



Density functional theory calculations for Pd adsorption on SO₄ adsorbed on h-BN[☆]



Mami Yokoyama^{*}, Kengo Nakada, Akira Ishii

Department of Applied Mathematics and Physics, Tottori University, Tottori, Japan

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ABSTRACT

We calculated the adsorption of SO₄ on h-BN and Pd on SO₄ adsorbed on h-BN by using first-principles calculations based on density-functional theory.

Six stable configurations were found for SO₄/h-BN, in which three O atoms of the SO₄ molecule bond to the h-BN surface. The adsorption energy of SO₄ to h-BN is 1.46 eV. When a Pd atom is added, Pd binds chemically to two O atoms of the SO₄. The stable position of Pd is located between the two O atoms and on top of the bridge site of h-BN. The B–O bond length near Pd is longer than that in SO₄/h-BN without Pd due to hybridization of the Pd orbital and the O orbital. This means that the B–O bond may be broken when Pd is present. Our results are highly valuable for experimentalists using h-BN as a catalyst substrate.

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1. Introduction

Isolated hexagonal boron nitride (h-BN) monolayers, consist of a well known two-dimensional (2D) honeycomb arrangement linked by sp² hybridized B–N bonds similar to graphene, but with carbon atoms replaced by alternating boron and nitrogen atoms, are and the basic material used to form nanotubes. Graphite and h-BN are two-dimensional planar layer structures and have no chemical bonding among the layers. Thus it is very reasonable to calculate it as a cluster model of monolayers. The most common phase of BN is known to be a very good electrical insulator with good thermal conductivity and stability. In recent theoretical study [1–5], the adsorption sites and adsorption energies for some atomic species and molecules have been reported. These studies introduced the adsorption mechanism, atomic structures, stability, migration barrier energies and electronic properties of the adatom system on graphene and h-BN plane for the most species using the density functional theory. The migration energies and adsorption energies of each atom are very small. Therefore, h-BN may be used as substrate for Pd catalyst.

Recently, Arisawa et al. [6,7] found that SO₄ exist on gold surfaces after a Piranha treatment [8] during a process of making a

Pd catalyst. The Piranha treatment had been traditionally used to remove organic residues from gold surfaces [9–14] and to make self-assembled monolayers (SAMs) of alkylthiols (RSH) on metal surfaces [9–15]. When the SO₄ group stays on the gold surface, it might have a huge effect on generating nano particles on the substrate [7]. Such nanoparticles are known as effective catalysts for chemical transformations due to their large surface area. However, unfortunately, most of metals are not a tolerable substrate during Piranha treatment. It means that we should look for non-metal substrate for such catalyst, because gold substrate is too expensive. The reason for the selection of gold as substrate is that gold is not dissolved during piranha treatment. The h-BN can also be the candidate for a substrate for this type of catalysis, because h-BN is not dissolved by sulfuric acid [16]. Moreover, h-BN is far cheaper than gold.

In this study, we have carried out first-principles calculations based on the density-functional theory for SO₄/h-BN and (Pd&SO₄)/h-BN, to explore the implications of Piranha treatment for h-BN, since h-BN is conceived as a possible substrate for a Pd catalyst. We further propose a new Pd catalyst that is a Pd catalyst on h-BN. Before we propose the new Pd catalyst using a h-BN substrate, we will discuss how SO₄ exists around Pd on h-BN. For this purpose, we calculated the stable position, adsorption energy and electronic charge of SO₄ and Pd on h-BN.

2. Models

In this study, we used a first-principles band calculation technique based on density functional theory (DFT) [17,18] using the pseudopotential plane-wave method. The calculations were

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^{*} Corresponding author. Present address: Department of Applied Mathematics and Physics, Tottori University, 4-101 Koyama-Minami, Tottori 680-8550, Japan. Tel.: +81 857 31 5629.

E-mail address: m-yokoyama.lab3@damp.tottori-u.ac.jp (M. Yokoyama).

performed with the Vienna Ab-initio Simulation Package (VASP) [19–22]. We adopted the local density approximation (LDA) [23] with the usage of the Perdew and Zunger parameterization [24] as the term exchange correlation with a cutoff energy of 500 eV. Ion cores were modeled with projector augmented wave (PAW) potentials [25,26]. All calculations were carried out nonmagnetically in an initial stage. As a first step of this work, we set the unit cell for the h-BN sheet to a 3×3 structure for in order to explore dense SO_4 on h-BN. The sampling of the Brillouin zone was done using a $6 \times 6 \times 1$ Monkhorst–Pack grid [27], which was given by the convergence results from energy vs k -points. For the calculation of the density of states (DOS), we use a $18 \times 18 \times 1$ Monkhorst–Pack grid. The h-BN was simulated by a (3×3) super cell with a repeated slab model by a vacuum region of 15 Å between adjacent h-BN layers to avoid artificial interactions. We use a calculated h-BN lattice constant of 2.49 Å, which is slightly smaller than the experimental value of 2.50 Å. One edge atom of the 3×3 structure of the h-BN is fixed during the relaxation. Geometry optimizations were stopped when all the forces (of the degree of freedom set in the calculation) were smaller than 0.01 eV/Å. The charges for the SO_4 molecule and h-BN were calculated according to the Bader charge method [28].

3. Results

3.1. Stable structure of $\text{SO}_4/\text{h-BN}$ and $\text{Pd}/\text{SO}_4/\text{h-BN}$

First, we examined the stable configurations for the $\text{SO}_4/\text{h-BN}$, without Pd. We set eight configurations as starting structure for the structural optimization in the DFT calculations. The adsorption sites for SO_4 are the bridge site (B site), hollow site (H site) and top site (T site) as shown in Fig. 1. The configuration (B) and configuration (D) were stable at configuration (H) and configuration (G) after structural optimization, respectively. The other adsorption sites were not changed from the initial structure.

The starting structures, final structures and adsorption energies are shown in Table 1. From Table 1, it can be seen that the structures of SO_4 adsorbed on h-BN converge with the configurations (A, C, E–H), and the adsorption energy values of the configurations (A, C, E–H) are 1.14, 1.04, 1.05, 1.03, 1.07 and 1.46 eV, respectively. We have calculated the adsorption energy of the molecule (E_{ad}) defined by

$$E_{\text{ad}} = (E_{\text{h-BN}} + E_{\text{mol}}) - E_{\text{tot}}$$

where E_{ad} is the binding energy of the adsorbed atom to the h-BN sheet. E_{tot} is the total energy of the system per cell. $E_{\text{h-BN}}$ and E_{mol} are that of the isolated h-BN in the super cell and that of an isolated molecule, respectively. We defined that the positive values of

Table 1

Summary of the test structures and resulting adsorption energies for SO_4 adsorbed on h-BN.

Starting structure	Final structure	Adsorption energy (eV)
Configuration (A)	Same: Configuration (A)	1.14
Configuration (B)	Configuration (H)	1.46
Configuration (C)	Same: Configuration (C)	1.04
Configuration (D)	Configuration (G)	1.07
Configuration (E)	Same: Configuration (E)	1.05
Configuration (F)	Same: Configuration (F)	1.03
Configuration (G)	Same: Configuration (G)	1.07
Configuration (H)	Same: Configuration (H)	1.46

adsorption energy indicated exothermic process. According to the calculated adsorption energies, the most stable configuration can be determined, which is configuration (H). In this configuration, three O atoms from the SO_4 molecule are bound to B atoms of h-BN and a fourth O atom remains unbound to h-BN. Similar structures, where adsorbed SO_4 via three O atoms to surface metal were also investigated in the case of SO_4 on Pt and Au surfaces using first principle calculations [29–32]. These results imply strong adsorption energies of SO_4 on the surface.

Next, we performed a structural optimization for Pd near the adsorbed SO_4 on h-BN. The starting configuration of adsorbed SO_4 on h-BN is the most stable structure, which is the configuration H. The starting structures for Pd on $\text{SO}_4/\text{h-BN}$ are shown in Fig. 2. From Fig. 2, we set Pd on the hollow site, which show in configurations (a–c). In the case of configurations (d, f), Pd was set on top of O atoms. The other configurations (e, g) and configurations (h, i) were set on top of B atoms and N atoms, respectively.

The most stable structure of Pd with SO_4 adsorbed on h-BN is shown in Fig. 3. The Pd atom is located between the two O atoms of SO_4 and h-BN. The binding geometric data of SO_4 adsorbed on h-B are shown in Table 2. The B–O bond lengths of $(\text{Pd}\&\text{SO}_4)/\text{h-BN}$ are 3.06, 3.56 and 3.51 Å, respectively. These values are larger compared to $\text{SO}_4/\text{h-BN}$. This means that the B–O bond between the SO_4 and the h-BN weakens due to the interaction between Pd and SO_4 . In addition, the Pd–O lengths of $(\text{Pd}\&\text{SO}_4)/\text{h-BN}$ are 1.96, 1.95 and 3.76 Å, respectively. Two O atoms from the SO_4 molecule are bound to Pd and two O atoms remain unbound to Pd. The S–N (below S) length of $(\text{Pd}\&\text{SO}_4)/\text{h-BN}$ is 3.91 Å and thus longer than in the case of $\text{SO}_4/\text{h-BN}$. It means that SO_4 is desorbed from the h-BN surface due to Pd adsorption. For this most stable configuration, the adsorption energy ($E_{\text{ad,Pd}\&\text{SO}_4}$) between SO_4 and Pd is 5.14 eV. The adsorption energy ($E_{\text{ad,Pd-SO}_4}$) is defined as

$$E_{\text{ad,Pd-SO}_4} = E_{\text{tot}} - (E_{\text{Pd}} + E_{\text{SO}_4}),$$

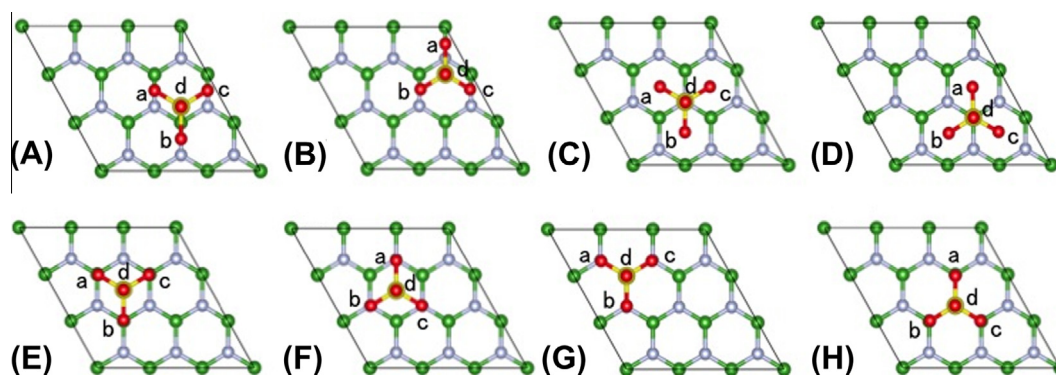


Fig. 1. Calculation models of SO_4 adsorbed on the h-BN (3×3) surface as starting structure of structural optimization in DFT calculation. The green, blue, yellow and red spheres correspond to B, N, S and O atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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