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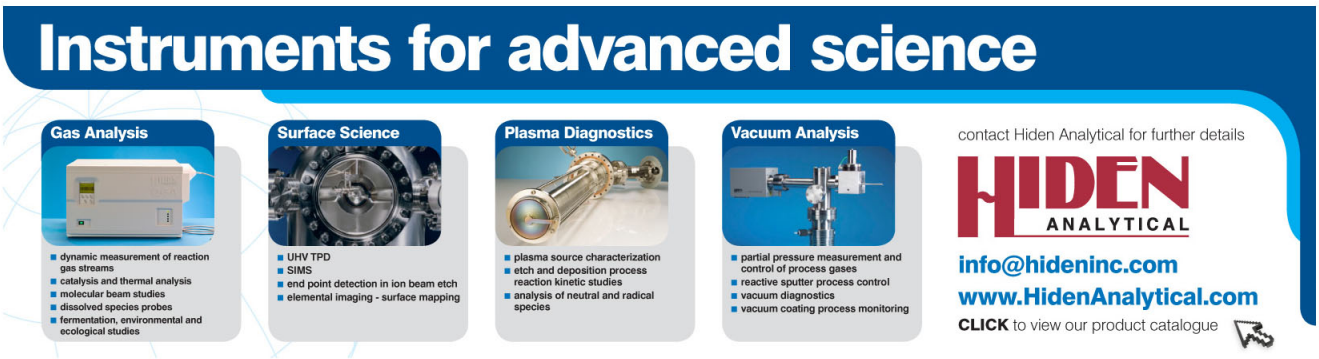
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CO oxidation on h-BN supported Au atom

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The mechanism of CO oxidation by O_2 on Au atoms supported on the pristine and defected hexagonal boron nitride (h-BN) surface has been studied theoretically using density functional theory. It is found that O_2 binds stronger than CO on an Au atom supported on the defect free h-BN surface and h-BN surface with nitrogen vacancy (V_N@h-BN), but weaker than CO on a free Au atom or Au trapped by a boron vacancy (V_B@h-BN). The excess of the positive or negative charge on Au can considerably change its catalytic properties and enhance activation of the adsorbed O_2. Coadsorption of CO and O_2 on Au, Au/V_N@h-BN, and Au/V_B@h-BN results in additional charge transfer to O_2. Various pathways of the CO oxidation reaction by molecular oxygen are studied. We found two different pathways for CO oxidation: a two-step pathway where two CO_2 molecules are formed independently, and a self-promotion pathway where oxidation of the first CO molecule is promoted by the second CO molecule. Interaction of Au with the defect-free and defected h-BN surface considerably affects the CO oxidation reaction pathways and barriers. Therefore, Au supported on the h-BN surface (pristine or defected) cannot be considered as pseudo-free atom and support effects have to be taken into account, even when the interaction of Au with the support is weak. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4774216]

I. INTRODUCTION

Since the pioneering work of Haruta on oxidation of carbon monoxide by small gold nanoparticles supported by metal oxides[1] it has become clear that gold can exhibit high catalytic activity in various oxidation reactions including the oxidation of carbon monoxide, aerobic alcohol oxidation, the direct synthesis of hydrogen peroxide, alkene epoxidation, etc.[2–10] The catalytic properties of gold are strongly size-dependent and emerge when the size of particles decreases to 1–5 nm, whereas larger particles and the bulk form of gold are catalytically inert.[1,2,5] The enormous interest in gold nanocatalysis is stipulated by the fact that gold nanoparticles are active and selective even at room temperatures that makes them unique catalysts for many industrial applications.

It is well established that there are several factors controlling catalytic activity of gold.[10–14] Apart from the strong size dependence of the catalytic activity of gold clusters one of the most important factors in gold nanocatalysis is the support effect.[15,16] It was demonstrated that the so-called active metal oxide supports (such as, MgO, TiO_2, Al_2O_3, Fe_2O_3, etc.) can considerably influence the catalytic properties of gold clusters and modify (enhance or suppress) their reactivity.[2,9,12,17] Such supports usually stabilize gold particles and can modify considerably their geometric structure and morphology,[18–22] which in turn can affect catalytic properties of the supported particles. Charge transfer from the metal oxide support to the gold results in formation of the highly reactive charged gold clusters.[17,23] Catalytic activity of the supported clusters can also be promoted by defects in the support. Defects can trap the metal cluster and enhance charge transfer between the support and the cluster. It was demonstrated that Au_8 clusters supported on the MgO(100) surface rich of F-center defects show high catalytic activity, while Au_8 deposited on the defect-poor MgO(100) surface are inert.[17,24]

One of the simplest and the most studied catalytic reaction on gold clusters is a low-temperature CO oxidation by molecular oxygen.[1,2,10,12,17,24–31] It has been demonstrated that dispersed gold supported on Co_3O_4, NiO, TiO_2, and Fe_2O_3 possesses high catalytic activity for CO oxidation.[32–35] These supports affect dramatically the catalytic activity of gold clusters. The choice of support, the method of preparation, and the pretreatment before use are very important factors controlling the reactivity.[36] The contact structure between the supported cluster and the surface is another important factor in the CO oxidation reaction.[9,32] It has also been suggested that adsorption of O_2 and CO on the gold particles of finite size becomes stronger at low-coordinated sites.[17,24,29,37–42]

Activation of the adsorbed O_2 is a crucial step in the CO oxidation reaction. A negative charge accumulated on the gold can weaken the O–O bond and activate the oxygen molecule for a further catalytic reaction; see, e.g., Refs. 43–49 and references therein. On the other hand, the positive charge accumulated on the gold can promote adsorption of CO and hydrocarbons.[7,50] It has been demonstrated that the CO oxidation reaction catalyzed by gold clusters can occur via Langmuir-Hinshelwood (LH) or Eley-Rideal (ER)

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mechanisms, depending on the cluster charge. Thus the neutral Au_{10} can catalyze oxidation of CO via the Langmuir-Hinshelwood mechanism even below room temperature.[41] CO oxidation on anionic gold clusters occurs via the Eley-Rideal mechanism,[38,51,52] while CO oxidation on cationic gold atoms can occur via both Eley-Rideal and Langmuir-Hinshelwood mechanisms.[52] Therefore, the charge state of gold particles (which can be controlled by the support) can considerably influence their reactivity and define the reaction mechanism.[47,48,53]

On the other hand it is commonly accepted that the inert supports, such as SiO_2 or hexagonal boron nitride (h-BN), do not affect the electronic and geometric structure of the supported clusters. Therefore, such clusters can be considered as pseudo-free.[3,54] This suggestion is widely used to study catalytic properties of gold clusters free of support effects. However, in our recent works we have demonstrated that adsorption, activation, and dissociation of O_2 on h-BN supported gold atoms and dimers can be affected by the interaction with the inert h-BN support via electron pushing and donor/acceptor mechanisms.[48,55,56] We have shown that even a weak interaction of Au and Au_2 with the defect-free inert h-BN surface can have an unusually strong influence on the binding and catalytic activation of the molecular oxygen.[56] This effect occurs due to the mixing of the 5*d* orbitals of the supported Au and Au_2 with the N-p_z orbitals. Although the defect-free h-BN surface does not act as a good electron donor for the supported O_2-Au, it promotes an electron transfer from the Au to O_2, pushing electrons from the gold to the adsorbed oxygen. In the case of a defected h-BN surface Au and Au_2 can be trapped effectively by an N or B vacancy or impurity point defect. Strong adsorption on the surface defects is accompanied by charge transfer to/from the adsorbate which can affect the catalytic activity of gold.[48] Very recently adsorption of small gold clusters on the h-BN/Rh(111) nanomesh has been studied theoretically.[57] The nanomesh is a strongly corrugated h-BN monolayer deposited on a metal surface that looks like an assembly of hexagonal pores at the nanometer scale.[58] The lowest regions bind strongly to the underlying metal, while the highest regions bind weakly. The size and depth of pores depend on the mismatch in h-BN and metal lattice parameters and strength of interaction between the h-BN monolayer and the metal. A recent review on 2D boron nitride nanostructures can be found in Ref. 59. It was noticed that all Au atoms in these clusters adsorbed on the h-BN/Rh(111) nanomesh are negatively charged and thus might be catalytically active.[57] However, to the best of our knowledge there were no attempts to study theoretically the specific catalytic reactions on h-BN supported Au clusters.

In the present paper we fill this gap and perform systematic theoretical investigation of the process of CO oxidation by O_2 on the h-BN supported gold atoms as the simplest model reaction. It is demonstrated that the inert h-BN support can affect the process of CO oxidation and corresponding reaction barriers. Coadsorption of CO and O_2 on Au/h-BN followed by formation of metastable intermediate CO–O_2 plays an important role in the CO oxidation mechanism. It is shown that the presence of the h-BN support can affect the CO oxidation barriers and overall probability of an oxidation reaction. Therefore, h-BN cannot be considered as an inert support for Au.

II. COMPUTATIONAL DETAILS

The calculations are carried out using density-functional theory (DFT) with the gradient-corrected exchange-correlation functional of Wu and Cohen (WC)[60] as implemented in the PWSCF package.[61] The choice of WC functional is stipulated by the fact that it allows to reproduce correctly the lattice constants, crystal structures, and surface energies of solids with layered structures such as graphite or h-BN, whose distances between the layers are determined by rather weak interactions.[62] Moreover, the WC functional provides a realistic description of the binding energies and geometries of h-BN layer on top of 3*d*, 4*d*, and 5*d* transition metal surfaces, correctly describing the interaction of transition metals with h-BN.[62–64] The WC functional was successfully used in our previous works to describe the adsorption of Au and Au_2 on the defect-free and defected h-BN surface as well as adsorption, activation and dissociation of molecular oxygen on h-BN supported Au particles.[48,55,56]

A plane-wave basis set and Troullier-Martins norm-conserving pseudopotentials are used.[65] Relativistic effects are taken into account for Au via scalar-relativistic pseudopotentials. All calculations are spin polarized. The energy cutoff of 80 Ry is chosen to guarantee convergence of the total energies and forces. The self-consistency of the density matrix is achieved with a tolerance of 10^{-9}. A climbing image nudged elastic band (CI-NEB) method has been used for finding transition states and minimum energy pathways.[66] We have checked that the total spin of the whole system does not change at transition states. The atoms in molecules method of Bader (AIM) has been used for the charge analysis.[67,68]

Periodic boundary conditions are used for all systems, including free molecules and clusters. In the case of finite size systems the supercell was chosen to be large enough to make intermolecular interactions negligible. In the present work the h-BN lattice has been optimized using the Monkhorst-Pack[69] $10\times10\times4$ k-point mesh for Brillouin zone sampling. The h-BN lattice has a layered structure which is very similar to graphite. The planar networks of B_3N_3 hexagons are regularly stacks on top of each other.[70] Due to the partially ionic character of the B–N bonding, the B atoms in one layer are located on top of the N atoms of the neighboring layer and vice versa. The calculated lattice parameters $a = b = 2.504$ Å, and $c = 6.656$ Å are in excellent agreement with the experimental values of $a = b = 2.524 \pm 0.020$ Å and $c = 6.684 \pm 0.020$ Å, reported in Ref. 71. The h-BN surface is represented by the two-layer slab containing 6×6 unit cells (72 units of BN per slab). In all calculations the bottom layer in the slab is fixed, and all other atoms are fully relaxed. The periodically replicated slabs are separated by a vacuum region of 15 Å in the (001) direction. Only the Γ point is used for sampling the Brillouin zone due to the large size of the supercell.

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In order to obtain the most stable configuration of the adsorbed O_2 and CO we have created a large number of initial geometries by adding adsorbents in different nonequivalent positions (up to 20 in each case) on the surface of the pristine and defected h-BN with the trapped Au atom. These structures have been optimized without any geometry constraints. The similar approach has been successfully used in our previous works to study structure of metal clusters[72–74] as well as adsorption and dissociation of O_2, H_2, and C_2H_4 molecules on free and supported gold clusters.[46–48,50,55,56,75]

To further validate our approach and choice of the WC functional we have calculated the dissociation energies and interatomic distances for CO and O_2. Our calculations demonstrate that the dissociation energy, D_e, and bond length in CO (11.75 eV, 1.14 Å) and O_2 (6.47 eV, 1.24 Å), are in a good agreement with the experimental data reported for CO (11.11 eV, 1.13 Å) and O_2 (5.23 eV, 1.21 Å), respectively.[76]

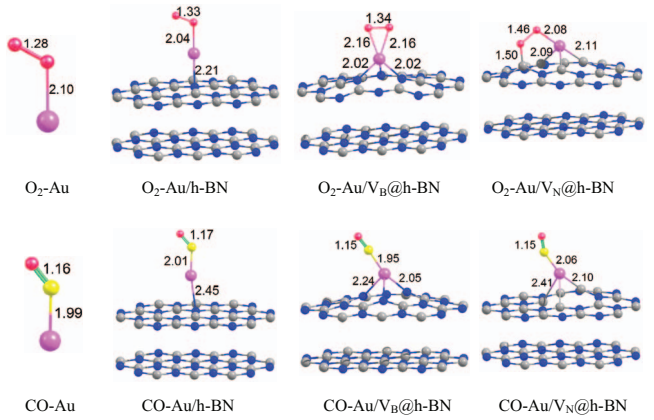


FIG. 1. Adsorption of CO and O_2 on free and supported Au atoms on a defect-free h-BN surface and on h-BN surface with boron (V_B) and nitrogen (V_N) vacancy defects (only part of the slab is shown).

III. RESULTS AND DISCUSSION

A. Adsorption of O_2 and CO on h-BN supported Au atoms

We start our study with an investigation of the independent adsorption of O_2 and CO on the gold atom supported on pristine or a defected h-BN surface. Two types of point defects are considered: vacancies of boron (V_B) and nitrogen (V_N) atoms. These are the simplest and relatively stable types of defects in h-BN. The stability of point defects in the h-BN surface has been intensively investigated.[77,78] It was found that nitrogen impurity defect is the most stable defect in h-BN under N-rich conditions followed by the nitrogen vacancy.[77] This is consistent with experimental findings of large concentrations of nitrogen interstitials and vacancies in the hexagonal phase of BN thin films grown by ion-bombardment-assisted deposition techniques; see, e.g., Ref. 77 and references therein. The relative stability of the particular type of defects in h-BN often depends on the experimental conditions and the environment. Therefore, in the present work we study only the simplest types of point defects in h-BN. In the previous works we have demonstrated that V_B and V_N defects on h-BN surface trap effectively Au atoms and modify their catalytic properties due to the electron transfer between the surface defects and the adsorbed gold particles.[48,55,56]

The optimized geometries of O_2 and CO adsorbed on Au/h-BN, Au/V_B@h-BN, and Au/V_N@h-BN centers are shown in Fig. 1. These structures have been fully optimized on the surface, with accounting for relaxation of gold atom, O_2 and CO molecules as well as the top layer of h-BN. The bottom layer of h-BN in the slab was fixed. Thus, we have taken into account structural relaxations on the h-BN surface due to its interaction with the supported gold. In the case of the defect-free h-BN surface, the gold atom adsorbs on top of the N atom, V_B and V_N point defects. Note that the defected h-BN surface undergoes strong structural relaxations upon Au adsorption.[55] Figure 1 shows that the oxygen molecule adsorbs on top of the Au atom that is supported either on the defect-free h-BN surface or trapped by the V_B defect, but it bridges Au and the surface B atom in the case of O_2 adsorption on the Au/V_N@h-BN center. As was demonstrated in Ref. 55 the interaction of Au with the h-BN support results in an additional activation of the adsorbed O_2 and weakening of the O–O bond in comparison with the free gold atom. This effect is especially strong for the V_N defect, which acts as an electron donor for the supported Au.

In the case of CO adsorption on Au/h-BN, Au/V_B@h-BN, and Au/V_N@h-BN centers, CO always binds on top of the Au atom, forming a Au–C bond. This result is consistent with the previous study on CO adsorption on small cationic, neutral, and anionic Au_n (n = 1–6) clusters where it was found that among the various possible CO adsorption sites, the on-top (one-fold coordinated) sites are the most favorable, irrespective of the cluster charge.[79] Table I summarizes the results of our theoretical calculations on binding energies, E_b, Bader charges, Q, and spin multiplicity of the whole system,

TABLE I. Binding energy, E_b, Bader charge, Q, and spin multiplicity of the whole system, $2S + 1$, calculated for the most stable configurations of O_2 and CO adsorbed on a free and h-BN supported Au atom. Numbers in parentheses are taken from Refs. 55 and 56.

	Oxygen molecule			Carbon monoxide		
Adsorption center	E_b (eV)	Q ($\|e\|$)	Spin ($2S + 1$)	E_b (eV)	Q ($\|e\|$)	Spin ($2S + 1$)
Au	0.58 (0.49)	−0.20 (−0.19)	2	1.09	−0.03	2
Au/h-BN	1.25 (1.05)	−0.47 (−0.46)	2	1.03	−0.16	2
Au/V_B@h-BN	1.09 (0.90)	−0.39 (−0.33)	3	1.52	−0.03	3
Au/V_N@h-BN	1.44 (1.10)	−1.37 (−1.31)	1	0.82	−0.09	1

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$2S + 1$, obtained for O_2 and CO adsorbed on a free gold atom and a gold atom supported on the pristine or defected h-BN, V_B@h-BN, and V_N@h-BN surfaces. The binding energy of a molecule M (O_2 or CO) to the free or supported Au atom is defined as

$$E_b = E_{tot}(\mathrm{M}) + E_{tot}(\mathrm{Au}) - E_{tot}(\mathrm{M-Au}), \qquad (1)$$

where $E_{tot}(\mathrm{M-Au})$ denotes the total energy of the complex system M − Au, while $E_{tot}(\mathrm{M})$ and $E_{tot}(\mathrm{Au})$ are the total energies of the non-interacting M and Au species, respectively. Here M denotes the O_2 or CO molecule, while Au corresponds to a free or supported Au atom.

Adsorption and catalytic activation of O_2 on Au/h-BN, Au/V_B@h-BN, and Au/V_N@h-BN have been studied in our previous works[55,56] using the SIESTA code[80–82] with the basis set of strictly localized numerical atomic orbitals. Table I demonstrates that the binding energy and Bader charge of O_2 adsorbed on free and h-BN supported Au atoms obtained within the plane-waves basis sets approach as implemented in PWSCF code are in a good agreement with previously reported data.[55,56]

Our calculations demonstrate that O_2 and CO adsorb on free Au with a binding energy of 0.58 and 1.09 eV, respectively. Pristine and defected h-BN support considerably affects the binding of O_2 and CO to Au/h-BN, Au/V_B@h-BN, and Au/V_N@h-BN adsorption centers. Thus, O_2 adsorbs on Au/h-BN, Au/V_B@h-BN, and Au/V_N@h-BN with the binding energies of 1.25, 1.09, and 1.44 eV, respectively. These values are approximately twice as large as the binding energy of O_2 to a free Au. In the case of CO adsorption on the supported Au, CO binds weaker (in comparison to CO binding to a free Au) to Au/h-BN and Au/V_N@h-BN with binding energies of 1.03 and 0.82 eV, respectively. However, in the case of CO adsorption on Au/V_B@h-BN, the binding energy is 1.52 eV, which is larger than the calculated binding energy of CO to the free Au. In addition, we found that O_2 binds stronger to Au/h-BN and Au/V_N@h-BN centers, but weaker to the free Au atom and Au/V_B center compared to the CO adsorption. Thus pristine and defected h-BN supports dramatically affect O_2 and CO adsorption to the supported gold atoms. Our calculations demonstrate that an Au atom adsorbed on h-BN or V_N@h-BN surfaces possesses a Bader charge of $-0.08e$ and $-0.39e$, respectively; but in the case of Au adsorption on a V_B@h-BN center the Bader charge localized on Au is +0.70e.[56] Thus, V_N donates electrons to the adsorbed Au, while V_B acts as an electron acceptor. The charge excess on the supported Au atom results in a stronger binding of O_2 to the gold; while charge deficiency on Au results in stronger binding of CO. We found that the charge state of the supported Au strongly influences the adsorption of O_2 and CO. The interaction between CO and Au depends on a balance between the electron donation from CO to Au and the back donation from Au to CO.

Next, let us consider the simultaneous adsorption of O_2 and CO on Au. Figure 2 demonstrates the optimized geometries of CO and O_2 coadsorbed on a free or supported Au atom. It is seen from Fig. 2 that O_2 and CO can bind to Au in three different ways: (a) without a direct interaction between O_2 and CO (A_1 and B_1); (b) forming a COO_2 intermediate, where O_2 is directly coupled with CO (A_2, B_2, and C_1); (c) without direct interaction between O_2 and CO, when O_2 bridges Au and the surface atoms (D_1). In the case of O_2 and CO coadsorbed on Au and Au/h-BN (A_1, A_2, B_1, and B_2) the spin multiplicity of the whole system is doublet, while in the case of O_2 and CO coadsorption on Au/V_B@h-BN and Au/V_N@h-BN centers the spin state is a singlet.

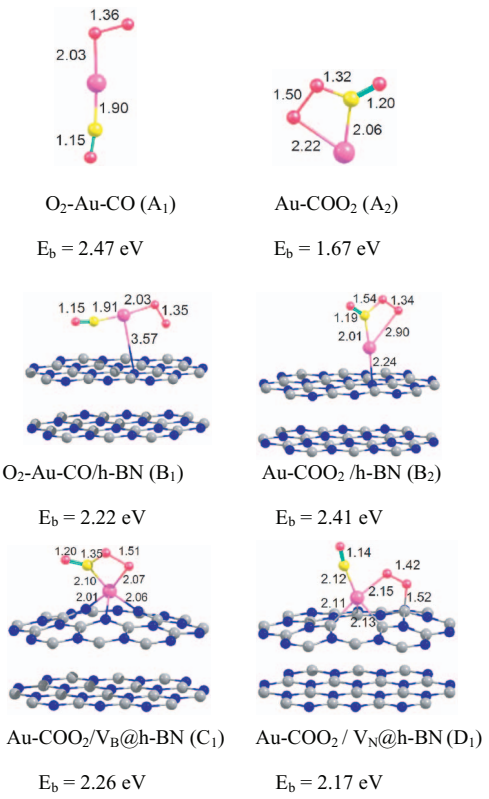


FIG. 2. Coadsorption of CO and O_2 on a free Au atom (A_1, A_2); a Au atom supported on the defect-free h-BN surface (B_1, B_2) and Au trapped by boron (C_1) and nitrogen (D_1) vacancy defects on a h-BN surface. Only part of the slab is shown. The interatomic distances are given in Å.

The results of our calculation demonstrate that the h-BN support considerably influences the geometry and binding energies of Au–COO_2 complexes. Thus, in the case of a free Au atom the most stable configuration of coadsorbed O_2 and CO is the one without a direct interaction between the two adsorbants (A_1). However, the Au–COO_2 complex, where O_2 is directly coupled with CO (B_2), becomes energetically favorable on the pristine h-BN support. In several cases, such as A_1 and B_2 the binding energies of coadsorbed CO and O_2 are larger than the sum of the binding energies of the independent adsorption of O_2 and CO on Au. This fact demonstrates the appearance of a cooperative effect in coadsorption of O_2 and CO, similar to those discussed in Refs. 46, 47, 83, and 84 and references therein.

Figure 3 presents the calculated Bader charges localized on O_2 and CO in the case of the most stable configurations when CO and O_2 are coadsorbed on free and supported Au atoms. The Bader charges localized on O_2 in configurations A_1, B_2, C_1, and D_1 are $-0.53e$, $-0.45e$, $-1.48e$, and $-1.22e$, respectively. In the case of O_2 and CO coadsorption on a free Au atom and Au/V_B@h-BN center the Bader charge

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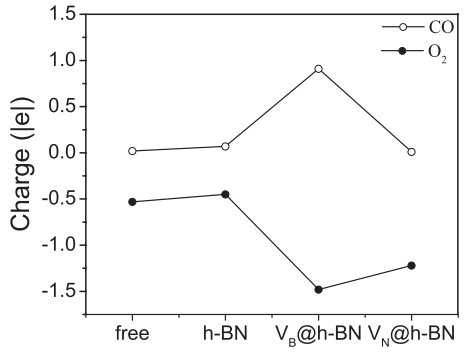


FIG. 3. The calculated Bader charges localized on O_2 (filled dots) and CO (open dots) in the case of the most stable configurations when CO and O_2 coadsorbed on the free and supported Au atoms.

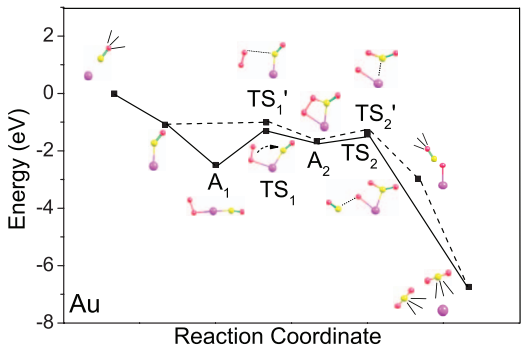


FIG. 4. Reaction pathways for the CO oxidation by O_2 on the free Au atom. The key geometry structures are shown in insets.

localized on O_2 is much larger than for the corresponding configurations without CO. It is interesting that in the case of O_2 and CO coadsorption on the free Au, the extra charge on O_2 originates from the Au atom: coadsorbed CO pushes electrons from Au to O_2. In the case of O_2 and CO coadsorption on Au trapped by a V_B defect the extra charge on O_2 originates from the CO molecule itself, i.e., the CO molecule plays the role of an electron donor.

B. CO oxidation catalyzed by free and supported Au atoms

In order to understand the role of the h-BN support on the catalytic activity of a Au atom, we have investigated the reaction pathways of CO oxidation by O_2 on free and supported Au. It has already been mentioned that there are two possible routes for a catalytic oxidation on small gold clusters. The first route consists in a preliminary dissociation of the adsorbed O_2 followed by consequential oxidation of CO by atomic oxygen. The second route is a direct oxidation reaction between an activated O_2 and CO. It has been shown that the barrier of O_2 dissociation on a single Au atom is too high.[46] Although the presence of h-BN support can lower the barrier of O_2 dissociation, it remains relatively high and thus O_2 dissociation cannot occur spontaneously with the exception of a Au/V_N adsorption center.[55] Therefore, in the present work, we focus on the mechanism of the direct oxidation of CO by an activated O_2. Geometry structures of all transition states calculated below are provided in the supplementary material.[85]

Let us consider the CO oxidation reaction on the free Au atom:

$$O_2 + 2CO \xrightarrow{Au} 2CO_2. \quad (2)$$

Figure 4 demonstrates the possible reaction pathways for this process. The results of our calculations demonstrate that CO adsorbs on Au with a binding energy of 1.09 eV, which is larger than the binding energy of O_2 to Au. After adsorption of the first CO on Au two different pathways for O_2 adsorption are possible, as is shown in Fig. 4. The first is the coadsorption of O_2 on Au without a direct interaction with CO (Langmuir-Hinshelwood mechanism) resulting in the formation of the intermediate A_1. This is a barrierless process. After A_1 is formed it can be transformed to the intermediate A_2 via transition state TS_1 with a barrier of 1.16 eV. However, this is an energetically unfavorable process, since the A_1 intermediate has a larger adsorption energy than A_2. The second pathway consists of a direct O_2 attack of Au–CO and the formation of the A_2 intermediate via transition state TS_1' with a barrier of 0.09 eV.

In order to obtain the final product CO_2 from the intermediate A_2 there are two possibilities: (i) a two-step process, when the CO_2 molecule extracts from the A_2 intermediate via transition state TS_2' with a barrier of 0.31 eV forming a highly reactive AuO species. The second CO attacks AuO resulting in the formation of the second CO_2; (ii) a single step process when the second CO attacks the intermediate A_2 forming $2CO_2$ via transition state TS_2 with the barrier of 0.24 eV. It is important to note that in the latter pathway the oxidation of the first CO molecule is promoted by the second CO molecule (the self-promotion effect).[27,30]

Figure 5 demonstrates the possible reaction pathways for CO oxidation on the h-BN supported Au. The results of our calculations demonstrate that O_2 adsorbs on Au/h-BN with a larger binding energy than CO. After O_2 adsorption takes place, there are two ways for CO adsorption. On the first way CO binds directly to the AuO_2/h-BN forming the intermediate B_1 without any barrier. Intermediate B_1 is metastable and can be transformed to B_2 via transition state TS_1' with a barrier of 0.98 eV. On the second way CO directly attacks AuO_2/h-BN to form intermediate B_2 via transition state TS_1 with a barrier of 0.04 eV.

The reaction pathways from the intermediate B_2 to final products of $2CO_2$ are quite similar to those described

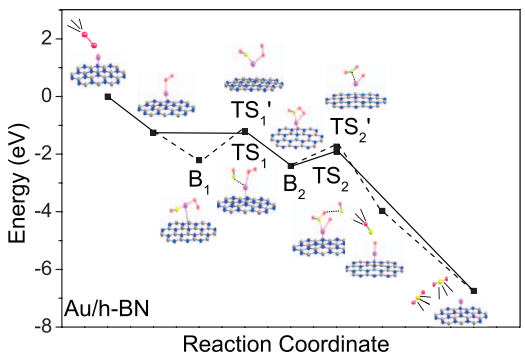


FIG. 5. Same as Fig. 4, but for Au/h-BN adsorption center.

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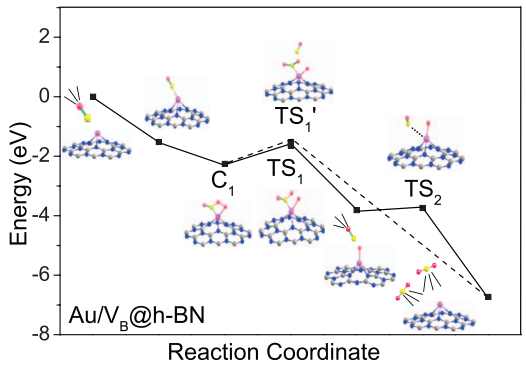


FIG. 6. Same as Fig. 4, but for Au/V_B@h-BN adsorption center.

for the free Au: (i) a two-step process with the formation of the first CO_2 product via transition state TS_2' with a barrier of 0.67 eV, and the consequent oxidation of the second CO by atomic oxygen on AuO/h-BN; (ii) a self-promoting path, when the second CO reacts with intermediate B_2 forming $2CO_2$ via transition state TS_2 with a barrier of 0.49 eV. As it is seen from our calculations the self-promoted pathway is favorable.

Let us consider the CO oxidation on Au trapped by the nitrogen and boron point defects on a h-BN surface. As was discussed above, the boron vacancy V_B plays the role of an electron acceptor. Therefore, Au trapped by V_B@h-BN is positively charged (Fig. 6). The positive charge localized on Au promotes the CO adsorption. After the first adsorption of CO on Au/V_B@h-BN the intermediate C_1 can be formed directly without any barrier. After intermediate C_1 is formed there are two possible pathways to get $2CO_2$ as the final product. These pathways are similar to those obtained for the unsupported Au. However, in the case of Au trapped by V_B@h-BN the intermediate C_1 disintegrates, releasing one CO_2 with a barrier of 0.58 eV. After that the second CO attacks O-Au/V_B@h-BN and forms CO_2 overcoming the small barrier of 0.07 eV. This barrier is related to the formation of the CO–Au–O/V_B@h-BN complex, where both CO and O reactants are attached to the supported Au atom. After that step, oxidation of CO by O occurs spontaneously without any barrier. This path is energetically favorable in comparison with the self-promoting pathway. It is important to note that as the CO_2 product departs from the Au/V_B@h-BN center the total spin

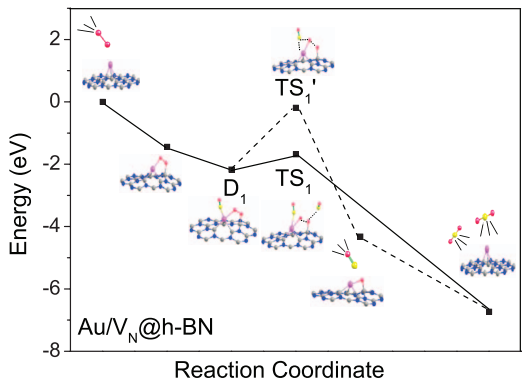


FIG. 7. Same as Fig. 4, but for Au/V_N@h-BN adsorption center.

of the whole system changes from singlet to triplet. However, this change occurs on the down-hill slope of the reaction path and does not affect the barrier.

For the CO oxidation reaction on the Au/V_N@h-BN center, Au is negatively charged, favoring O_2 adsorption and activation as a first step (Fig. 7). After that the intermediate D_1 can be formed directly without any barrier. The route from D_1 to the final products consists of two paths: a two-step pathway with a barrier of 1.98 eV and a self-promoting pathway with a barrier of 0.49 eV. Thus in the case of Au/V_N@h-BN center the self-promoting pathway is energetically favorable in comparison with a two-step pathway.

IV. CONCLUSION

In the present work, we have studied the CO oxidation reaction on a free and h-BN supported gold atom. The pristine h-BN surface and the h-BN surfaces with boron and nitrogen vacancies have been considered. We have found that O_2 binds stronger than CO on Au/h-BN and Au/V_N@h-BN support, but weaker than CO on Au and V_N@h-BN adsorption centers. The excess of the positive or negative charge on Au can considerably change its catalytic properties and enhance the activation of the adsorbed O_2. Coadsorption of CO and O_2 on Au, Au/V_N@h-BN, and Au/V_B@h-BN results in an additional charge transfer to O_2.

Various pathways of the CO oxidation reaction by molecular oxygen are studied. We have found two different pathways for the CO oxidation: a two-step pathway, where two CO_2 molecules are formed independently, and a self-promotion pathway, where the oxidation of the first CO molecule is promoted by the second CO molecule. Interaction of Au with the defect-free and defected h-BN surface considerably affects the CO oxidation reaction pathways and barriers.

Our finding leads to a very important conclusion that Au supported on the h-BN surface (pristine or defected) cannot be considered as a pseudo-free atom. The support effects have to be taken into account, even when the interaction of Au with the support is weak.

The important task is to investigate how the h-BN support influences the catalytic properties of gold clusters of larger sizes up to 1–3 nm, where the strong size-dependence of the catalytic activity of gold clusters has been observed experimentally. Whether or not h-BN support can affect catalytic properties of large gold clusters is an open question. One can suggest that mixing of the N-p_z and B-p_z orbitals of h-BN with Au-d_{z^2} orbitals can modify the local electronic structure of the gold atoms in the contact area between the cluster and the support. As it is known, such an interface can play a crucial role in the catalytic activity of the supported clusters.[9,75,86,87] Therefore, it is necessary to clarify whether or not the perimeter interface between a large gold cluster and the h-BN support affects the catalytic activity of gold.

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