Exploration of Long-Life Pt/Heteroatom-Doped Graphene Catalysts in Hydrogen Atmosphere

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Supporting Information

ABSTRACT: We investigated the H and H2 adsorption effects on the stability of a Pt atom on various heteroatom-doped graphene supports using first-principles calculations based on density functional theory. We show that H and H2 adsorptions on the Pt atom weaken the interaction between the Pt atom and graphene support and decrease the adsorption energy of Pt atoms. H2 adsorption on Pt atoms decreases the adsorption energy of Pt atoms on all graphene supports by more than 30%, whereas H adsorption only affects pristine, O-, and S-doped graphene. These results indicate that the hydrogen atmosphere enhances the detachment of Pt catalysts. However, the B-, O-, Si-, P-doped, and monovacant graphene still maintained large adsorption energies of PtH and PtH2 of more than 1.5 eV. In addition, the diffusion barriers of PtH and PtH2 on pristine graphene were calculated to be less than 0.07 eV, which further demonstrated that H and H2 enhance the degradation of Pt catalysts. Even after H and H2 adsorptions on a Pt atom, O-, Si-, P-doped, and monovacant graphene still maintained large diffusion barriers of more than 1 eV. Therefore, we concluded that O-, Si-, and P-doped graphene are suitable supports for Pt catalysts in a hydrogen atmosphere.

1. INTRODUCTION

Recently, metal subnanoclusters, which are composed of several to tens of metal atoms, have attracted considerable attention for various applications, such as catalysts and optical materials, thanks to their unique property originating from confined electrons in molecular dimensions and discrete energy levels.1 The properties of metal subnanoclusters vary greatly with their size because the atomic and electronic structures of metal subnanoclusters are highly dependent on the number of metal atoms. For instance, Imaoka and coworkers showed that a Pt10 catalyst exhibited higher catalytic activity for a hydrogenation reaction for styrene than Pt8, Pt9, and Pt nanoparticle catalysts2 and that a Pt19 catalyst exhibited the highest catalytic activity for an oxygen reduction reaction among various size-controlled Pt subnanoclusters and bulk Pt.3 Similar to the above examples, metal subnanoclusters exhibit superb properties with specific size; it is thus critical to maintain the size of metal subnanoclusters during operation for their practical use. Thus, support materials that strongly interact with metal subnanoclusters and suppress the detachment and diffusion of metal subnanoclusters are required for their practical use. Additionally, due to their very fine size, catalytic activities of metal subnanoclusters also highly depend on the support materials.4 This indicates that properties of metal subnanoclusters can be tuned by choosing a proper support through so-called “support effects”.

Graphene is considered a promising support for metal subnanoclusters because of its high mechanical and chemical durability, relative surface area, and electron conductivity. However, the planar structure and delocalized π electrons of graphene hardly interact with adsorbates. Therefore, the detachment, diffusion, and agglomeration of metal atoms can easily occur,5 resulting in degradation of the metal subnanoclusters. It has been reported that heteroatom doping of graphene improves the durability of metal clusters on graphene.5 We previously investigated the effect of dopant dependence on the adsorption states and diffusion behavior of metal atoms, that is, Pt and Fe, and showed that dopant atoms improve the interaction between a metal atom and graphene, preventing agglomeration of metal subnanoclusters.6,7 As mentioned, properties of metal subnanoclusters highly depend on support materials; therefore, a large variety of heteroatom-doped graphene can give many options for designing catalysts.
Atmospheric gas adsorption on metal subnanocluster catalysts also enhances the degradation. It has been reported that the activity of a Pt subnanocluster catalyst on Ketjenblack gradually decreased in a H₂ environment, causing agglomeration and detachment of the subnanocatalysts. Additionally, it is well known that water gas changes the shape of Cu nanoclusters. That is, the (111) and (100) surfaces dominantly surround the Cu nanoclusters, whereas after water gas adsorbs on Cu nanoclusters, the ratios of lower index surfaces such as (100) and (110) increase. In the field of hydrogen storage, it has been reported that H atoms and H₂ decrease the interaction between a metal atom and carbon substrates, such as carbon nanotube and graphene. Therefore, even though heteroatom-doped graphene has been shown to suppress the degradation of metal subnanoclusters in vacuum, atmospheric gas adsorption may enhance the detachment, diffusion, and agglomeration of metal subnanoclusters on heteroatom-doped graphene. However, dopant dependence on the interaction between a metal atom and light-element-doped graphene in atmospheric gas is still unclear. Thus, the adsorption and diffusion properties of atmospheric gas adsorbed metal subnanoclusters on heteroatom-doped graphene should be investigated to evaluate the lifetime of catalysts under operating conditions.

In this study, we considered adsorptions of H₂ and H, which are important substances for the hydrogenation of organic compounds and oxygen reduction reactions, on a Pt atom supported on light-element-doped graphene. As a first step, we adopted the Pt atom as a catalyst to focus on the junction point between Pt subnanoclusters and heteroatom-doped graphene. Using first-principles calculations based on density functional theory (DFT), we investigated the adsorption states of H and H₂ on Pt/heteroatom-doped graphene systems and the adsorption and diffusion behaviors of PH and PtH₂ to identify suitable dopants that would prevent detachment and agglomeration of Pt subnanoclusters in the hydrogen atmosphere.

2. COMPUTATIONAL METHODS

We performed DFT calculations using the Vienna ab initio simulation package (VASP 5.4.1) and the projector-augmented wave method. We adopted the rev-vdW-DF2 exchange-correlation functional. The rev-vdW-DF2 functional is composed of a revised Becke’s exchange and the nonlocal correlation of vdW-DF2 and accurately accounts for the van der Waals interaction. The plane-wave basis set was used with an energy cutoff of 600 eV. The supercell consisted of a periodically repeated 4 × 4 graphene monolayer with a 25 Å vacuum layer. For the heteroatom-doped graphene, we considered graphene in which one of its C atoms is substituted by the heteroatom, as shown in Figure 1. The concentration of the heteroatom was 3.1 at. %, which is a reasonable value identified from previous experimental reports. To determine the dependence of the Pt adsorption and diffusion properties on the dopant used, we investigated six dopants (X), where X = B, N, O, Si, P, and S. These light-element-doped graphene supports have been observed in experiments. For comparison, we also considered monovacant graphene as a case of strongly adsorbing supports. We adopted the optimized lattice parameters of each graphene support and the most stable configurations of the Pt/graphene systems reported in our previous study. We used a 5 × 5 × 1 Γ-point centered Monkhorst–Pack grid for Brillouin zone sampling to calculate the total energy, with a Gaussian smearing σ of 0.2 eV. All the atoms were fully relaxed until the force on each atom was less than 0.02 eV/Å.

In order to investigate the hydrogen adsorption effects on Pt adsorption states, we also introduced one H atom or H₂ molecule in the supercell. Figure 2 shows the initial adsorption sites of H and H₂ on each Pt/graphene system. For the H₂ molecule, we considered two directions of the molecular axis of the H₂ molecule, that is, perpendicular and parallel to the graphene basal plane, as shown in Figure 3. The initial distance between hydrogen adsorbates from a single Pt atom was set to 2 Å. We defined the adsorption energies of H E_ads(H) and H₂ E_ads(H₂) on Pt/X-doped graphene using the following equations.

![Figure 1](image1.png)

Figure 1. Schematic illustration of 4 × 4 supercell of heteroatom-doped graphene. The brown and blue balls denote C atoms and heteroatoms, respectively.

![Figure 2](image2.png)

Figure 2. Initial adsorption structure for a H atom and a H₂ molecule on a Pt atom for (a) pristine, (b) B-doped, (c) N-doped, (d) O-doped, (e) Si-doped, (f) P-doped, (g) S-doped, and (h) monovacant graphene. The black points denote the position of the H atom and the center of the H₂ molecule axis. The brown, green, white, blue, and silver balls represent C, B, N, Si, and Pt atoms, respectively.

![Figure 3](image3.png)

Figure 3. Schematic illustration of the initial structure of H₂ molecule: (a) direction of axis of H₂ molecule perpendicular to Pt atom and (b) direction of axis of H₂ molecule parallel to Pt atom.
where $E_{\text{X}(\text{gra})}$, $E_{\text{X}H}$, and $E_{\text{X}H_2}$ are the total energies of isolated X-doped graphene, PtH, and PtH$_2$, respectively.

We calculated the diffusion barriers of PtH and PtH$_2$ on pristine graphene using a climbing image nudged elastic band (CI-NEB) method. For heteroatom-doped graphene, it has been reported that the potential energy change through diffusion of a single Pt atom changes monotonically with the distance from the dopants and that the diffusion barrier of a single Pt atom is nearly identical to the adsorption energy differences between the corresponding heteroatom-doped graphene and pristine graphene. Thus, we defined the diffusion barriers of PtH and PtH$_2$ on heteroatom-doped graphene in this manner.

To compensate for the dipole–dipole interaction between graphene layers, a dipole moment correction was incorporated. We used Visualization for Electronic and Structure Analysis (VESTA) to visualize the atomic models and electron density distributions.

3. RESULTS AND DISCUSSION

3.1. Single Pt Atom Adsorption States on Heteroatom-Doped Graphene. We revisited the adsorption states of a single Pt atom on pristine and heteroatom-doped graphene using the rev-vdW-DF2 functional. Figure 4 shows the most stable adsorption sites of the single Pt atom on pristine and heteroatom-doped graphene. From Figure 4, a single Pt atom tends to adsorb on low coordination sites such as top and bridge sites. We note that the most stable adsorption configurations do not change whether the conventional PBE functional or rev-vdW-DF2 was used. Figure 5 shows the adsorption energy of a single Pt atom on pristine graphene and each heteroatom-doped graphene support. We note that the adsorption energy of a single Pt atom on monovacant graphene is approximately the same as the previous report. As shown in Figure 5, the Pt atom adsorbs more stably on heteroatom-doped graphene than on pristine graphene. In particular, O-, Si-, P-, S-doped, and...
monovacant graphene exhibit high adsorption energy of a single Pt atom. The adsorption energy calculated using the rev-vdW-DF2 functional was approximately 0.3 eV larger than that calculated using the PBE functional. The energy difference corresponds to more than 10% of the corresponding adsorption energy in the cases of weak adsorbed Pt/graphene, that is, pristine, B-doped, and N-doped graphene. However, the chemical bonding behaviors determined using the PBE and rev-vdW-DF2 functionals correspond well to each other. Therefore, the origin of the adsorption energy difference is the London dispersion interaction.

In Figure 6, the electron density distributions are used to briefly explain why O-, Si-, P-, and S-doped graphene exhibit high negative adsorption energies for a Pt atom. Figure 6a−c shows that the Pt atom does not interact with the pristine, B-doped, and N-doped graphene strongly because of the delocalized π orbital of graphene. Thus, the pristine, B-doped, and N-doped graphene exhibit low adsorption energy for the Pt atom. For O-doped graphene, the valence number of the O atom is six; thus, one of the C atoms near the O atom has a dangling bond. In addition, a Pt atom also has a covalent bond with a C atom adjacent to an O atom, which has an sp³-like orbital because of its bending structure of C−C−O. Therefore, a Pt atom strongly bonds with O-doped graphene. For Si-, P-, and S-doped graphene, Si, P, and S atoms protrude from the basal graphene surface because the atomic radii of Si, P, and S are much larger than the atomic radius of C. Therefore, there is a dangling sp³ orbital around the Si, P, and S atoms and Pt atom that can strongly bond with the Pt atom. We note that the sp³ dangling bond orbitals are nearly unoccupied, half-filled, and fully occupied in Si-, P-, and S-doped graphene, respectively. Monovacant graphene shows the highest adsorption energy for a Pt atom thanks to its dangling bonds of adjacent three C atoms. More details about the adsorption states of a single Pt atom on pristine and heteroatom-doped graphene are provided in our previous report.

3.2. Effect of H Atom on Pt Adsorption States on Heteroatom-Doped Graphene. In this section, we focus on the effect of H adsorption on Pt adsorption and the diffusion properties on pristine and heteroatom-doped graphene. First, we investigated the most stable adsorption states of PtH on pristine and heteroatom-doped graphene. Figure 7 shows the adsorption energies of PtH and H atoms; the adsorption energies largely decrease with H adsorption for pristine, O-doped, and S-doped graphene, where the decrease ratios are more than 30%. In the case of monovacant graphene, the adsorption energies of PtH and H atoms are −6.32 and −2.87 eV, respectively. These results indicate that H adsorption on a Pt atom weakens the interaction between Pt atoms and the graphene support and enhances the detachment of Pt catalysts. We note that the adsorption energies of H atoms are larger than those of PtH except for the cases of O-doped and monovacant graphene and, therefore, the detachment of PtH occurs before H desorption. From the viewpoint of H adsorption energy, H adsorption energy varies depending on the support material. Adsorbate adsorption energies are crucial factors for catalytic reactions and hydrogen storage materials. Thus, this may indicate that appropriate combinations of the Pt atom and modified graphene realize both durability and good performance for various applications.
Figure 8 shows the most stable adsorption configurations of PtH on pristine and heteroatom-doped graphene. Comparison of Figures 4 and 8 reveals that H adsorption on Pt atoms increases the bond length between Pt atoms and pristine and B-, N-, and S-doped graphene. For Si-doped graphene, Pt atoms move to Si on-top sites after H adsorption because the H atom breaks the bonding between a Pt atom and a C atom adjacent to a Si atom. In addition, before H adsorption on a Pt...
atom on O-doped graphene, the Pt atom strongly bonds with a C atom, as shown in Figure 6d. However, after H adsorption, the bond length between Pt and C atoms increases, as shown in Figure 8d. This longer bond length also indicates that H atoms decrease the interaction between Pt atoms and the graphene support and enhance the detachment of Pt catalysts.

Next, we discuss the interaction in PtH/X-doped graphene systems. Figure 9 shows the electron density distributions around a Pt atom on pristine and each heteroatom-doped graphene. For pristine graphene, comparison of Figures 6a and 9a reveals that a Pt atom bonds with two C atoms through a covalent bond before H adsorption; however, the electron density between Pt and one of the C atoms decreased after H atom adsorption. However, the Pt atom bonds with a H atom through a strong interaction, as observed in Figure 9a, which indicates that the Pt atom prefers to bond with a H atom and break the interaction with the C atom. To more precisely analyze the chemical bonding of Pt/graphene systems, we also obtained the projected density of states (PDOS), as shown in Figures S1a and S2a. In Figure S2a, a clear peak corresponding to the covalent bond between Pt and H atoms is observed in the energy range of −5 to −3 eV, and the peak corresponding to the covalent bond between Pt and C2 in the energy range of −8 to −7 eV in Figure S1a disappears. This result also indicates that one of two covalent bonds between Pt and graphene is broken by H adsorption. This mechanism can be understood as follows. The electron configuration of the Pt atom is [Xe]4f145d96s1, which indicates that the neutral Pt atom has two unoccupied electron orbitals and can form covalent bonds with at most two atoms. In addition, a Pt atom cannot form strong covalent bonds with pristine graphene because of the delocalized π electrons of graphene. Therefore, the Pt atom forms a strong Pt−H covalent bond and a weak Pt−C covalent bond after H adsorption, and the adsorption energy of PtH on pristine graphene greatly decreases.

For B-doped graphene, the electron density distribution between the Pt atom B-doped graphene slightly decreases after H adsorption, as observed in Figures 6b and 9b. For N-doped graphene, we observed that the electron density distribution between the Pt atom and C2 atom, which is not adjacent to an N atom, decreases. These results indicate that a H atom also weakens the interaction between a Pt atom and B- and N-doped graphene, similar to the case for pristine graphene. We note that the electron transfer from the C atom to a neighboring N atom occurs because of the difference in electron negativity. Therefore, a C atom adjacent to a N atom becomes an active site,33 and the reduction of the adsorption energy of Pt/N-doped graphene is smaller than that of pristine graphene. We also determined the PDOS of B- and N-doped graphene to further investigate the adsorption states of a single Pt atom and PtH. As observed in Figure S1b,c, the peaks of the C atom of B-doped graphene and C atoms of N-doped graphene are in energy ranges of −5 to −1 and −9 to −3 eV, respectively. These peaks can be assigned to bonding orbitals as peaks of Pt d orbitals in the same energy range. As shown in Figure S2b,c, we observed that there are definitive peaks of covalent bonds between Pt and H atoms in the energy range of −6 to −4 eV for B-doped graphene and in the energy range of −5 to −3 eV for N-doped graphene. These electrons contributed to form covalent bonds between Pt and graphene before H adsorption. These results indicate that the Pt atom prefers to bond with a H atom, which results in the weak
interactions of Pt/B- and N-doped graphene. As previously mentioned, the origin of these trends is the weak covalent bonds between Pt atoms and B- and N-doped graphene, which have a planar structure. Therefore, the H atom decreases the adsorption energy of the Pt atom on B- and N-doped graphene.

For Si-doped graphene, as previously mentioned, PtH adsorbs at the top of the Si atom. This behavior is also observed because a Pt atom prefers a strong covalent bond with a H atom instead of a weak covalent bond with a C atom. Pt atoms form covalent bonds with Si-doped graphene through the active sp³ dangling bond of Si atoms after H adsorption. A clear peak of Pt dₓᵧ−Si pₓ covalent bonds is observed in the energy range of −5 to −3 eV in the PDOS, as shown in Figure S2c. Therefore, the large adsorption energy of PtH on Si-doped graphene is maintained after H adsorption, even though the Pt atom loses the covalent bond with a C atom. For P-doped graphene, Figure 9f shows the large electron density of Pt and adjacent C atoms after H adsorption, which indicates that PtH and P atoms maintain strong interaction similar to the case of a single Pt atom adsorption. Pt atoms form covalent bonds with P-doped graphene through the active sp³ dangling bond of P atoms similar to the case of Si-doped graphene. Clear peaks corresponding to the covalent bonds of Pt dₓᵧ−H s orbitals and Pt dₓᵧ−P pₓ orbitals are observed in the energy range of −6 to −5 eV in Figure S2f. Therefore, P-doped graphene also exhibits a large adsorption energy of PtH.

For O- and S-doped graphene, the adsorption energy of a Pt atom decreases more than 30% through H adsorption, which is larger than those of other heteroatom-doped graphene supports. For O-doped graphene, a Pt atom forms a strong covalent bond with C atoms before H adsorption. Figure S2d shows that the antibonding orbital of Pt−C adjacent to an O atom is partially occupied after H adsorption, whereas the orbital lies just above the Fermi level before H adsorption, as observed in Figure S1d. Therefore, the interaction between a Pt atom and O-doped graphene weakens through H adsorption, resulting in a large reduction of the adsorption energy. For S-doped graphene, the Pt d orbital is fully occupied through a coordinate bond with the fully occupied sp³ orbital of a S atom before H adsorption. After H adsorption, as previously mentioned, PtH only has one half-filled orbital, which results in weakening of the coordinate bond between Pt and S atoms. In addition, bonding and antibonding peaks between Pt and H atoms are observed in energy ranges of −3 to −2 and −1 to 0.5 eV, respectively, in Figure S2g. Because of the slight electron donation from the fully occupied sp³ orbital of a S atom, the antibonding orbital of Pt−H atoms is partially occupied, which results in weakening of the covalent bond between Pt and H atoms. These findings indicate that the adsorption energy of PtH is smaller than that of a single Pt atom.

For monovacant graphene, the Pt atom keeps its high adsorption energy after H adsorption because of strong interaction between the Pt atom and monovacant graphene as shown in Figure 9h. Compared to Figures S1h and S2h, the PDOS of Pt and adjacent C atoms show only slight changes through H adsorption, which means that H atoms do not change the adsorption states of the Pt atom on monovacant graphene. In addition, Figure S2h shows the PDOS of an H atom on Pt/monovacant graphene does not show clear peaks indicating Pt−H bonds. This shows that H atoms weakly interact with the Pt atom on monovacant graphene because the Pt atom prefers forming strong covalent bonds with dangling bonds in monovacant graphene. Thus, PtH shows large adsorption energy on monovacant graphene.

3.3. Effect of H2 Molecule on Adsorption States of a Pt Atom on Heteroatom-Doped Graphene. In this section, we focus on the effect of H2 adsorption on the adsorption states of a Pt atom on pristine and heteroatom-doped graphene. First, we investigated the most stable adsorption configuration and corresponding adsorption energies of PtH2 and H2. Figure 10 shows the adsorption energies of PtH2 on pristine and all the heteroatom-doped graphene supports, which are smaller than those of a single Pt atom. In the case of monovacant graphene, the adsorption energies of PtH2 and H2 are −4.77 and −0.14, respectively. These findings indicate that H2 adsorption on a Pt atom weakens the interaction between Pt and the graphene supports and enhances the detachment of Pt catalysts. However, for O-, Si-, P-, S-doped, and monovacant graphene, the adsorption energy of H2 was smaller than that of PtH2, indicating that desorption of the H2 molecule occurs preferentially compared with detachment of Pt atoms. Therefore, O-, Si-, P-, S-doped, and monovacant graphene are promising supports for preventing the detachment of Pt subnanoclusters in environments containing H2 molecules, whereas H2 adsorption enhances the degradation of Pt catalysts on pristine, B-doped, and N-doped graphene. Similar to the case of H adsorption on Pt atom, H2 adsorption energy varies depending on the support material. Therefore, these results also indicate that appropriate combinations of the Pt
atom and modified graphene realize both durability and good performance for various applications.

Figure 11 and Table 1 show the most stable adsorption configuration of PtH2 and the bonding distances of H2 on pristine and heteroatom-doped graphene, respectively. The results indicate that there are two types of H2 adsorption, that is, molecular and dissociative adsorption, depending on the graphene supports. For pristine and B-, N-, and Si-doped graphene, dissociative adsorption after structural relaxation is observed, whereas molecular adsorption is observed for the O-, P-, S-doped, and monovacant graphene. We note that the dissociative adsorption of H2 molecules also occurs on an isolated Pt atom. Comparison of Figures 4 and 11 reveals that the dissociatively adsorbed H2 molecule elongates the bond distance between Pt atoms and graphene except for Si-doped graphene. For O-, P-, and S-doped graphene, spontaneous dissociation of the H2 molecule does not occur; however, the intramolecular bond distance of the H2 molecule is lengthened, as shown in Table 1. We also calculated the dissociative adsorption states of H2 on Pt/O-, P-, S-doped, and monovacant graphene using CI-NEB methods. Table 2 lists the adsorption energies of PtH2 with H2 molecular and dissociative adsorption. The adsorption energy of PtH2 with H2 dissociative adsorption is nearly identical to that with molecular adsorption except for O-doped graphene. This

Table 1. Bonding Distances between Two H Atoms in the Most Stable Adsorption Configuration on Each Pt/Heteroatom-Doped Graphene

| system                        | bond distance (Å) |
|-------------------------------|-------------------|
| isolated H2                   | 0.75              |
| isolated PtH2                 | 2.07              |
| PtH2/pristine graphene        | 1.84              |
| PtH2/B-doped graphene         | 1.96              |
| PtH2/N-doped graphene         | 1.86              |
| PtH2/O-doped graphene         | 0.85              |
| PtH2/Si-doped graphene        | 1.76              |
| PtH2/P-doped graphene         | 0.85              |
| PtH2/S-doped graphene         | 0.87              |
| PtH2/monovacant graphene      | 0.84              |

Figure 11. Most stable configurations of Pt atom with H2 on (a) pristine, (b) B-doped, (c) N-doped, (d) O-doped, (e) Si-doped, (f) P-doped, (g) S-doped, (h) monovacant graphene, and (i) isolated Pt with H2 in vacuum. The brown, green, white, red, blue, purple, yellow, silver, and pink balls represent C, B, N, O, Si, P, S, Pt, and H atoms, respectively. The corresponding bonding distances between Pt and the coordinated atoms are also shown.
means that whether dissociation of H$_2$ occurs on Pt/P-, S-doped, and monovacant graphene or not, the stabilities of a Pt atom on these graphene do not change so much. In addition, Table 2 shows that the H$_2$ dissociative adsorption states on Pt/O-doped graphene are much unstable than that of H$_2$ molecular adsorption states and the activation barrier of H$_2$ dissociation on Pt/O-doped graphene is larger than the desorption energy of a H$_2$ molecule. These results indicate that detachment of H$_2$ preferentially occurs over H$_2$ dissociation on Pt/O-doped graphene. Therefore, we concluded that H$_2$ molecularly adsorbs on Pt/O-doped graphene. We investigated the detailed interaction between PtH$_2$ and the graphene support by examining the electron density distribution and PDOS. For pristine graphene, Figure 12a shows that the electron density between Pt and C atoms is reduced by approximately 30% through the H$_2$ adsorption. It can be considered that the Pt atom breaks the two weak interactions between C atoms and forms two covalent bonds with two H atoms, resulting in an electronic closed shell structure for the same reason as for H atom adsorption. In the PDOS in Figure S3a, there is a distinctive peak corresponding to covalent bonds between Pt and C atoms in the energy range of $-$6 to $-$4 eV and the peak corresponding to the covalent bond between a Pt atom and pristine graphene is diminished. These results indicate that a Pt atom forms covalent bonds

| support  | adsorption energy of PtH$_2$ (eV) | dissociative adsorption energy (eV) | activation barrier (eV) |
|----------|-----------------------------------|-------------------------------------|-------------------------|
| O-doped  | −2.25                             | −1.12                               | 1.57                    |
| P-doped  | −1.90                             | −1.81                               | 0.21                    |
| S-doped  | −1.34                             | −1.43                               | 0.11                    |
| monovacant | −4.95                             | −4.97                               | 0.19                    |

Figure 12. Electron density distributions of (a) pristine graphene around a Pt atom with a H$_2$ molecule, (b,c) B-doped graphene around a Pt atom with a H$_2$ molecule, (d) N-doped graphene around a Pt atom with a H$_2$ molecule, (e,f) O-doped graphene around a Pt atom with a H$_2$ molecule, (g,h) Si-doped graphene around a Pt atom with a H$_2$ molecule, (i) P-doped graphene around a Pt atom with a H$_2$, (j) S-doped graphene around a Pt atom with a H$_2$ molecule, and (k) monovacant doped graphene around a Pt atom with a H$_2$ molecule. The contour interval is 0.1 e/Å$^3$. 

DOI: 10.1021/acsomega.9b00750
ACS Omega 2019, 4, 6573–6584
with H atoms using the electrons that have been contributed for Pt–C bonds. Therefore, the adsorption energy of PtH₂ greatly decreases compared with that of a single Pt atom. For B- and N-doped graphene, Figure 12b−d shows that the electron density between a Pt atom and B- and N-doped graphene is also reduced by approximately 40% through the H₂ adsorption, which originates from the electronic closed shell structure of PtH₂ similar to the case of pristine graphene. The PDOS in Figure S3b,c show that there is no peak of interaction between a Pt atom and B- and N-doped graphene, whereas there are distinctive peaks of Pt–H covalent bonds in the energy region of −5 to −4 eV for both doped-graphene supports. Therefore, the H₂ molecule also largely decreases the adsorption energy of a Pt atom on B- and N-doped graphene.

For Si-doped graphene, dissociative adsorption of the H₂ molecule also occurs. Comparing Figures 6e and 12g, we observed that although the H₂ molecule decreases the electron density between Pt and C atoms, the electron density between Pt and Si atoms remains the same as the case without H₂ adsorption. In Figure S3e, the corresponding clear peaks of Pt dₓz−H s and Pt dₓz−Si pₓ bonds are observed in energy ranges of −6 to −5 and −4 to −3 eV, respectively. However, the peak of Pt–C covalent bonds is diminished. These results indicate that H₂ adsorption weakens the interaction between the Pt atom and Si-doped graphene; however, the Pt atom still maintains the strong interaction with the Si atom. This behavior occurs because the Si atom has a nearly fully unoccupied electron orbital and PtH₂ can adsorb on Si-doped graphene through the coordinate bond. Therefore, Si-doped graphene exhibits a large adsorption energy of more than 2 eV in the H₂ atmosphere.

Figure 12f,i−k shows that a Pt atom on O-, P-, S-doped, and monovacant graphene interacts weakly with H₂, whereas a high electron density is maintained between a Pt atom and O-, P-, S-doped, and monovacant graphene. Comparing the corresponding PDOS in Figures S1d,f,g and S3d,f,g, we observe that the peaks of the interaction between a Pt atom and O- and P-doped graphene, which are in energy ranges of −6 to −4 and −5 to −3 eV, respectively, become weaker than those without H₂ adsorption and the peaks of bonding between a Pt atom and H₂ appear. For S-doped graphene, no peaks assigned to Pt–S bonds are observed because the PtH₂ cannot accept the lone pair of S atoms. Therefore, the adsorption energy of a Pt atom on S-doped graphene decreased more than that on O- and P-doped graphene. As previously mentioned, the Pt atoms on O-, P-, and S-doped graphene are close to having a closed shell structure through the covalent and coordinate bonds, which leads the Pt atoms to be inert. Therefore, H₂ cannot dissociate at the Pt atoms on O-, P-, and S-doped graphene.

For monovacant graphene, the electron density distributions shown in Figure 12k and PDOS shown in Figure S3h show that a Pt atom forms strong covalent bonds with monoatomic graphene even after H₂ adsorption and weak covalent bonds with H₂. This is because the covalent bonds through the dangling bonds of adjacent C atoms are very stable and a Pt atom prefers forming covalent bonds with monovacant graphene. Thus, monovacant graphene shows large adsorption energy of PtH₂.
3.4. Effect of H and H$_2$ on Diffusion Behavior of a Pt Atom on Heteroatom-Doped Graphene. Finally, we discuss the diffusion behaviors of PtH and PtH$_2$ on pristine and heteroatom-doped graphene. Figure 13a,c shows the potential energy change through diffusion of PtH and PtH$_2$ on pristine graphene determined using CI-NEB methods. We observed that H and H$_2$ adsorptions decrease the diffusion barrier of the Pt atom, whose value is less than 0.07 eV, while the diffusion barrier of a single Pt atom on pristine graphene is 0.15 eV. These results indicate that Pt subnanoclusters on pristine graphene agglomerate rapidly in a hydrogen atmosphere even at room temperature. Therefore, pristine graphene is not a suitable support. Figure 13b,d shows the electron density distributions of PtH and PtH$_2$ at the transition states, respectively. The Pt atoms have weak chemical bonds with C atoms at the diffusion transition states, whereas the interaction of Pt–H is strong. These trends do not change from the most stable adsorption configurations, and therefore, smaller adsorption energy with a relative increase of the significance of van der Waals interactions results in the smaller potential corrugation. We note that our previous reports$^{6,7}$ also showed that the diffusion barriers of metal atoms on graphene supports are proportional to their adsorption energy of a metal atom. Thus, H atom and H$_2$ adsorption decrease the diffusion barrier of a Pt atom. Figure 14 shows the corresponding diffusion barriers of PtH and PtH$_2$ on each heteroatom-doped graphene. In the case of monovacant graphene, the diffusion barriers of Pt, PtH, and PtH$_2$ are 5.51, 5.25, and 3.73 eV, respectively. The diffusion barriers of a Pt atom decreased on all the graphene supports considered in this study because of the larger decrease of the adsorption energy on heteroatom-doped graphene caused by H and H$_2$ adsorptions than that on pristine graphene. However, O-, Si-, P-doped, and monovacant graphene exhibited high diffusion barriers of PtH and PtH$_2$ of more than 1 eV. We note that the corresponding Boltzmann factors of PtH$_2$ diffusion on O$_x$, Si$_x$, P-doped, and monovacant graphene at 100 °C are $10^{-12}$ order smaller than the one on pristine graphene. Therefore, from the viewpoints of the adsorption energy and diffusion barrier, O-, Si-, P-doped, and monovacant graphene are promising supports for Pt subnanoclusters in a hydrogen atmosphere.

4. CONCLUSIONS

In this study, we investigated the effect of a H atom and H$_2$ molecule on the adsorption states and diffusion behaviors of a single Pt atom on pristine and heteroatom-doped graphene using first-principles calculations based on DFT. As a result, we revealed that effects of H and H$_2$ on Pt adsorption states on graphene supports highly depend on the dopant species. We observed that heteroatom doping of graphene increases the interaction between a Pt atom and the graphene support. However, when a H atom or H$_2$ molecule adsorbs on a Pt atom, the interaction between the Pt atom and graphene support is weakened because the Pt atom prefers to form covalent bonds with H or H$_2$ rather than with graphene. Therefore, H and H$_2$ adsorptions on the Pt atom weaken the interaction between the Pt atom and graphene support and decrease the adsorption energy of Pt atoms. We revealed that H$_2$ adsorption on Pt atoms decreases the adsorption energy of Pt atoms on all the graphene supports studied by more than 30%, whereas H adsorption only affected the cases of pristine, O$_x$, and S-doped graphene. These results indicate that the hydrogen atmosphere enhances detachment of Pt catalysts. However, B-, O$_x$, Si$_x$, P-doped, and monovacant graphene still maintained large adsorption energies of PtH and PtH$_2$ of more than 1.5 eV. In addition, the diffusion barriers of PtH and PtH$_2$ on pristine graphene were calculated to be less than 0.07 eV, which indicates that H and H$_2$ enhance the diffusion and coarsening of Pt catalysts. Even after H and H$_2$ adsorptions on the Pt atom, O$_x$, Si$_x$, P-doped, and monovacant graphene still maintained large diffusion barriers of more than 1 eV. Therefore, from the viewpoints of the adsorption energy and diffusion barrier, we concluded that O$_x$, Si$_x$, P-doped, and monovacant graphene are suitable supports for Pt catalysts in a hydrogen atmosphere. Additionally, we revealed that adsorption energies of H and H$_2$ vary depending on the dopant in graphene. From these points, we believe that our findings can give many support options for designing new catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00750. Projected density of states of single Pt atom and atoms around Pt atom in each graphene, projected density of states of PtH and atoms around PtH$_2$ in each graphene (PDF).

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**ACKNOWLEDGMENTS**

This work was performed using the facilities of the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

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