsible for HDS activ-

TABLE 6

Charge Densities of Catalyst (**XIV**) And Thiophene (Non-interacting)[a]

S(18) = +0.98	C(20) = +0.10	H(24) = +0.15	C(21) = +0.19
H(25) = +0.05	Mo(6) = +0.76	S(17) = −0.53	H(14) = +0.08
Mo(10) = +0.51	O(9) = −0.35	O(8) = −0.08	O(12) = −0.08

[a] See Fig. 2 for atom labeling.

ity. On the other hand there is very little in the literature that provides a detailed explanation in terms of the actual interaction of Co with the catalyst which could explain the increase in HDS activity. The presence of Co^{2+} ions has been detected and there is experimental evidence for their migration from and to the sublayers (*24*) and for their localization in octahedral sites.

In trying to explain the promoter role of cobalt in the present work, we carried out some preliminary calculations, placing the cobalt in positions where it forms oxygen bridges with the Mo vacancy. All these calculations were performed with respect to structure (XIV). It was observed that the presence of Co had a negligible effect on the catalyst (XIV) when it was bridged through oxygens. Another type of interaction, which may occur because of the mobility of the Co^{2+} ions was then considered. Cobalt was placed in the position of one of the oxygen atoms surrounding the Mo vacancy. In particular, we have considered the site lying underneath the vacancy (see Fig. 1) which is an empty site in our catalyst model. Since the molybdenum is only tetrahedrally bound to the oxygen atoms, the empty oxygen site belongs to the adjacent molybdenum oxide chain and is an octahedral site with respect to the Mo vacancy. In addition, we have assumed that the cobalt occurs as a sulfide. The model for the Co–catalyst complex is given in Fig. 4 and is labeled as structure (XIX). The distance Mo–Co is 2.33 Å; this is precisely the Mo–O distance given in Fig. 1. The distance Co–S is 2.41 Å (*75*). Since the sulfur atom is then accessible to hydrogenation, we have assumed in our model that there is a hydrogen atom on the upper layer attached to this sulfur.

XIX

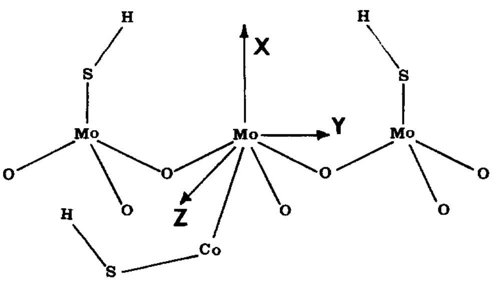

FIG. 4. Interaction of cobalt with reactive catalyst.

TABLE 7

Effect of Co On the Reactive Catalyst

	(XIV)	(XIX)
HOMO	−0.47	−0.52
LUMO	−0.18	−0.29
E	−177.85	−217.72
B.E.	−3.15	−6.58
Charge on Mo(6)	+0.76	+0.46
LUMO Coefficients on Vacancy		
s	0.0004	−0.1833
p_x	0.0005	−0.2229
p_y	−0.0887	0.0210
p_z	−0.0002	−0.0306
d_{z^2}	−0.0009	0.1880
d_{xz}	−0.0013	−0.1677
d_{yz}	0.1087	−0.0222
$d_{x^2-y^2}$	0.0	−0.3844
d_{xy}	−0.1726	0.1662

The results of this calculation are given in Table 7, where for comparison purposes we have also listed the pertinent values for the active catalyst (XIV) without cobalt. The results show that the presence of Co decreases the charge on the Mo vacancy from +0.76 to +0.46. There is, however, a dramatic change in the nature of the LUMO at the vacancy site. Not only is the LUMO energy substantially lowered but there is also more than a sixfold increase in the reactivity index for an electron transfer reaction at the vacancy site. Hence, the present results suggest that a plausible explanation of the role of Co as a promoter could stem from the electronic charges in the LUMO at the vacancy site induced by Co when it is directly joined to the Mo atom. In view of the approximate nature of the quantum mechanical method and also because of the limited number of structures studied, this result cannot be taken as conclusive. It is very indicative, nonetheless, of a plausible mechanism for the catalyst's promotion by Co.

The stability of structure (**XIX**) can be inferred from the reaction:

$$\mathrm{CoSH} + (\mathbf{XIV}) \rightarrow (\mathbf{XIX}), \qquad \Delta E = -1.07 \text{ a.u.} \quad (11)$$

This stability is also reflected in the larger bond energy, −6.58 a.u. of structure (**XIX**), compared with −3.15 a.u. for structure (**XIV**).

IV. DISCUSSION

The study of the HDS reaction of thiophene and related compounds over a $Mo{-}Al_2O_3$ catalyst promoted by Co has been the subject of a large number of experimental works. Due to the complexity of the reaction there is as yet no clear-cut explanation of its mechanism, although several models have been proposed. Because of this, we have undertaken in this work the systematic study, by means of molecular orbital calculations, of very simple molecules which may be taken as the basic blocks for more complicated catalyst structures. In particular, after studying a number of simple molybdenum structures, we have been able to determine that a linear chain of Mo_3O_{10} may be regarded as a suitable oxidic precatalyst structure. The processes of hydrogenation leading to vacancy formation have been studied with reference to this molecule. According to our calculations the reaction whereby a vacancy is formed is favored on energetic grounds. Also, the sulfidation process leading to the production of an oxysulfide chain structure (**XIV**) may readily occur. With respect to this structure, it is of interest to point out that the vacancy position may be easily shifted.

We have also considered the interaction of this sulfided catalyst with thiophene. The reaction of this molecule with the catalyst has been generally assumed to proceed via a cleavage of the C–S bond, induced by an attack of one of the labile hydrogens of the catalyst on the α carbon in thiophene. We observe, however, that energetically the most likely process involves an intermediate structure, where this hydrogen is shared by both the C and the S atoms. The following hydrogenation step, according to our calculations could occur either at the C(20) or C(22) atoms, leading in this case to a partial saturation of the olefinic bonds. This would preclude the formation of butadiene as an intermediate as the concurrent hydrogenation of the C(22) carbon atom is also possible. In any event, it seems that a simple picture of a direct C–S cleavage is not warranted and that instead the HDS reaction might go through fairly complicated transition states.

Concerning the role of Co as a promoter, we have shown that there is a negligible effect when Co is bridged through an O atom to the Mo vacancy-holding atom. On the other hand, Co exerts a considerable effect on the vacancy site, favoring a charge transfer from thiophene, when it is placed in one of the oxygen octahedral sites. This implies, however, a direct Co–Mo interaction. Although the net charge on the vacancy is diminished, the reactivity index for the LUMO at this site is greatly increased. This conclusion is, however, tentative and more work must be done on other types of simple catalyst models in order to properly determine the role of Co as a promoter.

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