Density Functional Theory Studies of Chemisorption and Diffusion Properties of Ni and Ni Complexes on MoS_2 Basal Planes

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Introduction

Among various sulfide catalysts proposed for the hydrodesulfurization (HDS) process, molybdenum sulfide is one of most promising candidates for technological applications.[1,2] In practice it is used as well-dispersed MoS_2 nanocrystallites supported on γ-alumina and can be used both as an unpromoted or promoted catalyst[1] with Co or Ni atoms.

Despite a relative large number of experimental studies the role of the metallic promoters in HDS processes is still under intense debate. Recently, Weiss *et al.*[3-5] provided new insight based on low-temperature scanning tunneling microscopy investigations of the dynamics of Ni and Co clusters on MoS_2 basal planes. These studies indicate that both these species have a low barrier for surface diffusion. It was suggested that these promoters can be used to increase the sticking probability of sulfur-containing hydrocarbons and to transport these hydrocarbons to the active sites for reaction. However, several issues were not clarified by these studies. For example the location of the promoters on the basal plane or the electronic modifications induced upon adsorption of these metallic atoms is not well established. Moreover, the transport properties, particularly the diffusion characteristics as well as the clustering processes of these promoters on MoS_2 have not yet been well characterized and understood. Another issue raised by experimental investigations is that of the role played by various sulfur defects on the chemisorption properties of promoter atoms. In general, it would be very useful to understand how the adsorption and dissociation of various hydrocarbon species containing sulfur are changed in the presence of the promoters and of the vacancies on MoS_2 surface.

The properties of promoted MoS_2 catalysts have also been considered in several recent theoretical studies based on density functional theory (DFT) calculations.[6-7] However, these studies have focused exclusively on description of the binding properties of promoter species at edge surfaces where the catalytic activity is the highest but have not analyzed the properties of basal surfaces. In the present study we describe a DFT study that focuses on analyzing the interaction of Ni promoters with the basal plane of MoS_2 in an effort to clarify some of the mechanisms proposed by Weiss *et al.*[3-5] based on their STM investigations.

Computational Method

The calculations performed in this study were done using the Vienna *ab initio* simulation package (VASP).[8-10] This program evaluates the total energy of periodically repeating geometries based on density-functional theory and the pseudopotential approximation. In this case the electron-ion interaction is described by fully non-local optimized ultrasoft pseudopotentials similar to those introduced by Vanderbilt.[11,12] Periodic boundary conditions are used, with the one electron pseudo-orbitals expanded over a plane-wave basis set. The expansion includes all plane waves whose kinetic energy, $\hbar^2 k^2 / 2m < E_{cut}$ where k is the wave vector, m the electronic mass and E_{cut} is the chosen cutoff energy. A cutoff energy of 242 eV has been used in our studies.

Calculations have been done using the spin polarized PW91 generalized gradient approximation (GGA) of Perdew *et al.*[13] The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme.[14] The minimization of the electronic free energy was performed using an efficient iterative matrix-diagonalization routine based on a sequential band-by band residuum minimization method (RMM) or alternatively, based on preconditioned band-by-band conjugate-gradient (CG) minimization.[15] The optimization of different atomic configurations was performed based on a conjugate-gradient minimization of the total energy.

The minimum energy paths between different minima were optimized by use of the nudged elastic band (NEB) method of Jónsson and Mills.[16] In this approach the reaction path is "discretized", with the discrete configurations, or images, between minima being connected by elastic springs to prevent the images from sliding to the minima in the optimization. In the NEB searches either 8 or 16 images were employed between minima.

The periodic nature of the surface was represented in our simulations using a supercell model with periodic boundary conditions in all three directions. Most calculations have been done using a slab model consisting of one S-Mo-S layer. However, additional tests have been performed for the case of supercells with three S-Mo-S trilayers. In all calculations a vacuum layer of at least 10 Å has been used parallel to the MoS_2 basal plane

Results and Discussions

Based on full optimizations of the Ni atoms on the MoS_2 basal plane we have identified three stable adsorption configurations. The first one (1F) (see Fig.1a) corresponds to Ni atoms adsorbed on top of the sulfur atoms, the second one (6F) corresponds to a six-fold configuration of Ni (see Fig.1b).The last one (3F) is represented by adsorption on top of Mo atom with a three-fold binding to neighbor sulfur atoms (see Fig.1c).

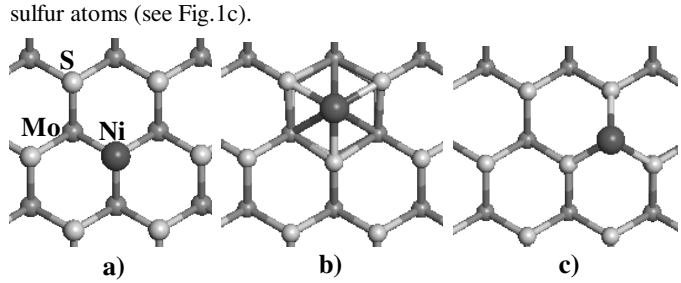

Figure 1. Adsorption configurations of Ni on MoS_2(0001) surface: (a) 1F on top of S atoms, (b) 6F in a six-fold configuration and (c) 3F on top of Mo atom.

Our results indicate a stability order E(3F) > E(6F) > E(1F). For the most stable adsorption configuration (3F), the adsorption energy, 77 kcal/mol, is large. In this configuration the Ni atom sits above the Mo atom at a distance of 2.59 Å while the Ni-S distances are 2.13 Å.

We have also investigated the minimum energy paths for diffusion of a Ni atom between different adsorption configurations using NEB calculations. In particular, we have analyzed three diffusion pathways suggested by the surface symmetry: 3F→6F→3F, 3F→6F→1F and 3F→1F. Our calculations indicate that among these the 3F→6F→3F pathway has the smallest barrier for diffusion. The corresponding profile determined in our studies is represented in Figure 2. As can be seen from this figure the barrier height is about 20 kcal/mol. This value is about 3.8 times smaller than the corresponding adsorption energy at the 3F site. This ratio of the

diffusion barrier to the adsorption energy is consistent with values obtained for other adsorbate/surface systems.[17] However, our results indicate much larger diffusion barriers than those expected from the analysis of STM data by Weiss et al.[3,4]

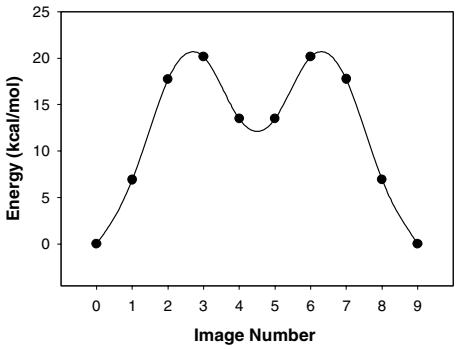

Figure 2. Minimum energy path for diffusion of Ni atom between two 3F sites and passing through the 6F configuration.

We have also analyzed the case when a Ni_3 cluster adsorbs on MoS_2 basal plane. We have identified an adsorption configuration on top of S atoms in which the adsorption energy per Ni atom decreases significantly to about 20.4 kcal/mol. However when this cluster is moved away from the on-top position the Ni atoms are adsorbed at the corresponding 3F sites, leading to cluster deformation and dissolution at the surface sites.

Another set of investigations we have pursued is related to adsorption of Ni atoms at S vacancy sites. Our calculations indicate that independent on the starting optimization configuration the Ni atom will adsorb at the position of S vacancy on the basal plane. The corresponding adsorption energy increases for this configuration to about 98.5 kcal/mol, indicating the existence of a very stable adsorption configuration.

As indicated by Weiss et al.[3-5] the presence of Ni atoms on MoS_2 surface is important to increase the sticking of sulfur-containing hydrocarbons. We have analyzed this aspect by performing studies of the adsorption of thiophene molecules on the promoted and unpromoted surfaces.

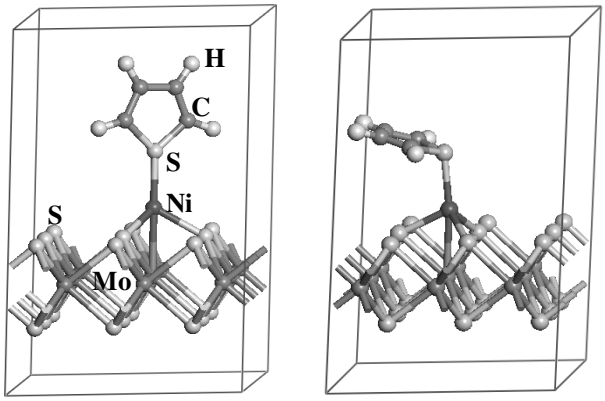

Figure 3. Vertical and tilted adsorption configurations of thiophene on Ni promoted MoS_2 basal plane.

In the case of adsorption of thiophene molecules on the unpromoted surface the calculated adsorption energies of thiophene are very small indicating a physisorption interaction mechanism. This result is in agreement with previous experimental findings determined by Salmeron et al.[18] based on TPD investigations. However, when Ni atoms are present on the surface the binding energies significantly increase. For example, in Figure 3 we present two possible adsorption configurations of thiophene molecule on Ni atoms positions at 3F sites. Our calculations indicate adsorption energies of about 20 kcal/mol for thiophene on the promoted surface. These results support the experimental findings related to the increased sticking probability of sulfur-containing hydrocarbons on basal surface.

Conclusions

The main results of our investigations related to adsorption and diffusion studies of Ni and Ni complexes on $MoS_2(0001)$ surface can be summarized as follows:

a) there are several adsorption configuration of Ni atoms on MoS_2 basal planes with large adsorption energies.

b) a simple hopping mechanism of Ni atoms between different adsorption sites indicate diffusion barriers in excess of 20 kcal/mol. This results contradict the experimental findings of Weiss et.al.[3,4] where metallic promoters were found to move easily on the surface even in the case of low temperatures.

c) the binding energy of Ni atoms to the surface increases when S vacancies are present.

d) the Ni promoter species increase the binding of thiophene molecule to the surface. In the absence of these promoters, thiophene physisorbs on the surface.

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