The h-BN surface effect on CO oxidation reaction catalyzed by supported gold atom

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Abstract. The mechanism of CO oxidation by O2 on Au atoms supported on the pristine and defected hexagonal boron nitride (h-BN) surface has been studied theoretically using density functional theory. Two possible routes for catalytic oxidation are considered. The first route consists in a preliminary dissociation of the adsorbed O2 followed by consequential oxidation of a reactant molecule by atomic oxygen. Although the presence of h-BN surface can change the O2 dissociation barrier, it remains relatively high. The second route is a direct oxidation reaction between the activated molecular oxygen and the reactant. We have found two different pathways for CO oxidation: a two-step pathway where two CO2 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.

1. 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 up to 1-5 nm, while 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]. Thus, it was demonstrated that the so-called active metal oxide supports (such as, MgO, TiO2, Al2O3, Fe2O3,

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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 \( \text{Au}_8 \) clusters supported on the \( \text{MgO}(100) \) surface rich of F-center defects show high catalytic activity, while \( \text{Au}_8 \) deposited on the defect-poor \( \text{MgO}(100) \) 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 \( \text{Co}_3 \text{O}_4 \), \( \text{NiO} \), \( \text{TiO}_2 \), and \( \text{Fe}_2 \text{O}_3 \) 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 been also suggested that adsorption of \( \text{O}_2 \) and CO to the gold particles of finite size becomes stronger at low-coordinated sites [17, 24, 29, 37–42].

Activation of the adsorbed \( \text{O}_2 \) is a crucial step in CO oxidation reaction. A negative charge accumulated on the gold can weaken the \( \text{O} \cdash \text{O} \) bond and activate oxygen molecule for 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]. There are two possible routes for catalytic oxidation on gold clusters. The first route consists in a preliminary dissociation of the adsorbed \( \text{O}_2 \) followed by consequential oxidation of a reactant molecule by atomic oxygen. The second route is a direct oxidation reaction between the activated molecular \( \text{O}_2 \) and the reactant. It has been demonstrated that CO oxidation reaction catalyzed by gold clusters can occur via Langmuir-Hinshelwood (LH) or Eley-Rideal (ER) mechanisms, depending on cluster charge. Thus the neutral \( \text{Au}_{10} \) can catalyze oxidation of CO via Langmuir-Hinshelwood mechanism even below room temperature [41]. CO oxidation on anionic gold clusters occurs via 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 \( \text{SiO}_2 \) or h-BN, do not affect the electronic and geometry structure of the supported clusters. Therefore in the absence of strong support interactions 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 \( \text{O}_2 \) 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 weak interaction of Au and \( \text{Au}_2 \) 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 5d orbitals of the supported Au and \( \text{Au}_2 \) with the N\(-\text{p}_{z}\) orbitals. Although the defect-free h-BN surface does not act as a good electron donor for the supported \( \text{O}_2\text{-Au} \), it promotes an electron transfer from the Au to \( \text{O}_2 \), pushing electrons from the gold to the adsorbed oxygen. In the case of defected h-BN surface Au and \( \text{Au}_2 \) can be trapped effectively by N or B vacancy and impurity point defects. Strong adsorption on the surface defects is accompanied by charge transfer to/from the adsorbate which can affect catalytic activity of gold [48]. Very recently adsorption of small gold clusters
on the h-BN/Rh(111) nanomesh has been studied theoretically [57]. It was noticed that all Au atoms in these clusters 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 found that there are 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. It is demonstrated that the inert h-BN support can affect the process of CO oxidation and corresponding reaction barriers. It is shown that presence of h-BN support can affect the CO oxidation barriers and overall probability of oxidation reaction. Therefore h-BN cannot be considered as an inert support for Au.

2. Theoretical Methods

The calculations are carried out using density-functional theory (DFT) with the gradient-corrected exchange-correlation functional of Wu and Cohen (WC) [58] as implemented in the PWSCF package [59]. 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 like graphite or h-BN, whose distances between the layers are determined by rather weak interactions [60]. The WC functional was successfully used in our previous works to describe 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, 61].

A plane-wave basis sets and Troullier-Martins norm-conserving pseudopotentials are used [62]. 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 [63]. We have checked that the total spin of the whole system does not change at transition states.

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. 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 the vacuum region of 15 Å in the (001) direction. Only the $\Gamma$ point is used for sampling the Brillouin zone due to the large size of the supercell.

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 adsorbants 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 [64–66] as well as adsorption and dissociation of O$_2$, H$_2$, and C$_2$H$_4$ molecules on free and supported gold clusters [46–48, 50, 55, 56, 67].

The binding energy of a molecule M (O$_2$ or CO) to a free or supported Au atom is defined as

$$E_b = E_{\text{tot}}(M) + E_{\text{tot}}(\text{Au}) - E_{\text{tot}}(M - \text{Au}),$$

(1)
where $E_{\text{tot}}(M - \text{Au})$ denotes the total energy of the complex system $M - \text{Au}$, while $E_{\text{tot}}(M)$ and $E_{\text{tot}}(\text{Au})$ are the total energy of non-interacting $M$ and $\text{Au}$ species, respectively. Here $M$ denotes $O_2$ or CO molecule, while $\text{Au}$ corresponds to a free or supported Au atom.

3. Theoretical Results

There are two possible routes for catalytic oxidation on gold clusters. The first route consists in a preliminary dissociation of the adsorbed $O_2$ followed by the consequential oxidation of a reactant molecule by the atomic oxygen. The second route is a direct oxidation reaction between the activated molecular oxygen and the reactant. In the present work both of the possible processes are considered.

3.1. Dissociation of $O_2$ on h-BN supported gold atoms

First, we have studied the $O_2$ dissociation on Au atoms trapped by pristine and defected h-BN surfaces. Figure 1 presents potential energy profiles for $O_2$ dissociation on supported h-BN supported Au. It can be seen that oxygen molecule adsorbs on top of the Au atom supported on the defect-free h-BN surface and trapped by the $V_B$ defect, but bridges Au and the surface B atom in the case of $O_2$ adsorption on the $\text{Au}/V_N@h-$BN center. Interaction of Au with the defect-free h-BN support stabilizes the initial state of $O_2$ adsorbed molecularly on $\text{Au}/h$-BN. As a result, the barrier for $O_2$ dissociation on $\text{Au}/h$-BN become 2.92 eV. The barrier for $O_2$ dissociation on a defected-free h-BN supported Au atom is too high and the dissociated configuration of $O_2$ is not favorable energetically; thus $O_2$ dissociation cannot occur spontaneously. The barrier for $O_2$ dissociation on $\text{Au}/V_B@h$-BN adsorption center is 2.48 eV, which lower than those calculated for $\text{Au}$ and $\text{Au}/h$-BN adsorption centers, however the final dissociated state of oxygen is not favorable energetically. Figure 1 demonstrates that the potential energy profile calculated for $O_2$ dissociation on the $\text{Au}/V_N@h$-BN adsorption center differs considerably from those obtained for free Au atom and Au adsorbed on $V_B@h$-BN. Figure 1 also demonstrates the final configuration of the dissociated oxygen on $\text{Au}/V_N@h$-BN is energetically favorable. Thus, dissociation of $O_2$ can occur even on a single Au atom if it is trapped by the $V_N$ defect on h-BN surface. Although the presence of h-BN support can lower the barrier of $O_2$ dissociation, it remains relatively high and $O_2$ dissociation cannot occur spontaneously with an exception of $\text{Au}/V_N$ adsorption center [55]. It has been shown that the barrier of $O_2$ dissociation on a single Au atom is too high. Therefore, in the next step, we focus on the mechanism of direct oxidation of CO by activated $O_2$.

3.2. CO oxidation with activated $O_2$ on h-BN supported Au atoms

The optimized geometries of CO adsorbed on $\text{Au}/h$-BN, $\text{Au}/V_B@h$-BN and $\text{Au}/V_N@h$-BN centers are shown in Fig. 2. It is seen from Fig. 2 that CO adsorption on $\text{Au}/h$-BN, $\text{Au}/V_B@h$-BN and $\text{Au}/V_N@h$-BN centers, CO always binds on top of Au atom, forming Au–C bond.

This result is consistent with the previous study on CO adsorption on small cationic, neutral, and anionic $\text{Au}_n$ ($n = 1$-$6$) 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 [68].

Figure 3 demonstrates possible reaction pathways for this process. The results of our calculations demonstrate that CO adsorbs on $\text{Au}/h$–BN with the binding energy of 1.03 eV, which is larger that the binding energy of $O_2$ to $\text{Au}/h$–BN. After adsorption of the first CO on $\text{Au}/h$–BN two different pathways for $O_2$ adsorption are possible, as it is shown in Fig. 3(a). The first is the coadsorption of $O_2$ on Au without direct interaction with CO (Langmuir-Hinshelwood
Figure 1. (a) Potential energy profiles for $O_2$ dissociation on Au/h-BN. The zero energy corresponds to the noninteracting $O_2$ and Au/h-BN, Au/V$_B$@h-BN, or Au/V$_N$@h-BN adsorption centers. The relative energies are given in eV. Adsorbed configurations of oxygen are marked by the star (*); (b) Optimized geometries of transition (TS) and intermediate (INT) states (only part of the slab is shown).
mechanism) resulting in formation of the intermediate $A_1$. This is the 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 0.98 eV. The second pathway consists in a direct $O_2$ attack of $Au-CO$ and formation of the $A_2$ intermediate via transition state $TS_1'$ with the barrier of 0.04 eV.

In order to obtain the final product $CO_2$ from the intermediate $A_2$ there are two possibilities: (i) a two-step process with formation of the first $CO_2$ product via transition state $TS_2$ with barrier of 0.67 eV, and 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 the barrier of 0.49 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].

Let us consider CO oxidation on Au trapped by the nitrogen and boron point defects on h-BN surface. As it was discussed above, the boron vacancy $V_B$ plays a role of the electron acceptor. Therefore, Au trapped by $V_B@h-BN$ is positively charged. The positive charge localized on Au promotes 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 $B_1$ 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 formation of CO-$AuO/V_B@h-BN$ 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 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. After that CO can react with the dissociated O atom with a barrier of 1.21 eV, or with the activated $O_2$ molecule. Intermediate $C_1$ can be formed directly without any barrier after $O_2$ activation. 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. The barrier of CO oxidation with dissociated O atom is higher than the case of reaction with activated $O_2$ molecule. The
Our finding leads to an important conclusion that Au supported on the h-BN surface (pristine pathways except for the case of V_B is promoted by the second CO molecule. CO oxidation reaction follows the self-promoting formed independently; (ii) the self-promoting pathway when oxidation of the first CO molecule O_2 atom is too high. The CO oxidation reaction follows the pathways that CO react with activated Au/V_B it remains relatively high and O_2 dissociation cannot occur spontaneously with an exception of Au/V_N adsorption center. It has been shown that the barrier of O_2 dissociation on a single Au atom is too high. The CO oxidation reaction follows the pathways that CO react with activated O_2 molecule. There are two possibilities: (i) the two-step pathway when two CO_2 molecules are formed independently; (ii) the self-promoting pathway when oxidation of the first CO molecule is promoted by the second CO molecule. CO oxidation reaction follows the self-promoting pathways except for the case of V_B@h-BN center. 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 an important conclusion that Au supported on the h-BN surface (pristine or defected) cannot be considered as pseudo-free atom.

4. Conclusion
In the present work, we have studied mechanism of CO oxidation reaction on free and h-BN supported gold atom. The pristine h-BN surface and h-BN surfaces with boron and nitrogen vacancies have been considered. Various pathways of CO oxidation reaction by molecular oxygen are studied. Although the presence of h-BN support can lower the barrier of O_2 dissociation, it remains relatively high and O_2 dissociation cannot occur spontaneously with an exception of Au/V_N adsorption center. It has been shown that the barrier of O_2 dissociation on a single Au atom is too high. The CO oxidation reaction follows the pathways that CO react with activated O_2 molecule. There are two possibilities: (i) the two-step pathway when two CO_2 molecules are formed independently; (ii) the self-promoting pathway when oxidation of the first CO molecule is promoted by the second CO molecule. CO oxidation reaction follows the self-promoting pathways except for the case of V_B@h-BN center. 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 an important conclusion that Au supported on the h-BN surface (pristine or defected) cannot be considered as pseudo-free atom.
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