The $(\sqrt{3} \times \sqrt{3})$ R30° sulfur over layer on the iridium (111) surface: a DFT study

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Abstract—Iridium (Ir) is used as a selective reducing exhaust gas catalyst in the lean-burn car engine technology. In this paper we investigated the energetics of adsorption of adatom sulfur on the iridium (111) surface for the $(\sqrt{3} \times \sqrt{3})$ R30° structure at .33 monolayer coverage using first-principles calculations. We have calculated electronic structure and total energy for three possible sites i.e. on-top site, threefold site in the hollow (substrate atom located beneath) and threefold site in the hollow (vacancy located beneath). We found threefold site, with a vacancy located beneath it in the second layer, is the most stable which is in good agreement with the experimental results.

Keywords—density functional theory; coverage; adsorption; slab.

I. INTRODUCTION
Sulfur adsorption on metal surfaces has been of considerable interest due to the poisoning activity of sulfur with respect to the catalytic properties of surfaces. The potential use of Ir surfaces is motivated by reducing exhaust gas catalysts [1]. The $(\sqrt{3} \times \sqrt{3})$ R30° sulfur over layer on the iridium (111) surface was experimentally investigated by C.M. Chan and W. H. Weinberg [2]. The most symmetric and hence most probable adsites on Ir(111) surface are a linear (on-top) site and a threefold site in the hollow among three surface atoms. There are two different types of the latter, either with a vacancy below the hollow in the second substrate layer or with a substrate atom below the hollow in the second layer [2].

Fig. 1 Hard sphere representation of S adsorption on Ir(111) surface on-top site.

Fig. 2 Hard sphere representation of S adsorption on Ir (111) surface for threefold site in the hollow (substrate atom located beneath) [red dotted line represents the iridium atom in the second substrate layer is beneath the sulfur atom].

Fig. 3 Hard sphere representation of S adsorption on Ir (111) surface for threefold site in the hollow (vacancy located beneath) [red dotted line represents the iridium atom in the third substrate layer is beneath the sulfur atom].

Very few researchers have performed DFT calculations regarding sulfur adsorption on iridium surface. Results for the adsorption energetics and structures for S adsorption on Ir (100) surface were reported elsewhere [3]. Reference [3] reported that Sulfur atom prefers hollow sites for the adsorption on Ir (100) surface. DFT calculations for the sulfur adsorption
on iridium (111) plane for the (√3X√3) R30° structure were not reported elsewhere.

To understand the favorable adsorption site of sulfur atom on iridium (111) surface; we performed first principle calculations based on density functional theory and implemented in (Cambridge Serial Total Energy Package) CASTEP code [4]. The ground state energies of S-Ir(111), Ir(111) and S systems are being calculated from following equations [5]

\[ \hat{H}_{S-Ir(111)} \Psi_{S-Ir(111)} = E_{S-Ir(111)} \Psi_{S-Ir(111)} \] (1)

\[ \hat{H}_{Ir(111)} \Psi_{Ir(111)} = E_{Ir(111)} \Psi_{Ir(111)} \] (2)

\[ \hat{H}_S \Psi_{S} = E_{S} \Psi_{S} \] (3)

Hamiltonian operator depends on

\[ \hat{H} = \hat{T} + \hat{V}_e - \hat{V}_{e-n} + \hat{V}_{n-n} \] (4)

where \( \hat{T} \) is the kinetic operator and \( \hat{V}_e - \hat{V}_{e-n} + \hat{V}_{n-n} \) are the operators of electron-electron interactions, electron-nucleus interactions and nucleus-nucleus interactions respectively. As nucleus is heavy, its influence has been omitted. According to Khon-Sham [6], ground state energy and charge density of interacting electrons in any external potential were exactly the same as those of non-interacting electrons in a specially modified potential by following equation

\[ E_{\text{kin}} + E_{\text{e-e}} = E_{\text{kin}} + E_{\text{e-e}} \] (5)

where \( \rho \) is the density of electrons and \( E_{\text{ex}} \) is the exchange-correlation functional.

As systems are periodical and particles in the systems can be treated as non-interacting; we found the following single particle Schrodinger equation through the k space.

\[ \Psi_{m,k} = e^{i \mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{G}} c_{Gmk} e^{i \mathbf{G} \cdot \mathbf{r}} \] (6)

\( \Psi_{m,k} \) is the wave function of \( m^{th} \) non-interacting particle, \( \mathbf{k} \) is the wave vector, \( c_{Gmk} \) are complex Fourier coefficients, \( e^{i \mathbf{G} \cdot \mathbf{r}} \) represents a plane-wave travelling in space; perpendicular to the vector \( \mathbf{G} \) and \( \mathbf{G} \) is the vector in the reciprocal space.

We finally solved the following single particle equation in reciprocal space and we got the ground state energies of our mentioned systems.

\[ \hat{H} \Psi_{m,k} = E_{m,k} \Psi_{m,k} \] (7)

To solve this equation, exchange-correlation functional \( E_{xc} \) is treated within the generalized gradient approximation (GGA) according to Perdew et al. (PW91) [7]. The wave functions near the nuclei are less important, because they don’t affect the electronic properties very much. The Coulomb potential near each nucleus was replaced with a modified, weaker potential i.e. pseudo potential. The interaction between ions and electrons are represented by ultra-soft Vanderbilt-type pseudo-potential.

The Monkhorst-pack [8] scheme k point’s grid sampling was set at 4×4×1 to replace integration over the Brillouin zone. The plane wave basis set cut off energy was taken at 310 eV for better convergence. To characterize the surface relaxation effect, the Ir (111) surface was modeled by a four-layer slab periodically repeated in a super cell geometry with 10 Å of vacuum between any two successive slabs. All the results presented below are from energy minimizations in which all degrees of freedom of the adsorbed S and the Ir layers were allowed to relax, except the bottom two layers.

III. RESULTS AND DISCUSSION

A. Relaxation for the Ir(111)- (√3X√3) R30°

Surface relaxation implies that the relaxed surface has a lower energy than the original ideal surface [9]. The geometry of the relaxed surface was determined by performing an energy minimization as a function of the positions of the atoms in the super cell. In this calculation only top layers are allowed to move. In case of top site and hollow (vacancy beneath) site contraction occur between the first substrate layer and second substrate layer (d12) but expansion occurs in the case of hollow site (atom beneath). The distance between the second substrate layer and third substrate layer (d23) reduce for all the cases; represents structures are in ground state.

B. Adsorption energetics

The adsorption energies for various possible sites are calculated by following equation [10]

\[ E_{\text{ads}} = (E_{S-Ir(111)} - E_{Ir(111)} - nE_{S})/n \] (8)

where \( E_{S-Ir(111)} \) and \( E_{Ir(111)} \) are the total energy of the Ir(111) system with and without S atoms adsorbed on the surface respectively; \( n \) denotes the number of S atoms per unit cell and \( E_{S} \) represents the energy of the isolated S atom.

Calculated adsorption energies are given in table 1. It is clear that hollow site (vacancy beneath) is the most stable
because of their lowest energy. The adsorption energy for this site is -6.241 eV. This result is completely in agreement with the LEED experiment. The top site and Hollow site (atom beneath) are less favorable because of their higher adsorption energies. At .33 coverage, sulfur first layer come .03 Å closer to the second layer and second layer come .0047 Å closer to the third iridium layer for the top site. For threefold site in the hollow (substrate atom located beneath), first layer expand from second layer by .17% i.e. .0044 Å closer to the third iridium layer for the top site. For threefold site in the hollow (substrate atom located beneath), first layer expand from second layer by .17% i.e. .0044 Å closer to the third iridium layer for the top site. For the most stable site, hollow site (vacancy beneath) first Ir layer come .002 Å closer to second layer. For the top site sulfur atom is 2 Å above the first Ir layer.

Adsorbate sulfur is 1.65 Å above for two kinds of hollow sites corresponding to bond length 2.28 Å which are in good agreement with LEED beam analysis.

C. Density of states (DOS)

The DOS analysis for threefold site in the hollow (vacancy located beneath) is given in fig.5. Sulfur 3s localized bands extend from -12.5 eV to -11 eV. A little DOS of 3s is found near -4.8 eV. 3p states of sulfur extend from valence band to conduction band i.e. -5eV to 5 eV. 5d states of iridium are non-localized and extend from -7 eV to 5 eV. Iridium 6s states and 5p states are extended extensively from valence band to conduction band. Strong hybridization occurs between Ir-5d and S-5p which make resonance. As a result bonding occurs between sulfur and iridium. The strong hybridization between S-3p states and Ir-5d states explain the large adsorption energy and why S atoms like to sit tightly on the Ir. Surface bonding is also assisted by the small hybridization between Ir-6s with S-3p and Ir-5p with S-3p. Continuous DOS at Fermi energy represents strong bond between sulfur atom and iridium surface.

<table>
<thead>
<tr>
<th>Possible sites</th>
<th>$E_{ads}$</th>
<th>h</th>
<th>$\Delta d_{12}$ (%)</th>
<th>$\Delta d_{23}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>top site</td>
<td>-4.139</td>
<td>2.00</td>
<td>-1.19</td>
<td>.52</td>
</tr>
<tr>
<td>Hollow site (atom beneath)</td>
<td>-6.125</td>
<td>1.65</td>
<td>+.17</td>
<td>-.22</td>
</tr>
<tr>
<td>Hollow site (vacancy beneath)</td>
<td>-6.241</td>
<td>1.65</td>
<td>-.09</td>
<td>-.19</td>
</tr>
</tbody>
</table>

Fig. 5 The partial density of states (PDOS) for adatom S in Ir(111) surface: (a) S PDOS and (b) Ir PDOS for hollow site (vacancy beneath).
IV. CONCLUSION

For the first time DFT calculations were performed for $(\sqrt{3} \times \sqrt{3})$ R30° sulfur over layer on the iridium (111) surface. From adsorption energies it is clear that sulfur atom prefer hollow site having vacancy located beneath the second layer. Excellent agreement has been obtained between the theoretical and experimental results for the optimized structure parameters of the Ir (111) surface.

REFERENCES