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Enhanced CO tolerance of Pt clusters supported on graphene with lattice vacancies

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The adsorption of CO on Pt₄ clusters supported on graphene with lattice vacancies is studied theoretically using the first-principles calculation. Our results show that the electronic structure of the graphene-supported Pt₄ clusters is significantly modified by the interaction with carbon dangling bonds. As a result the adsorption energy of CO at a Pt site decreases almost linearly with the lowering of the Pt d-band center, in analogy with the linear law previously reported for CO adsorption on various Pt surfaces. An exceptional behavior is found for Pt₄ supported on graphene with a tetravacancy, where CO adsorption is noticeably weaker than predicted by the shift in the d-band center. Detailed electronic structure analyses reveal that the deviation from the linear scaling can be attributed to lack of Pt d states near the Fermi level that hybridize with CO molecular orbitals. The weakening of CO adsorption on the Pt₄ clusters is considered as a manifestation of the support effect of graphene, and leads to the enhancement of CO poisoning tolerance that is crucial for developing high-performance Pt cluster catalysts.

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I. INTRODUCTION

The extraordinary electronic and structural properties of graphene hold considerable potential for a wide variety of industrial applications. Among them, one of the most promising candidates is the application of graphene as a support material for metal nanoparticle catalysts. While platinum (Pt) supported on carbon (C) materials has been regarded as the most practical electrocatalyst for polymer electrolyte membranes fuel cells, the position of conventional carbon support materials is now challenged by graphene, since its large specific surface area, high chemical and electrochemical stability, and high carrier mobility are well suited for a catalyst support. A great number of experiments have been carried out in the last decade (see reviews [1–11] and references therein) and it has been demonstrated that Pt supported on graphene exhibits improved catalytic activity [12], durability [13], and carbon monoxide (CO) tolerance [12] as compared with on carbon black. In particular, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) has revealed the existence of extraordinarily small Pt clusters on graphene, suggesting a possible contribution of these clusters to the high catalytic performance [12,14]. In addition, more recent HAADF-STEM measurements have even observed single Pt atoms dispersed on undoped [15,16] and nitrogen-doped [17] graphene, which show high catalytic activities and CO tolerance. Theoretically, on the other hand, first-principles calculations based on density functional theory (DFT) have been performed extensively to clarify the properties of graphene-supported Pt clusters from viewpoints of geometric [18–34] and magnetic [35–44] structures, molecular adsorptions [45–50], CO tolerance [51–54], and catalytic reactions such as CO oxidation [55–60], decomposition of O₂ [61] and methanol [62], and reduction of O₂ [63–65] and CO₂ [66]. However, the fundamental mechanism of the support effect of graphene has yet to be clarified.

In this work, we shed light on the physical aspects of the support effect of graphene on Pt clusters, with a special emphasis on CO adsorption. We perform DFT calculations of a Pt₄ cluster supported on graphene with a lattice vacancy, in which the interaction with C dangling bonds is expected to exert a significant impact on the electronic structure of Pt₄. Our results show that the center of the d band is lowered dramatically for Pt atoms near the vacancy, on which CO adsorption is weakened. Intriguingly, the CO adsorption energy decreases almost linearly with the lowering of the d-band center, indicating that the linear law previously reported for various Pt surfaces [67] is also applicable to graphene-supported Pt clusters. However, the CO adsorption energy on Pt₄ supported on graphene with a tetravacancy turns...
out to be exceptionally small relative to the corresponding
\(d\)-band center, suggesting that the \(d\)-band center alone is not
sufficient to describe the whole trend of CO adsorption on
graphene-supported Pt clusters. To address the problem, we
propose overlap population (OP) as a more useful descriptor,
on which the CO adsorption energy displays a roughly linear
dependence, including the system with a tetravacancy. We
also derive the perturbation formula for OP, which reveals a
close relation between OP and the CO adsorption energy as
described below.

II. METHODS

The DFT calculations in the present paper are carried out
using the state [34,68] code with norm-conserving pseudo-
potentials [69]. The plane-wave basis set is used to expand
wave functions (charge density) with cutoff energy of 64 Ry
(400 Ry). Pristine graphene is modeled with a periodically
repeated \(5 \times 5\) unit cell of freestanding graphene with the
lattice constant of 2.46 Å, and \(6 \times 6 \times 1\) \(k\) points are sampled
in the Brillouin zone (BZ). A lattice vacancy is formed by
removing \(n\) C atoms with \(n = 1, 2, 3, 4\) from the pristine
graphene, and a supported Pt nanoparticle is modeled with
a tetrahedral cluster composed of four Pt atoms (Pt4). The
finite-size effect in the system with \(n = 4\) is examined by
using a \(10 \times 10\) unit cell, for which \(3 \times 3 \times 1\) \(k\) points are
sampled in the BZ. As a probe of the support effect, a CO
molecule is adsorbed on the graphene-supported Pt4 clus-
ter. The exchange-correlation energy and potential are de-
scribed within the generalized gradient approximation using
the Perdew-Burke-Ernzerhof (PBE) [70] functional, which
has been widely adopted in previous calculations of Pt clusters
on graphene [51,52,55–60]. The structure of each system is
relaxed until the atomic forces fall below \(8.24 \times 10^{-2}\) nN
(5.14 \(\times 10^{-2}\) eV/Å). Spin polarization is taken into account
for a free Pt4 cluster and graphene with an odd-numbered
vacancy, while the other systems are assumed to be spin unpolarized. A vacuum layer of 30 Å is introduced and the
effective screening medium method [71,72] is used to elim-
nate the spurious electrostatic interaction with the periodic
images.

III. RESULTS AND DISCUSSION

A. Pt4 clusters supported on graphene with lattice vacancies

The relaxed structures of graphene with lattice vacancies
are depicted in the first column of Fig. 1, where \(V_n\) stands
for graphene with \(n\) C vacancies with \(n = 0, 1, \ldots, 4\). Around
the lattice vacancies, the honeycomb lattice is reconstructed
to saturate dangling bonds by forming nonhexagonal rings.
For example, Jahn-Teller distortion breaks \(D_{3h}\) symmetry of
a monovacancy in \(V_1\) [73,74]. The formation energy of \(V_n\) is
defined as

\[ E_{\text{form}}(V_n) = E(V_n) - E(V_0) + n\mu_C, \]

where \(E(V_n)\) denotes the total energy of \(V_n\), and \(\mu_C\) is the
C chemical potential defined as the total energy of pristine
graphene \(V_0\) per C atom. The formation energies for \(V_1, V_2, V_3,\) and \(V_4\) are calculated to be 7.77, 8.10, 11.31, and
12.17 eV, respectively, which compare well with previous
calculations; see Refs. [75–77] and references therein. The
value of \(E_{\text{form}}(V_1)\) is also in agreement with the experimental
results of \(> 6.6\) eV estimated from vacancy concentration in
quenched graphite [78] and 7.3 ± 1 eV from lattice parameter
change in irradiated graphite [79].

FIG. 1. Schematic views of graphene sheets without (a) and with carbon vacancies (b)–(e), and the corresponding graphene-supported Pt4
clusters and CO adsorption structures. In the first column, crosses (×) stand for the positions of the carbon vacancies. In the second column,
inequivalent Pt atoms in each Pt4/V_n are indicated by different labels.
The formation energies of large vacancies can be reduced by removing C atoms one by one, whose energy cost is given by the difference

$$\Delta E_{\text{form}}(V_n) = E_{\text{form}}(V_n) - E_{\text{form}}(V_{n-1})$$  \hspace{1cm} (2)

$$= E(V_n) - E(V_{n-1}) + \mu_C.$$  \hspace{1cm} (3)

We plot $E_{\text{form}}(V_n)$ and $\Delta E_{\text{form}}(V_n)$ as a function of the number of C vacancies in Fig. 2, where odd-numbered vacancies still give larger $\Delta E_{\text{form}}(V_n)$ than even-numbered ones. This is because the formation of an odd-numbered vacancy is accomplished by at least one unsaturated dangling bond [75], which results in spin polarization of odd-numbered vacancies [80].

We next consider adsorption of a Pt$_4$ cluster on top of each vacancy and calculate the adsorption energy

$$E_{\text{ads}}(\text{Pt}_4/V_n) = E(\text{Pt}_4/V_n) - E(\text{Pt}_4) - E(V_n),$$  \hspace{1cm} (4)

where $E(\text{Pt}_4/V_n)$ and $E(\text{Pt}_4)$ denote the total energies of the adsorbed system Pt$_4$/V$_n$ and a free Pt$_4$ cluster, respectively. By comparing the adsorption energies for several structures, we determine the most stable adsorption structure of Pt$_4$ on each vacancy as shown in the second column of Fig. 1. On pristine graphene, a three-legged adsorption structure is in fact slightly more stable than the two-legged one shown in Fig. 1(a), with $E_{\text{ads}}$(Pt$_4$/V$_0$) = $-1.27$ and $-1.25$ eV, respectively. However, the former is destabilized upon adsorption of a CO molecule, and thus we here adopt the latter as the adsorption structure for Pt$_4$/V$_0$. In contrast to the weak adsorption on V$_0$, Pt$_4$ adsorbs more strongly on graphene with the vacancies; i.e., the Pt$_4$ adsorption energies on V$_1$, V$_2$, V$_3$, and V$_4$ are calculated to be $7.00$, $7.23$, $-10.60$, and $-11.58$ eV, respectively. Note that the Pt$_4$ adsorption energies tend to balance the large energy costs for the formation of the vacancies. Namely, if we assume that V$_n$ is formed along with the adsorption of Pt$_4$, the formation energy of Pt$_4$/V$_n$ defined as

$$E_{\text{form}}(\text{Pt}_4/V_n) = E_{\text{form}}(V_n) + E_{\text{ads}}(\text{Pt}_4/V_n)$$  \hspace{1cm} (5)

$$= E(\text{Pt}_4/V_n) - E(\text{Pt}_4) - E(V_0) + n\mu_C$$  \hspace{1cm} (6)

is much smaller than $E_{\text{form}}(V_n)$ as shown in Fig. 2, although the formation of Pt$_4$/V$_n$ is still endothermic. In analogy with Eq. (3), we also consider the difference

$$\Delta E_{\text{form}}(\text{Pt}_4/V_n) = E_{\text{form}}(\text{Pt}_4/V_n) - E_{\text{form}}(\text{Pt}_4/V_{n-1})$$  \hspace{1cm} (7)

$$= E(\text{Pt}_4/V_n) - E(\text{Pt}_4/V_{n-1}) + \mu_C,$$  \hspace{1cm} (8)

which describes the energy cost to form Pt$_4$/V$_n$ by removing a C atom from Pt$_4$/V$_{n-1}$. Although it costs large energy of 2 eV to remove the first C atom, $\Delta E_{\text{form}}(\text{Pt}_4/V_n)$ becomes even negative, i.e., $-0.17$ and $-0.12$ eV for $n = 3$ and 4, respectively, as shown in Fig. 2. This reveals that Pt$_4$ adsorbed on graphene acts as a catalyst that facilitates the expansion of lattice vacancies, justifying our models of Pt clusters supported on large vacancies. This is qualitatively consistent with the results of TEM measurements, in which Pt atoms catalyze the dissociation of C–C bonds at graphene edges [81,82]. Note that, by definition, $\Delta E_{\text{form}}(\text{Pt}_4/V_1)$ is larger than $E_{\text{form}}(\text{Pt}_4/V_1)$ by $E_{\text{ads}}(\text{Pt}_4/V_0)$, and thus forming V$_1$ along with the adsorption of Pt$_4$ is a more possible scenario for the formation of Pt$_4$/V$_1$.

**B. Local density of states projected onto the Pt d states**

To investigate the support effect of graphene on the electronic structure of Pt$_4$, we first examine the local density of states (LDOS) projected onto the d states of each Pt atom in Pt$_4$/V$_n$. The calculated LDOS ($\rho_d$) is plotted as a function of energy $\varepsilon$ measured from the Fermi level $\varepsilon_F$ in Fig. 3, where, e.g., Pt$_4$/V$_n$ in each panel stands for the Pt atom(s) labeled as A on V$_n$ in the second column of Fig 1. Special care should be taken for treating $\varepsilon_F$, since it is ill defined for the DFT calculations of gapped systems. In Fig. 3 (and Fig. 5 seen below), we determine $\varepsilon_F$ using the method as illustrated in Appendix A.

The LDOSs reflect the interactions between the Pt d states and graphene, and their trend can be captured by introducing the d-band center defined as

$$\varepsilon_d = \frac{\int \varepsilon \rho_d(\varepsilon) d\varepsilon}{\int \rho_d(\varepsilon) d\varepsilon},$$  \hspace{1cm} (9)

where the energy integral is taken from $-15$ eV to 4 eV with respect to $\varepsilon_F$. The calculated d-band centers are indicated by the vertical lines in Fig. 3, and the detailed values are summarized in Table 1. From Fig. 3(a), one can see that PtA/V$_0$ and PtB/V$_0$ have little difference in $\rho_d$, but the latter shows high peaks at slightly lower energies than the former. As a result the d-band centers of PtA/V$_0$ and PtB/V$_0$ are calculated to be $-1.64$ and $-2.39$ eV, respectively. On the other hand, PtA/V$_1$ and PtB/V$_1$ exhibit significant difference in LDOS; i.e., the peak structures are retained for the former, while the d band of the latter is broadened dramatically as shown in Fig. 3(b). The difference is due to the strong interaction between PtB and three dangling bonds of the monovacancy, which is also reflected in the d-band centers of $-1.65$ and $-4.15$ eV for PtA/V$_1$ and PtB/V$_1$, respectively. A similar difference is found between PtA/V$_2$ and PtC/V$_2$, whose d-band centers are $-1.82$ and $-4.25$ eV, respectively. The even deeper d-band center of the latter reflects the broader d band due to the interaction between PtC and four dangling bonds of the divacancy. Apparently, PtB/V$_2$ also interacts with a dangling bond, but its narrower d band with $\varepsilon_d = -2.33$ eV suggests that the d states of PtB/V$_2$ are rather close to those of PtA/V$_2$. 

**FIG. 2.** Formation energies of graphene sheets with a lattice vacancy V$_n$ (○) and graphene-supported Pt$_4$ clusters Pt$_4$/V$_n$ (□). Filled circles (●) and squares (■) correspond to the energy differences defined by Eqs. (3) and (8), respectively.
The site dependence of the LDOS can be observed more clearly for Pt\(_4\)/V\(_3\), since the highly asymmetric adsorption structure makes the four Pt atoms inequivalent [see Fig. 1(d)]. Namely, the \(d\)-band center is shifted downward monotonically as \(-1.97, -2.75, -3.48, \) and \(-3.87\) eV for Pt\(_4\)/V\(_3\), Pt\(_A\)/V\(_3\), Pt\(_C\)/V\(_3\), and Pt\(_D\)/V\(_3\), respectively, as shown in Fig. 3(d). Pt\(_C\)/V\(_3\) and Pt\(_D\)/V\(_3\) are analogous to Pt\(_B\)/V\(_3\) in that they interact with two dangling bonds of a vacancy. As a result, \(\varepsilon_d = -3.29\) eV for Pt\(_A\)/V\(_3\) is close to the \(d\)-band centers of Pt\(_C\)/V\(_3\) and Pt\(_D\)/V\(_3\). From the comparison among the four graphene-supported Pt\(_4\) clusters, one can also find that the \(d\)-band center of the topmost Pt atom is lowered monotonically with the size of the lattice vacancy. In particular, Pt\(_A\)/V\(_3\) exhibits a relatively deep \(d\)-band center of \(-2.31\) eV, despite the fact that the Pt atom has no direct bond to the tetravacancy.

**C. CO adsorption on the graphene-supported Pt\(_4\) clusters**

We next investigate the support effect of graphene on molecular adsorption. We here take CO as an example, which exhibits a relatively deep orbital contribution to Pt\(_4\)/V\(_3\), since CO adsorbs less strongly at bridge and hollow sites of a free Pt\(_4\) cluster. The calculated adsorption energies and relevant bond lengths are summarized in Table I. Comparison of the adsorption energies reveals that CO prefers to adsorb at the topmost site, i.e., Pt\(_A\), as depicted in the third column of Fig. 1, while CO gets destabilized as the adsorption site gets closer to graphene, and the adsorption at the bottom-most Pt atoms turns out to be unstable except for Pt\(_4\)/V\(_0\). The site dependence of the CO adsorption energy is closely related to the geometry of the adsorption system as shown in Figs. 4(a) and 4(b), where the adsorption energy is plotted as functions of Pt–C and C–O bond lengths, respectively, with C being the C atom in CO. Figure 4(a) clearly indicates that \(E_{ads}(CO/Pt_4/V_n)\) increases monotonically as the Pt–C bond is shortened, in agreement with the tendency that CO closer to Pt\(_4\)/V\(_n\) has larger overlap between CO molecular orbitals (MOs) and Pt \(d\) states. In contrast, Fig. 4(b) displays a monotonic increase in \(E_{ads}(CO/Pt_4/V_n)\) with the elongation of the C–O bond, suggesting that the back-donation from Pt \(d\) states to the antibonding CO \(2\sigma\) orbital contributes to the CO adsorption on Pt\(_4\)/V\(_n\). Note, however, that the contribution of the donation from the CO \(5\sigma\) orbital to Pt \(d\) states cannot be inferred from Fig. 4(b), since CO \(5\sigma\) is predominantly localized at the C atom.

In Fig. 4(c), we also plot \(E_{ads}(CO/Pt_4/V_n)\) as a function of \(\varepsilon_d\) in the spirit of the \(d\)-band model [83–85], where the nature of the \(d\) states of a metal surface is represented by \(\varepsilon_d\). Intriguingly, \(E_{ads}(CO/Pt_4/V_n)\) displays an almost linear
FIG. 4. CO adsorption energy plotted as a function of the Pt–C bond length (a), the C–O bond length (b), the \( d \)-band center (c), the total overlap population (d), and the number of Pt \( d \) states near \( \varepsilon_F \) (e). In each panel, pluses (+), crosses (×), circles (◦), triangles (△), and squares (□) correspond to the results for Pt\(_4\)/V\(_n\) with \( n = 0, 1, \ldots, 4 \), respectively. Solid, dashed, and dotted lines are drawn to guide the eye. In panel (e), the number of Pt \( d \) states near \( \varepsilon_F \) is estimated by integrating the LDOS in Fig. 3 from −0.25 eV to 0.25 eV with respect to \( \varepsilon_F \).

relation with \( \varepsilon_d \), in analogy with CO adsorbed on various Pt surfaces [67]. An exception is CO adsorbed at Pt\(_A\)/V\(_4\), whose adsorption energy deviates significantly from the linear law. It is tempting to think that the deviation is attributed to the fact that the tetravacancy is too large relative to the unit cell or that the structure of Pt\(_4\)/V\(_4\) is distorted significantly upon the adsorption of CO. However, \( E_{\text{ads}}(\text{CO}/\text{Pt}_4/\text{V}_4) \) remains almost unchanged even though the 10 × 10 unit cell is adopted, and is decreased to −1.12 eV if the geometry of Pt\(_4\)/V\(_4\) is fixed during CO adsorption, the latter of which suggests that CO adsorption is in fact stabilized by the distortion of Pt\(_4\)/V\(_4\). The deviation from the linear law indicates that the \( d \)-band center alone is not sufficient to explain the mechanism of CO adsorption on Pt\(_4\)/V\(_n\). It should be noted that \( E_{\text{ads}}(\text{CO}/\text{Pt}_4/\text{V}_4) \) is even smaller than the CO adsorption energy of −1.70 eV at the on-top site of the Pt(111) surface at 1/9 coverage. This is particularly important from an applicational point of view, since the tolerance for CO poisoning is crucial for developing high-performance metal catalysts. Our results demonstrate that the interaction with large vacancies in graphene can enhance the CO tolerance of supported Pt clusters, which has indeed been suggested experimentally as an origin of the high catalytic activity of graphene-supported Pt clusters [12,14]. Note that the graphene supports used in these experiments are expected to have lattice vacancies introduced in the preparation process of reducing graphene oxide.

D. Overlap population analysis

To gain more insight into the role of CO MOs in CO adsorption on Pt\(_4\)/V\(_n\), we finally investigate the density of states weighted by OP [86–88], often referred to as crystal
The calculated COOP curves between CO MOs and all the states of Pt₄/Vₙ are shown in Fig. 5, where positive (negative) peaks represent bonding (antibonding) states formed as a result of CO adsorption. The behavior of the COOP peaks can easily be understood from the perturbative expression for the OP-weighted density of states, i.e., Eq. (B30) in Appendix B. Among the four CO MOs considered here, low-lying 4σ and 1π have both positive and negative peaks below εₓ, which indicates that the bonding and antibonding contributions of these MOs almost cancel each other out. On the other hand, the existence of negative (positive) peaks derived from 5σ (2π) above (below) εₓ suggests that this MO contributes attractively to the CO adsorption through the donation (back-donation) processes. The latter behavior is consistent with the Blyholder model of CO adsorption on Pt surfaces [91].

The contributions of these MOs can be compared quantitatively by calculating OP per MO, which is obtained from the integral of COOP below εₓ. The calculated results for OP are summarized in Table I, which shows that 5σ contributes slightly more than 2π except for Pt₄/V₉, while the contributions from 4σ and 1π orbitals are negligibly small. More importantly, the results for 5σ exhibit a characteristic dependence on the CO adsorption site. Namely, adsorption sites farther away from graphene tend to give larger OPs except for Pt₄/V₃. In addition, OP for 5σ is largest at Pt₄/V₁, while it is relatively small at Pt₄/V₄ as compared with other topmost Pt atoms. These behaviors are quite similar to the site dependence of E_ads(CO/Pt₄/Vₙ) discussed in the previous section. On the other hand, the relation with E_ads(CO/Pt₄/Vₙ) is less clear for 2π, unlike the dependence of E_ads(CO/Pt₄/Vₙ) on the C–O bond length shown in Fig. 4(b), where the elongation of the C–O bond indicates the hybridization of 2π. Still, the OPs of 5σ and 2π tend to decrease with the size of the vacancy. In the last column of Table I, we also show the total OP for each CO adsorption structure, which retains the similarity to the CO adsorption energy. Indeed, the CO adsorption energy as a function of the total OP exhibits roughly linear dependence including CO/Pt₄/V₄ as shown in Fig. 4(d), indicating that the CO adsorption energy is sensitive to the apparently small difference in the total OP.

The relation between the CO adsorption energy and the total OP can be understood from the fact that the hybridization between CO MOs and Pt d states is mainly responsible for the CO adsorption on Pt₄/Vₙ. We consider the interaction between two states k and l with unperturbed energies εₓ and εₙ, respectively. To the second order in the interactions, OP between k and l is approximated as

$$p_{kl} = \frac{2 \text{Re}[S_{kl} V_{kl}]}{e_{k} - e_{l}},$$  

(11)

where εₙ < εₓ < εₙ, and S_{kl}(V_{kl}) denotes the overlap integral (coupling matrix element) between k and l. See Appendix B for the derivation of Eq. (11). Specifically, k and l correspond to an occupied state of CO (Pt₄/Vₙ) and an unoccupied state of Pt₄/Vₙ (CO), respectively, for a donation (back-donation) process. In the Mulliken-Wolfsberg-Helmholz (MWH)
approximation \( V_h \approx -\alpha S_{hk} \) with \( \alpha > 0 \) \cite{92,93}. \( \nu_k \) is proportional to the first term of the energy correction to state \( k \) given by

\[
\Delta \varepsilon_{kl} = \frac{|\langle \phi_l | V_{kl} | \phi_k \rangle|^2}{\varepsilon_k - \varepsilon_l} - S_{kl} V_{kl},
\]

where the second term describes the energy cost for orthogonalization. \( E_{\text{ads}}(\text{CO}/\text{Pt}_4/\nu_n) \) is roughly given by the sum of \( \Delta \varepsilon_{kl} \) over \( k \) and \( l \), which correspond to an occupied (unoccupied) orbital of CO and an unoccupied (occupied) state of Pt\( _4/\nu_n \), respectively, in a donation (back-donation) process. Thus, \( E_{\text{ads}}(\text{CO}/\text{Pt}_4/\nu_n) \) is expected to scale linearly with the total OP as seen in Fig. 4(d).

To clarify the origin of the decrease in OP with the size of the vacancy, we also plot the LDOSs projected onto the \( dz \) and \( dz^* \) states of Pt\( _4/\nu_n \) in Fig. 3. In each system, we take the \( z \) axis perpendicular to the face of Pt\( _4 \) opposite to Pt\( _3 \) so that \( 5\sigma \) (2\( \pi \)) has largest overlap with \( dz \) (\( dz^* \)) when the CO axis is parallel to the \( z \) direction. However, the adsorbed CO is in general inclined from the \( z \) axis as can be seen from the third column of Fig. 1, suggesting that \( dz \) peaks distributed below \( \varepsilon_F \) interact repulsively with \( 5\sigma \). Alternatively, the inclined adsorption structure enables \( 5\sigma \) (2\( \pi \)) to overlap with \( dz \) and \( dz^* \), both of which hybridize with \( 5\sigma \) and 2\( \pi \). On the other hand, Pt\( _3/\nu_1 \) shows two peaks derived from \( dz^* \) near \( \varepsilon_F \), while a large \( dz \) peak appears at \(-1 \text{ eV} \), which indicates that the former predominantly hybridizes with \( 5\sigma \) and 2\( \pi \). For Pt\( _3/\nu_2 \) and Pt\( _3/\nu_3 \), the peak near \( \varepsilon_F \), which is composed of \( dz \) and \( dz^* \), is smaller than those for Pt\( _4/\nu_0 \) and Pt\( _4/\nu_1 \), in agreement with the decreases in OP. Pt\( _3/\nu_4 \) also shows a peak near \( \varepsilon_F \) but its \( dz^* \) component is negligibly small, while the large \( dz^* \) peaks at 0.6 and \(-1.9 \text{ eV} \) scarcely hybridize with \( 5\sigma \) and 2\( \pi \), respectively. Moreover, the \( dz \) states at Pt\( _4/\nu_4 \) are almost fully occupied, and the large \( dz \) peak at \(-1.6 \text{ eV} \) interacts repulsively with \( 5\sigma \). To confirm the importance of the \( d \) states near \( \varepsilon_F \), we also plot the CO adsorption energy as a function of the number of \( d \) states near \( \varepsilon_F \) (\( N_F \)) as shown in Fig. 4(e), where \( N_F \) is estimated by integrating the LDOS in Fig. 3 from \(-0.25 \text{ eV} \) to \( 0.25 \text{ eV} \) with respect to \( \varepsilon_F \). Note that the peaks in the energy range mainly consist of \( d_z \) and/or \( d_{xz} + d_{zx} \) states. Figure 4(e) shows that \( E_{\text{ads}}(\text{CO}/\text{Pt}_4/\nu_n) \) increases roughly linearly with \( N_F \), in analogy with the dependence on the total OP seen in Fig. 4(d). From these observations, we conclude that OP is mainly determined by the electronic structures of Pt \( d_z \) and \( d_{xz} + d_{zx} \) states, and in particular the exceptionally small CO adsorption energy at Pt\( _4/\nu_4 \) can be attributed to the lack of these \( d \) states near \( \varepsilon_F \), as well as the repulsion between Pt \( d_z \) and CO \( 5\sigma \).

### IV. SUMMARY

We have investigated theoretically CO adsorption on Pt\( _4 \) clusters supported on graphene with lattice vacancies. The analysis of the LDOS projected onto the Pt \( d \) states has revealed that the \( d \)-band center is lowered significantly for Pt atoms near a vacancy, reflecting the interaction with C bonding bands. As a result the adsorption energy of CO at a Pt site decreases almost linearly with the lowering of the Pt \( d \)-band center with an exception of Pt\( _4/\nu_4 \), where CO adsorption is unusually weak relative to the corresponding \( d \)-band center. From a detailed analysis of OP between CO MOs and the states of Pt\( _4/\nu_n \), we have also shown that the total OP tends to decrease with the size of the vacancy, and that the CO adsorption energy depends roughly linearly on the total OP and on the number of \( d \) states near \( \varepsilon_F \), including CO adsorbed on Pt\( _4/\nu_4 \). Thus, we conclude that the exceptionally weak CO adsorption on Pt\( _4/\nu_4 \) can be attributed to the lack
of Pt $d$ states near $\varepsilon_F$ that have large overlap with CO $5\sigma$ and $2\pi$ orbitals. The approach based on OP is also applicable to other adsorption systems, in particular those in which the overlap between the electronic states of the adsorbate and the surface plays an essential role in the stability of the adsorption structure. Although further theoretical analyses are required for the elucidation of the origin of the high catalytic activity of graphene-supported Pt clusters, it is highly expected that the support effect of graphene on the Pt $d$ states not only enhances CO tolerance, but also has a significant impact on the catalytic activity.

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APPENDIX A: DETERMINATION OF THE FERMI LEVELS OF GAPPED SYSTEMS

In Secs. III B and III D, we have calculated the $d$-band center and overlap population, which depend on the reference from which energy levels are measured. Although the Fermi level $\varepsilon_F$ is often used as the energy reference, it is well known that $\varepsilon_F$ is ill defined for the DFT calculations of gapped systems. In the present systems, the formation of a vacancy or the interaction with a Pt cluster opens a finite gap in the otherwise gapless band structure of graphene. This hinders the comparison of the $d$-band center and overlap population among different systems, for which $\varepsilon_F$ varies with the size of the energy gap. To address this problem, we have corrected the energy levels in Figs. 3 and 5 through the helium (He) $1s$ level, as illustrated in what follows.

The first step of our approach is to determine the He $1s$ level by considering a system composed of pristine graphene and a He atom in the vacuum layer. The gapless band structure of graphene remains almost unchanged as long as the He atom stays far away from graphene. This enables us to measure the He $1s$ level from $\varepsilon_F$, which coincides with the Dirac point of the band structure of graphene. By comparing the results for several unit cells, the He $1s$ level is determined to be $-1.146$ eV below $\varepsilon_F$. We next add a He atom to the vacuum layer of Pt$_d$/V$_n$ or CO/Pt$_d$/V$_n$, in which the He $1s$ level obtained from the DFT calculation is in general shifted from the above value, reflecting the ambiguity in $\varepsilon_F$. Since the other energy levels are shifted parallel to the He $1s$ level, the correct energy levels as well as $\varepsilon_F$ are obtained by compensating the energy difference between the two He $1s$ levels. It is expected that the correction method presented here is also applicable to other systems with a sufficient vacuum layer.

APPENDIX B: PERTURBATION THEORY FOR ADSORPTION SYSTEMS

In Sec. III D, we have shown the perturbation formulas for the overlap population (11) and the energy correction (12) based on a nonorthogonal basis. Note that perturbation formulas are usually derived by using an orthogonal basis, since it is in general possible to form an orthogonal basis for a Hermitian Hamiltonian. However, this is not the case for the discussion of, e.g., overlap population, in which the basis for the system is assumed to consist of several orthogonal bases formed separately for respective subsystems. Here we briefly summarize the perturbation theory based on such a nonorthogonal basis, and show an application to molecular adsorption on a surface.

1. Preliminaries

Consider a system composed of several subsystems weakly interacting with each other. The Hamiltonian of the system consists of two terms as

$$H = H_0 + V,$$  \hspace{1cm} (B1)

where $H_0$ is the Hamiltonian of the respective subsystems and $V$ describe the interaction between them. We assume that orthonormal bases are obtained separately for the respective subsystems. A nonorthogonal basis $\{\psi\}$ is formed by combining these bases, since eigenstates in different subsystems are in general not orthogonalized. Using the nonorthogonal basis, we address the eigenvalue problem

$$H|\psi_k\rangle = E_k|\psi_k\rangle,$$ \hspace{1cm} (B2)

where $\psi_k$ ($E_k$) is the $k$th eigenstate (eigenenergy). $\psi_k$ is expanded in terms of the nonorthogonal basis as

$$|\psi_k\rangle = \sum_j |\phi_j\rangle c_{jk},$$ \hspace{1cm} (B3)

and substituted into Eq. (B2). Multiplying both sides by $\langle \phi_i |$ from the left, we have

$$\sum_j [S_{ij}(\varepsilon_j - E_k) + V_{ij}]c_{jk} = 0,$$ \hspace{1cm} (B4)

with the $j$th eigenenergy $\varepsilon_j$ of $H_0$, overlap integral $S_{ij} \equiv \langle \phi_i | \phi_j \rangle$, and coupling matrix element $V_{ij} = \langle \phi_i | V | \phi_j \rangle$. Since the eigenstates in $\{\psi\}$ are normalized but orthogonalized only in the respective subsystems, $S_{ij} = \delta_{ij}$ for $\phi_i$ and $\phi_j$ in the same subsystem, while $S_{i\neq j} \sim O(V_{\psi \psi})$ for those in different subsystems. The latter is justified by the MWH approximation \cite{92,93}

$$V_{ij} \propto S_{ij} \frac{V_{ii} + V_{jj}}{2}.$$ \hspace{1cm} (B5)

In what follows, we treat $V$ as a perturbation and develop a perturbation theory based on the nonorthogonal basis, considering $S_{i\neq j}$ to be of the first order of smallness in $V_{i\neq j}$.
2. Perturbation expansion

To solve Eq. (B4) perturbatively, eigenenergy $E_k$ and coefficient $c_{jk}$ are expanded as

$$E_k = E_k^{(0)} + E_k^{(1)} + \cdots,$$

and substituted into Eq. (B4). Here and in what follows, superscript $(n)$ stands for the $n$th order in $V$. From the zeroth- and first-order terms, we have

$$\delta E_k^{(1)} = \delta E_k^{(0)} + E_k^{(1)},$$

which take the same forms as those derived for an orthogonal basis. Clearly, Eq. (B8) is satisfied by setting

$$E_k^{(0)} = \epsilon_k, \quad c_{jk}^{(0)} = \delta_{jk},$$

respectively. In addition, $c_{jk}^{(1)}$ is determined from the normalization condition of $\psi_k$ as

$$1 = \langle \psi_k | \psi_k \rangle = 1 + 2 \text{Re} \left( c_{jk}^{(1)} \right) + O(V^2),$$

which results in $c_{jk}^{(1)} = 0$ by setting $c_{jk}^{(0)}$ to be real [94].

From the second-order terms in (B4), we have

$$-S_{kl}V_{lk} - \delta_{kl}E_k^{(2)} + \sum_{j(k\neq k)} [S_{ij}(\epsilon_i - \epsilon_k) + V_{ij}] c_{jk}^{(1)} - V_{kl} c_{jk}^{(1)} + (\epsilon_i - \epsilon_k) c_{jk}^{(2)} = 0,$$

where overlaps integrals appear explicitly. In the same way as for Eq. (B9), we obtain second-order corrections

$$E_k^{(2)} = \sum_{j(k\neq k)} \left[ \frac{|V_{jk}|^2}{\epsilon_k - \epsilon_j} - S_{kj}V_{jk} \right],$$

$$c_{jk}^{(2)} = \sum_{j(k\neq k)} \frac{V_{ij}V_{jk}}{(\epsilon_i - \epsilon_k)(\epsilon_j - \epsilon_k)} - \frac{V_{ik}V_{kl}}{(\epsilon_i - \epsilon_k)^2} + \frac{1}{\epsilon_i - \epsilon_k} \sum_j S_{ij}V_{jk} (i \neq k),$$

$$c_{kk}^{(2)} = -\frac{1}{2} \sum_{j(k\neq k)} \left[ \frac{|V_{jk}|^2}{(\epsilon_k - \epsilon_j)^2} + \frac{2 \text{Re}(S_{kj}V_{jk})}{\epsilon_k - \epsilon_j} \right].$$

One can readily confirm that the conventional perturbation formulas for an orthonormal basis can be reproduced by setting $S_{ij} = \delta_{ij}$ in Eqs. (B15)–(B17).

3. Adsorption energy

To apply the perturbation formulas derived above to molecular adsorption, we assume that $V$ acts only between the states of the adsorbate and those of the surface, i.e., $E_i^{(1)} = 0$ for all $i$. This means that, up to the second order in $V$, the energy correction to $\phi_i$ is given by Eq. (B15), which consists of interactions between $\phi_i$ and the remaining. In particular, the interaction energy with $\phi_i$ is given by

$$\Delta \epsilon_{kl} \simeq \frac{|V_{lk}|^2}{\epsilon_k - \epsilon_l} - S_{kl}V_{lk}.$$  

For simplicity, we assume that the adsorption has little influence on the occupations of the two states. If both $\phi_k$ and $\phi_l$ are occupied, the first term in Eq. (B18) is canceled out by the counterpart $\Delta \epsilon_{kl}$, while the second term, which is approximated to be

$$-S_{kl}V_{lk} \simeq \alpha |S_{kl}|^2$$

with $\alpha > 0$ [92,93], leads to destabilization. Conversely, a stable bonding state is realized when either of the two states is occupied; i.e., an occupied state of the adsorbate (surface) interacts with an unoccupied state of the surface (adsorbate), which can be considered as donation (back-donation) of electronic charge from the adsorbate (surface) to the surface (adsorbate). The contribution of hybridization to the adsorption energy is mainly described by the sum of Eq. (B18) over $k$ and $l$ with large $|V_{kl}|$ and $\epsilon_k \leq \epsilon_F \leq \epsilon_l$ or $\epsilon_l \leq \epsilon_F \leq \epsilon_k$.

4. Overlap population

We next consider the overlap of states between the adsorbate and the surface. To this end, we assume that the nonorthogonal basis set $\{ \phi \}$ is composed of two orthogonal subsets $A$ and $B$ formed separately for the free adsorbate and the clean surface, respectively, and rewrite Eq. (B3) as

$$|\psi_k\rangle = \sum_{i \in A} |\phi_i\rangle c_{ik} + \sum_{j \in B} |\varphi_j\rangle c_{jk}.$$  

Since $S_{ij} = \delta_{ij}$ for $i, j \in A$ or $B$, the normalization condition for $\psi_k$ is given by

$$1 = \sum_{i \in A} |c_{ik}|^2 + 2 \sum_{i \in A} \sum_{j \in B} \text{Re}(c_{ik}^* S_{ij} c_{jk}) + \sum_{j \in B} |c_{jk}|^2,$$

in which $|c_{ik}|^2$ and $|c_{jk}|^2$ are the net populations related to $\psi_k$ of $\phi_i$ the adsorbate and $\varphi_j$ of the surface, respectively, while

$$p_{ijk} = 2 \text{Re}(c_{ik}^* S_{ij} c_{jk})$$

is the overlap population between them [86–88]. It is convenient to introduce the density of states weighted by overlap population

$$\rho_{ij}(\epsilon) = \sum_k p_{ijk} \delta(\epsilon - \epsilon_k),$$

which visualizes the distribution of the overlap population as a function of energy. The contributions of all the occupied states to the overlap population between $\phi_i$ and $\varphi_j$ is obtained from a sum of $p_{ijk}$ over $k$ such that $\epsilon_k < \epsilon_F$, or equivalently from
an integral of $\rho_{ij}(\varepsilon)$ up to $\varepsilon_f$, as

$$P_{ij} = \sum_k p_{ijk} = \int_{\varepsilon_f}^{\varepsilon} \rho_{ij}(\varepsilon) d\varepsilon.$$  \hfill (B24)

Moreover, the states of the surface are usually treated collectively by defining

$$\rho_i(\varepsilon) = \sum_{j \in B} \rho_{ij}(\varepsilon) = \sum_j \sum_k p_{ijk} \delta(\varepsilon - \varepsilon_k),$$  \hfill (B25)

which is COOP discussed in Sec. III D.

To treat overlap population perturbatively, expansion

$$p_{ijk} = p_{ijk}^{(0)} + p_{ijk}^{(1)} + p_{ijk}^{(2)} + \cdots,$$  \hfill (B26)

and the perturbation formulas derived above are substituted to Eq. (B22). The zeroth-, first-, and second-order terms read

$$p_{ijk}^{(0)} = p_{ijk}^{(1)} = 0,$$  \hfill (B27)

$$p_{ijk}^{(2)} = \begin{pmatrix} 2 \text{Re}(S_{ij} V_{ji}) \\ \delta(\varepsilon - \varepsilon_j) \end{pmatrix} (\delta_{ik} - \delta_{jk}).$$  \hfill (B28)

Thus, up to the second order in $V$, we obtain approximate expressions for overlap population

$$p_{ijk} \simeq \frac{2 \text{Re}(S_{ij} V_{ji})}{\varepsilon_i - \varepsilon_j} (\delta_{ik} - \delta_{jk})$$  \hfill (B29)

and weighted density of states

$$\rho_{ij}(\varepsilon) \simeq \frac{2 \text{Re}(S_{ij} V_{ji})}{\varepsilon_i - \varepsilon_j} \left[ \delta(\varepsilon - \varepsilon_i) - \delta(\varepsilon - \varepsilon_j) \right],$$  \hfill (B30)

which enable a better understanding of these quantities. It is clear from Eq. (B29) that the contribution to $p_{ij}$ derives only from the situation in which either $\varphi_i$ or $\varphi_j$ is occupied, as in the case of adsorption energy (see Appendix B3). If $\varepsilon_i < \varepsilon_f < \varepsilon_j$, for example, the contributions of occupied states to overlap population add up to

$$p_{ij} \simeq \frac{2 \text{Re}(S_{ij} V_{ji})}{\varepsilon_i - \varepsilon_j}.$$  \hfill (B31)

Correspondingly, Eq. (B30) indicates that $\rho_{ij}(\varepsilon)$ displays a positive (negative) peak at $\varepsilon = \varepsilon_i (\varepsilon_j)$, signaling the formation of a bonding (antibonding) state, although the peak actually observed should be shifted by $\Delta \varepsilon_{ij} (\Delta \varepsilon_{ji})$. 

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