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An ab Initio Molecular Orbital Study of the Hydrogen Sorbed Site in Co/MoS_2 Catalysts

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A cluster model quantum chemical approach is used to study the electronic structure of Co in bimetallic sulfide catalysts Co/MoS_2. The oxidative addition of hydrogen to the Co−Mo component is considered. Ab initio HF/MP2 and DFT calculations show that hydrogen occluded in the catalyst bulk is sorbed on the cobalt ion and stabilizes the Co(III) d^6 electronic state of cobalt ions in the sulfide catalysts. This electronic state is rather active, when surface sites interact with the S-containing reagents participating in the HDS catalysis. A model of active sites on the Co/MoS_2 catalyst is used to discuss the suggested molecular mechanism of the HDS catalysis.

I. Introduction

Various models are suggested to represent the structure of active centers on the Co/MoS_2 catalysts.[1−3] One of these models, which is based on single slabs of MoS_2 with the Co atoms localized in the edge plane, is accepted most widely. However, still there is no universally adopted opinion about the electronic state of Co, which enters the active component composition in the sulfide HDS catalysts. The cobalt state seems to be of key importance for the understanding of the HDS catalysis mechanism.[4] According to our (A.N.S.) investigations,[3] Co $2p_{3/2}$ lines in XP spectra provided by the sulfide Co/MoS_2 catalysts, either bulk or supported on alumina, silica, and carbon, are shifted by 0.5 eV toward higher values of binding energy, when compared with the lines provided by the sulfide Co/Al_2O_3 catalysts. Therefore, in bimetallic catalysts a new electronic state of Co seems to form, which differs from the usual d^7 Co(II) oxidation state. Using these experimental data and our theoretical study related to an oxidative addition of dihydrogen onto the sulfide [Ni−Mo] catalysts,[4] we suggest a quantum chemical model of an active center of the Co/MoS_2 catalysts. In the present study, we focus on the special (d^6) electronic state of cobalt atoms, generated in the cobalt sulfide catalysts after their interaction with adsorbed hydrogen. A model representing the active center structure in the H_xCo/MoS_2 catalyst has been calculated, using the density functional theory (DFT), and then compared with the results obtained with the Hartree−Fock (HF) self-consistent field and second-order Moller−Plesset (MP2) levels of theory.

II. Quantum Chemical Model and Calculation Details

According to the quantum chemical ab initio study,[4] for the oxidative addition of dihydrogen to the sulfide [Ni−Mo] catalyst, one hydrogen atom is adsorbed on the surface (H_s) and another one is sorbed (occluded) in the bulk (H_o). The occluded hydrogen atom is situated under the Ni atom in the MoS_2 matrix right in the center of the trigonal prism formed by the sulfur atoms. We assume that this particular atom H_o is of key importance when an active center is generated in the HDS catalysts. We believe that a similar process occurs in the Co/MoS_2 catalysts, and H_o interacts with the Co atom surrounded by sulfur, thus producing the oxidation state Co(III) with a d^6 electronic configuration and coordination vacancy (see Figure 1a). We used the electronic structure of cluster (H)-$CoMo_2S_{10}H_{10}$ to model the active center in the H_xCo/MoS_2 catalysts, and to study the influence of H_o (Figure 1a) and H_s (Figure 1b). When we choose the model and cluster size, the most important problem is to take into account the real surrounding of metals:[3] the Mo atom is in the center of the sulfur trigonal prism, the Co atom is in the square-pyramidal surrounding, and the atomic ratio Co to Mo is 0.5. In this regard the cluster $CoMo_2S_{10}H_{10}$ is suitable. The influence of a nonstoichiometric S/Mo ratio is corrected by the boundary conditions.[4] Earlier, the MP2 method was used to study H_2 interaction with cluster $NiMo_2S_{10}H_{10}$,[4] and values of 70−75 kcal/mol have been predicted for the energy of H bonding to the Ni site with equilibrium distance r(Ni−H) = 1.5 Å.

All calculations were done using the LANL1 effective core potential for the inner shells of Co, Mo, and S atoms,[5] and single-ζ (MB) or double-ζ (DZ) basis sets for the valence shells provided with the Gaussian 92 package.[6] For H_s and H_o atoms, the basis set 4-31G was extended by adding a polarization p-orbital with exponent $\xi = 1.1$. Basis set STO-3G with a scale factor of 1.3 for H-"terminal" atoms, LANL1DZ for the Co and Mo atoms, and LANL1MB for S atoms were used to calculate the cluster (H)$CoMo_2S_{10}H_{10}$. Ab initio calculations were done with the Gaussian 92/DFT computer program[6] at the restricted Hartree−Fock (HF) level of self-consistent field theory, at the second-order Moller−Plesset (MP2) level of theory,[7] and compared with the results obtained with the density functional theory[8] (Becke3P86 exchange-correlation functional[9,10]). Vibrational frequencies were calculated at the DFT level. Mulliken population analysis was performed with the HF, MP2, and DFT wave functions. The $CoMo_2S_{10}$ fragment geometry was taken from experimental data[11] and was frozen at geometry optimization for the Co−H_s, Co−H_o, and for the S−H_t bonds of cluster (H)$CoMo_2S_{10}H_{10}$.

III. Electronic Structure of Cluster (H)$CoMo_2S_{10}H_{10}$ with d^6 Electronic Configuration of Co(III)

For the lowest energy state of cluster (H)$CoMo_2S_{10}H_{10}$, the electronic structure of the Co atom is calculated at the HF, MP2, and DFT levels. Table 1 presents the calculated atomic population of 3d orbitals of Co, as well as charge distribution

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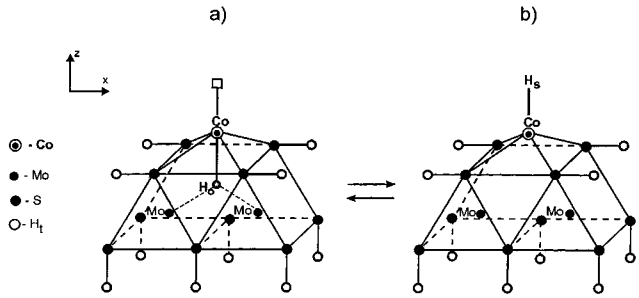

Figure 1. Proposed quantum chemical model [the $(H)CoMo_2S_{10}H_{10}$ cluster] for an active site of the trivalent cobalt ion (d^6) in the Co/MoS_2 catalysts with the occluded (a) and the adsorbed (b) hydrogen. □, coordination vacancy.

and vibrational frequency of the Co−H bonds. Calculations reveal the following features worth mentioning:

(i) "Surface-sorbed" hydrogen (H_s) represents terminal H adsorbed on atom Co.

(ii) "Bulk-sorbed" hydrogen is bonded to Co and is localized in the center of the trigonal prism of sulfur atoms in the MoS_2 unit cell. We call this hydrogen species as occluded hydrogen (H_o) in the Co/MoS_2 catalyst.

(iii) The calculated electronic structure of Co with valent d_{xy} and d_{z^2} orbitals (see Figure 1 for coordinate system) corresponds to an oxidation state Co(III) with d^6 electronic configuration.

(iv) The calculated IR spectrum shows that the vibrational frequency for Co−H_s ($\nu = 1972$ cm^{-1}, $\delta_x \approx \delta_y = 652$ cm^{-1}) fits the range of experimental vibrational frequencies, characteristic of monohydride molecular complexes[12] of Co and hydrogen species adsorbed on Ni/MoS_2 catalyst.[13]

(v) The calculated lowest electronic states of $(H)CoMo_2S_{10}H_{10}$ clusters with either H_s or H_o have very similar total energy at the HF, MP2, and DFT levels.

(vi) The calculated entropy difference between H_o and H_s in the active center is small, so either H_s or H_o hydrogen species may enter the active component.

(vii) Regarding the calculated net charges on the hydrogen atoms, one may assume that H_o forms a more hydride-like bond (the charge on H_o is more negative) than hydrogen H_s, because H_o is extra bonded to two Mo atoms (see Figure 1a).

(viii) The calculated IR spectrum shows that the vibrational frequency of Co−H_o ($\nu = 1696$ cm^{-1}, $\delta_x = 1764$ cm^{-1}, $\delta_y = 880$ cm^{-1}) agrees well with the neutron Compton scattering (NCS) study of hydrogen in the Co/MoS_2 catalyst.[14] It should be noted that the authors[14] have concluded that the chemisorbed hydrogen in the Co/MoS_2 catalyst is bonded to sulfur.

IV. Presence of Occluded Hydrogen in Molybdenum and Cobalt Sulfide Catalysts

Badger et al.[15] were the first to observe unusual hydrogen sorption when the amount of hydrogen sorbed by MoS_2 essentially exceeded the monolayer. Considering this phenomenon, Anderson et al.[16] proposed the HDS reaction to occur over the H_xMoS_2 catalyst. With this in view, it was necessary to identify different the hydrogen species sorbed in the MoS_2 and Ni(Co)-MoS_2 catalysts.

For example, let us consider tantalum−hydrogen bronze, H_x-TaS_2, where the hydrogen atom is localized in the center of a trigonal prism of sulfur atoms.[17] Blackburn and Sermon[18] assumed H_xMoS_2 and H_xTaS_2 to have similar structures. Quantum chemical calculations[16] with the semiempirical method of molecular orbitals (ASED-MO) for the MoS_2 cluster model (cluster $Mo_7S_{24}^{20-}$) show that occluded hydrogen H_o localized in the center of the trigonal prism S_6 is stable, but the calculated binding energy is lower (37 kcal/mol) than that of hydrogen adsorbed on Mo (100 kcal/mol). As follows from our calculations (Table 1), both H_o and H_s states are energetically equivalent if regarded with the cluster model $(H)CoMo_2S_{10}H_{10}$. Therefore, the existence of H_o seems to be quite probable and reasonable. We considered this idea for the first time[4] when we calculated the IR spectra of H_s and H_o in the Ni/MoS_2 catalysts using the cluster model $(H_s)(H_o)NiMo_2S_{10}H_{10}$. Comparing our calculations with the experimental spectrum of inelastic neutron scattering (INS), we see that the bands, experimentally observed at 795 and 1895 cm^{-1} for the Ni/MoS_2 catalysts,[13] are in a good agreement with the ones ($\nu_{Ni-H} = 1890$ cm^{-1}, $\delta_{Ni-H(x)} = 704$ cm^{-1}, $\delta_{Ni-H(y)} = 834$ cm^{-1}) calculated for H_s.[4] Note that experimental bands were obtained from the difference spectrum of two samples (a and b).[13] After hydrogen adsorption at 1 atm ($T = 473$ K), sample a was evacuated (10^{-4} Torr) at 573 K for 12 h to remove hydrogen from the gas phase. Sample b was exposed to high hydrogen pressure (30 bar) at 473 K for12 h. One may suggest that sample a contains no adsorbed hydrogen, since the reaction equilibrium

$$Ni-H_s + S-H_s \Leftrightarrow Ni + H_2S\ (H_2)\uparrow$$

is shifted toward gaseous products at low pressures. At the same time, sample a may still contain the occluded hydrogen, because according to the TPD data[19] this particular hydrogen is removed only at high temperatures ($T > 725$ K). Sample b should contain both adsorbed and occluded hydrogen. Therefore, in the difference spectrum one may observe solely H_s. This consideration agrees with our interpretation[4] of the INS spectra.[13]

Mitchell et al.[14] investigated the neutron Compton scattering (NCS) spectra of hydrogen adsorbed on the Mo and Co−Mo sulfide catalysts. Prior to the NCS experiments, samples were pumped down to 10^{-9} Torr at $T \approx 300$ K for 8 h. One might suppose these samples to contain no adsorbed hydrogen.[13] However, they might contain occluded hydrogen, which according to the TPD experiments[19] is removed from MoS_2 and from bimetallic sulfides at 500 and 725 K, respectively. There were no TPD peaks of hydrogen in the case of Co_9S_8 samples at 300−1000 K (see Figure 4 in ref 19). Most likely, either these samples contained only weakly bonded hydrogen or no dissociative adsorption of hydrogen occurred over the Co_9S_8 samples. This fact agrees with data,[14] where no hydrogen peak was detected in the NCS spectra.

Therefore, we may assume that hydrogen peaks, observed in the NCS spectra of MoS_2 and Co/MoS_2 catalysts, belong to occluded hydrogen H_o. Let us compare the IR bands calculated in this study for the active center model with the averaged bands $\nu_{av} = (\nu + \delta_x + \delta_y)/3$ observed elsewhere.[14] According to Mitchell et al.,[14] the fundamental vibration wavenumbers of hydrogen sorbed on Co/MoS_2 and MoS_2 catalysts are similar: 1392 ± 26 and 1430 ± 34 cm^{-1}, respectively. Our calculations of ν_{av} with values $\nu = 1697$ cm^{-1}, $\delta_x = 1764$ cm^{-1}, and $\delta_y = 880$ cm^{-1} for occluded hydrogen H_o (Table 1) give $\nu_{av} = 1447$ cm^{-1}, which is in rather good agreement with experiment.[14] Therefore, a Co/MoS_2 catalyst may indeed occlude stable hydrogen species H_o. Our assumption is supported by the results of a study[20] related to the hydrogenation of CoMoS films in high vacuum ($P \sim 10^{-9}$ Torr, $T \sim 300$ K), which show that films are not active toward molecular hydrogen. On the other hand, the same films exhibit a high activity toward atomic hydrogen, which partially penetrates into the bulk. The remaining surface hydrogen reacts with the surface sulfur atoms producing gaseous H_2S. It is mentioned that hydrogen species

TABLE 1: Calculated Electronic Parameters of Trivalent Cobalt Ion (d^6) for an Active Site in the (H)$CoMo_2S_{10}H_{10}$ Cluster with the Adsorbed Hydrogen (H_s) and the Occluded Hydrogen (H_o)[a]

	HF		MP2		DFT	
parameters	H_s	H_o	H_s	H_o	H_s	H_o
r_e(Co−H) Å	1.361	1.484	1.432	1.408	1.406	1.518
q(H)	+0.170	−0.217	+0.083	+0.118	+0.168	+0.120
q(Co)	+0.733	+0.658	+0.375	+0.206	+0.446	+0.431
d^N	$d^{6.0}\,d_{xy}^{0.90}d_{z^2}^{1.24}$	$d^{6.0}\,d_{xy}^{0.46}d_{z^2}^{1.10}$	$d^{6.0}\,d_{xy}^{0.91}d_{z^2}^{1.23}$	$d^{6.0}\,d_{xy}^{1.10}d_{z^2}^{1.21}$	$d^{6.0}\,d_{xy}^{0.98}d_{z^2}^{1.36}$	$d^{6.0}\,d_{xy}^{0.91}d_{z^2}^{1.41}$
ν(Co−H)[b] cm^{-1}					1972.7	1696.9
S_{298} (J/(mol K))					600.0	582.8
total energy (au)	−149.70846	−149.70880	−150.57526	−150.56240	−156.66100	−156.66295

[a] The $CoMo_2S_{10}$ fragment geometry: the Co−Mo bond length (2.80 Å) is taken from experimental data;[11] the chosen Mo−Mo (3.16 Å), Mo−S (2.41 Å), and S−S (3.16 Å) bond lengths are the crystallography values for MoS_2. [b] The calculated bending vibrations: $\delta_x \approx \delta_y = 652$ cm^{-1} of the adsorbed hydrogen (H_s); $\delta_x = 1764$ cm^{-1}, $\delta_y = 880$ cm^{-1} of the occluded hydrogen (H_o).

absorbed in the bulk are not active in H_2S generation. Only on heating this bulk does hydrogen desorb as dihydrogen. The authors[20] assume that hydrogen, sorbed in the bulk, may bond to coordination-unsaturated metal atoms in CoMoS. In our opinion, this assumption confirms our earlier expressed idea about the hydride type of the bond with hydrogen occluded in the CoMoS catalyst. On the other hand, the observed activity of the adsorbed atomic hydrogen species toward the evolution of gas phase H_2S confirms our assumption that at low pressures the surface reaction equilibrium $Co{-}H_s + S{-}H_s \Rightarrow Co + \square + SH_2\uparrow$ is shifted toward the gas phase products. That is why sulfide catalysts Co(Ni) and MoS_2 under the given conditions ($P \sim 10^{-9}$ Torr, $T \sim 300$ K) are not able to retain surface hydrogen H_s. Recently, a study of tunneling microscopy allowed the direct observation of the surface reaction $S{-}H_s + S{-}H_s \Rightarrow \square + SH_2\uparrow$ proceeding during the hydrogenation of monolayer MoS_2 films by atomic hydrogen ($P \approx 10^{-9}$ Torr, $T \approx 600$ K).[21]

Thus, we may draw the following main conclusion. Sulfide HDS catalysts cause a dissociative activation of molecular hydrogen and of S-containing molecules, and occlude atomic hydrogen in their bulk. This bulk hydrogen provides catalytically active Co sites with a d^6 electronic configuration. According to the TPD[19] and NCS[14] studies, unlike the Co/MoS_2 and MoS_2 samples, Co_9S_8 does not contain occluded hydrogen H_o. Note also that H_o is thermally more stable in the Co/MoS_2 catalysts than in MoS_2 ones.

V. Active Center and Catalytic Cycle of Thiophene Hydrogenolysis

Regarding the calculation results presented here, we consider that a Co(II) d^7 ion in a square-plane sulfur environment, which may be present in real catalysts, is not active in the HDS process. But an electronic state d^7 can transform to the d^6 state during the oxidative adsorption of hydrogen on Co. Only this d^6 electronic state is responsible for the adsorption of S-containing molecules.[22] Note that the key role of Co (Ni) atoms in the activation of S-containing molecules was demonstrated by Rodriguez et al.[23−26] In their study, the HDS activity and the catalyst's ability to interact with the S-containing molecules obviously correlate with each other.

Dihydrogen dissociative chemisorption on the HDS catalysts is most likely the major contributor of H_s. Hydrogen adsorption on different cluster models (Mo_yS_{2y} clusters, $y = 5{-}8$) was recently simulated with the ab initio SCF MO LCAO method.[27] The calculated data clearly demonstrate that Ni increases the adsorption ability of surface centers, and Ni itself is the most reactive site with respect to hydrogen adsorption. In this regard we assume that thermal stability of hydrogen is higher in the Co/MoS_2 catalysts than in the MoS_2 catalysts, which is also confirmed by the TPD data.[19]

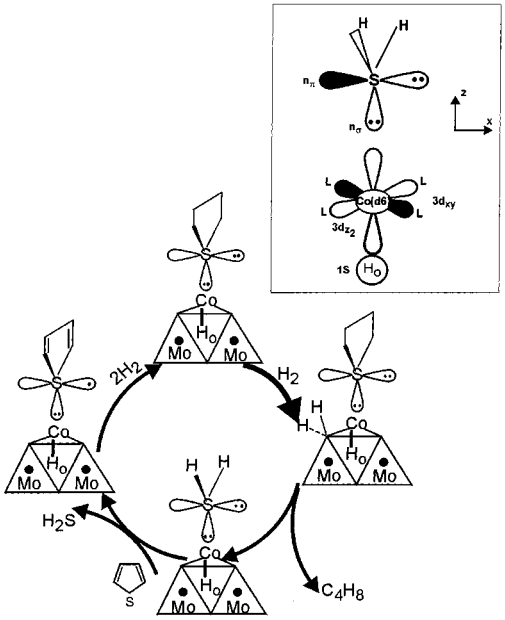

Figure 2. Proposed thiophene HDS catalytic cycle over Co/MoS_2.

We believe that actual active center generation should involve occluded hydrogen H_o. After H_2S adsorption on the Co atom, the d^6 electronic state is stabilized. According to our experience the Ni oxidation degree in the Ni/MoS_2 catalyst increases with the oxidative addition of H_2 only in the presence of H_2S.[28] Therefore, we suggest the HDS catalytic cycle to close through the H_2S adsorption complex on the (Ho)$CoMo_2S_{10}H_{10}$ active center (Figure 2).

A thiophene molecule adsorbs on the active Co(d^6) site replacing the H_2S molecule. The calculated values of E_{ads} (in the η^1-coordination shown in Figure 2) show H_2S adsorption to be partially reversible under reaction conditions, and there is replacement of adsorbed H_2S by thiophene. Thiophene hydrogenation destroys the π-system of the aromatic ring, and an additional lone pair appears at the sulfur atom of tetrahydrothiophene (THT). Since THT is more basic than thiophene, it does not desorb into the gas phase. Our preliminary ab initio calculations (at the Hartree−Fock level) of adsorption energy in the series H_2S (16.6 kcal/mol) < thiophene (18.4 kcal/mol) < THT (26.7 kcal/mol) support this assumption. Note that semiempirical calculations give the same results.[29]

After a tetrahydrothiophene molecule is stabilized on the active center, electron density transfers from the sulfur atom of THT onto the catalyst and localizes at terminal S atoms. This is the driving force for the dissociative adsorption of dihydrogen. The activated hydrogen is transferred to the adsorbed THT molecule, and the process is terminated with the C−S bond

scission and butene desorption into the gas phase (Figure 2). This mechanism does not contradict the one suggested before[3] but brings additional details. The most important thing is that adsorbed H_2S complex is regarded as initial and also final step of the HDS mechanism. In another recent version of the HDS catalytic cycle for thiophene over the Co−Mo catalysts[30] the Co atom is also suggested to be the active site for the C−S bond homolysis. Regarding the calculated H_2S and thiophene adsorption heats (16.6 and 18.4 kcal/mol, respectively), one may talk about the adsorption equilibrium between H_2S and thiophene. Such equilibrium was experimentally shown to occur.[33] As the reaction temperature increases, the thiophene adsorption capacity becomes higher than that of H_2S.[34] Relative adsorption constants for H_2S and various thiophenes such as thiophene, benzothiophene, and dimenzothiophene are considered in a study[35] according to which thiophenes adsorption constants are indeed higher than that of H_2S.

VI. Conclusion

On the basis of the calculations presented here, we assume the active center of sulfide Co−Mo catalysts to include Co(III) atoms in a d^6-electronic configuration, which is stabilized by hydrogen species occluded in the catalyst bulk. There are experimental data supporting our assumption:

(i) According to the XPS data, the electronic density on the Co atoms in the active center is lower than that in the highly dispersed CoS.[31] Therefore, the valence of Co is higher than II.

(ii) TPD data show that occluded hydrogen is indeed present in the active component. It desorbs at a temperature as high as 700 K.[19,32]

(iii) In the NCS spectrum[14] of the catalyst Co/MoS_2, a hydrogen peak may be ascribed to occluded hydrogen, whose possible existence in Ni/MoS_2 was earlier predicted by our calculations.[4]

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