

# MOLECULAR ORBITAL CALCULATIONS FOR IRON CATALYSTS

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One of the primary questions facing scientists working in the area of direct coal liquefaction (DCL) is the state of the iron in iron-based catalysts. While much work has been done on iron-based DCL catalysts, the mechanism of catalysis is poorly understood. In order to elucidate the possible catalytic action, we have begun modeling various surfaces of FeS and  $\text{Fe}_{(1-x)}\text{S}_y$  clusters with the ASED-MO method of Anderson. We have studied the adsorption of toluene and 1-methylnaphthalene at various sites on FeS and related defect clusters and have calculated bond breaking energies of the aromatic-aliphatic linkage. One explanation of the catalytic activity of the FeS is donation of electrons to the iron surface by the adsorbate, followed by a subsequent decrease in the bond breaking energies as compared to nonchemisorbed toluene or 1-methylnaphthalene.

## A. Introduction

The development of effective and economical catalysts is the key to making direct coal liquefaction a commercially viable goal. To this end, there has been a great deal of interest in sulfided iron catalysts for coal liquefaction. Several facts are known from experiments: the presence of sulfur increases the liquefaction conversion;<sup>1</sup> molybdenum is a 'more active catalyst' for liquefaction than iron;<sup>2</sup> molybdenum produces a more highly hydrogenated product; and the addition of molybdenum to the iron sulfided catalysts greatly increases the activity of the iron catalyst.<sup>1</sup> However, the question of the state of the iron in the iron-based catalysts is still unanswered. For instance, in experiments starting with iron oxide as the catalyst it is still not known whether the iron oxide undergoes a phase transition directly to  $\text{Fe}_x\text{S}_y$  phases or it transforms to metallic iron first and then goes to form  $\text{Fe}_x\text{S}_y$ .<sup>3</sup> We address such questions through quantum chemical modeling calculations.

Two methods, both based on the EHMO method of Hoffmann,<sup>4</sup> are particularly suited for these investigations. The first, a band structure tight binding EHMO approach, developed by Whangbo,<sup>5</sup> has already been successfully employed by Zonneville, *et al.*<sup>6</sup> in explaining thiophene desulfurization on  $\text{MoS}_2$  and the formation of negatively charged ions in the scattering of oxygen from silver. This method is well suited for investigating bulk and semi-infinite surface properties of the catalyst systems.

The second, the ASED-MO method developed by A.B. Anderson,<sup>7</sup> has been used by us in the study of the possible cleavage mechanisms of model compounds of interest to investigators in the field.<sup>8-11</sup> Anderson also has used the method to study ethylene hydrogenation mechanisms on Pt surfaces and ethylene and acetylene absorption on  $\text{MoS}_2$  clusters.<sup>12</sup> In this method one models a surface by a small number of atoms (i.e., as the surface of a cluster of atoms), and is ideal for the study of the small ultrafine particle catalysts. One can thus

address whether the departure from bulk properties when the catalyst size approaches 10nm is the cause of catalytic activity.

Our goal is to investigate the active sites in both nano-size and large particles of iron-based catalysts by quantum chemical methods. Initially the adsorption of small organic molecules such as ethylene and toluene on various sites on FeS, Fe<sub>7</sub>S<sub>8</sub>, other defect structures, and pure Fe surfaces will be investigated in order to try to determine the differences in adsorptive and catalytic activity as one progresses from pure iron to the defect pyrrhotite structure. As a prelude to these complex studies, we have begun to model these interactions with cluster studies using the ASED-MO method of Anderson.<sup>7</sup>

## B. Method Used

The ASED-MO method is an attempt to improve the binding energy curve calculation in EHMO theory. There are two significant modifications. The first one is in the Hamiltonian matrix. In the ASED-MO method, as in the EHMO method, the molecular orbitals are expanded in terms of Slater type orbitals for the valence electrons. The eigenenergies,  $\epsilon_j$ , and the expansion coefficients are obtained from a solution of the secular equation,

$$|H_{ij} - \epsilon_j S_{ij}| = 0 \quad (1)$$

The Hamiltonian matrix  $H$  in ASED-MO is defined by

$$H_{ii} = -VSIE, \quad (2)$$

$$H_{ij} = \frac{K}{2}(H_{ii} + H_{jj})S_{ij} \exp(-\delta R_{ij}). \quad (3)$$

The  $S_{ij}$ 's are overlap integrals and are calculated explicitly with Slater-type orbitals (STO). The valence state ionization energies (VSIE) and the exponents in the STO's are frequently adjusted slightly from experimental or theoretical norms in order to give numbers that are in closer agreement with experiment.<sup>13</sup> Note that the off-diagonal matrix elements in (3) are different from the usual EHMO form of the Wolfsberg-Helmholz expression by the inclusion of the exponential factor. The constant,  $K$ , is taken to be 2.25 in the ASED-MO version, and the exponent  $\delta$  is 0.13au<sup>-1</sup>. The  $R_{ij}$ 's are the distances between the various atom centers in the molecule. The practical effect of the exponential factor is to produce a sharper increase in the potential curve between any two atoms than the standard standard EHMO methods.

The second modification of EHMO in the ASED-MO method is the inclusion of specific pairwise repulsion terms, derived from the consideration of the Hellman-Feynman force theorem.<sup>7</sup> Nuclear repulsion terms, attenuated by nuclear attraction integrals, are included in each pairwise repulsion term. The attraction terms are computed with classical formulae, approximating the density due to  $p$  and  $d$  electrons by spherical distributions. Inclusion of the two modifications of Anderson significantly improves the validity of EHMO calculations.

## C. Results and Discussion

The first cluster we investigated is shown in Figure 1 and consists of 19 Fe atoms in the top layer, 12 sulfur atoms in the second layer and 19 iron atoms in the third layer. This particular cluster was chosen because of its simplicity, and more realistic surfaces will

be studied subsequently. The interatomic distances were chosen to correspond to those in the idealized pyrrhotite structure.<sup>14</sup> The nearest neighbor distance between iron atoms in the same layer is 3.43 Å but 2.84 Å between layers. The Fe-S distance is 2.44 Å. This is to be compared with the nearest neighbor distance in bcc pure iron of 2.48 Å. The inner iron atoms of the cluster exhibit a charge of about +0.6 |e|. While this cluster does not have the overall stoichiometry of FeS, it is representative of the correct stoichiometry in the immediate vicinity of the adsorption sites studied.

We started by studying the adsorption of a hydrogen molecule on this cluster. The hydrogen molecule was allowed to approach the top layer of the surface perpendicularly in several different sites—i.e. head-on, bridge, and interstitial (over the exposed sulfur atom in the second layer) sites. These positions are labeled A, B, and C, respectively, in the second panel of Figure 1. The iron pyrrhotite structure was modeled by removing an iron atom from the top layer, thereby creating a vacancy in this layer. The most stable positions for the hydrogen molecule at its ASED minimum energy distance were found. In several cases, once this position was found, the hydrogen atom closest to the surface was fixed and the position of the outermost hydrogen optimized with the grid search option of the ASED program. The binding energy of the hydrogen molecule to the surface was of the order of 0.04-0.07 eV, in other words, a physisorption process is occurring. However, in the presence of the vacancy the physisorption energies slightly decrease, indicating an inhibitory effect as the iron pyrrhotite structure is formed. We next investigated the adsorption of a simple organic molecule, ethylene. The ethylene molecule, at its ASED minimum energy configuration, was brought up parallel to the surface of the cluster. In this manner, the  $p_x$  orbitals of the carbon atoms can interact with the  $d$  orbitals of iron. The ethylene molecule was allowed to approach with one carbon atom fixed directly above an iron atom and the other carbon atom along the  $x$  axis. Once the minimum energy distance above the surface of the molecule was found, the  $\text{CH}_2$  fragment not above the iron was allowed to relax until the energy of that fragment was minimized. For each of the sites studied, the binding energy of ethylene to the surface was found to be about 1 eV—i.e., a chemisorption process is occurring. There was almost no difference in binding energies whether the adsorption site was the central iron atom or one removed from the central atom. However, when a vacancy was created, the binding energy of ethylene over the vacancy site (with the sulfur layer underneath) decreased to about 0.25 eV, even after considerable relaxation of the whole ethylene molecule.

In order to compare the effect of the sulfur layer, the second layer was changed to iron (i.e., a pure iron cluster) and the same procedure followed. The adsorption in the absence of the vacancy was the same as for the iron-sulfur cluster. However, in the presence of the vacancy the chemisorption energies did not decrease as much as in the presence of a sulfur layer. Therefore, the presence of sulfur appears to have an inhibitory effect on the chemisorption ability of the cluster surface.

We next studied the adsorption of toluene and 1-methylnaphthalene on the FeS cluster. A typical geometry studied is shown in Figure 2. The ring system of toluene was kept fixed at experimental distances and kept planar. The height of the toluene molecule above the surface and bond distances, angles, dihedral angles of the ring- $\text{CH}_3$  group were optimized coarsely in this preliminary study. The binding of toluene to an iron atom of the surface is about 2.5 eV and of 1-methylnaphthalene about 5 eV. We observe a transfer of charge from the ring systems to the cluster with a resultant decrease in the ring- $\text{CH}_3$  bond breaking energy as compared to unadsorbed toluene and 1-methylnaphthalene: from 4.25 to 2.8 eV for toluene and from 4.18 to 2.6 eV for 1-methylnaphthalene (the geometry of the adsorbed molecules has

not yet been fully optimized, and so the energies are still approximate). Our initial results lead to the conclusion that the compounds are strongly chemisorbed on the catalyst surface, with a resultant transfer of charge from the molecule to the catalyst, leading to a decrease in bond breaking energies. This appears to be similar to the mechanism proposed by Farcasiu, *et al.*<sup>15</sup> in the context of the catalytic decomposition of 4-(1-naphthylmethyl)biphenyl in the presence of carbon black. We are now in the process of doing more rigorous geometry optimizations for the cases considered above and studying other adsorption sites, the effect of iron vacancies, and modeling other surfaces which have sulfur exposed.

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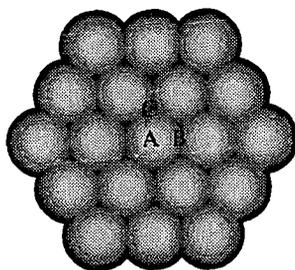
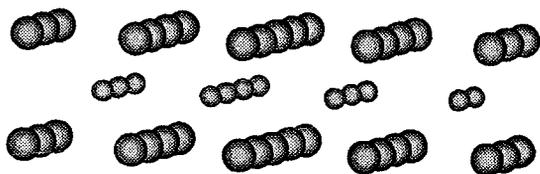


Fig. (1) Top Panel: FeS Cluster  
Bottom Panel: Adsorption site labels

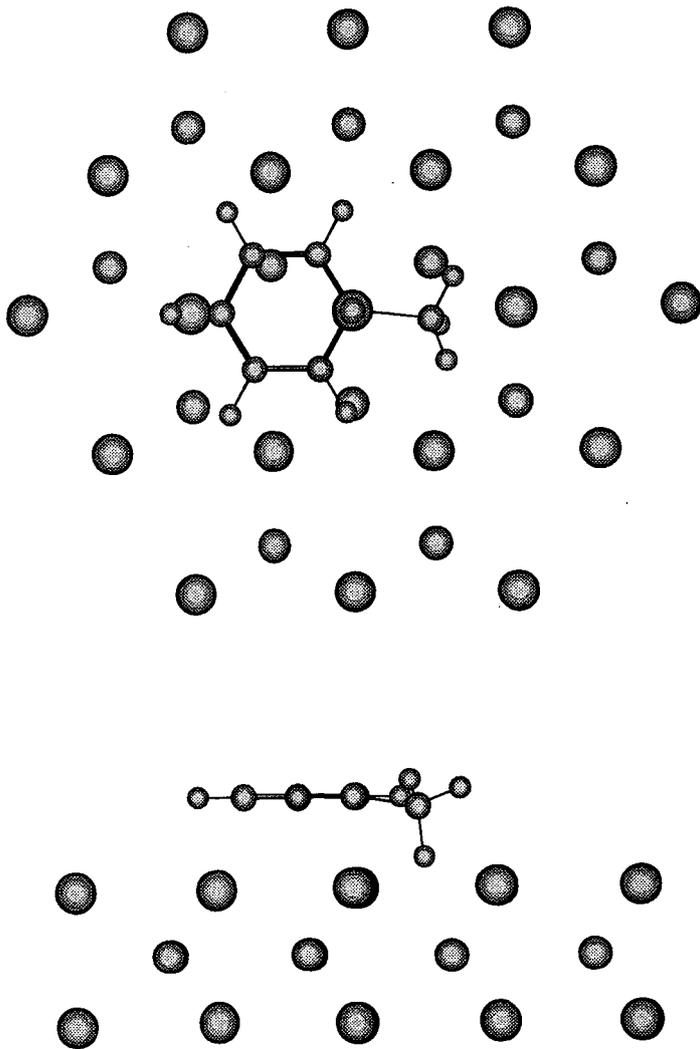


Fig. (2) Chemisorption of toluene on FeS cluster: top and side views