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# Catalytic activity of Au clusters on the "inert" h-BN surface

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## I. Introduction

We present results of the systematic theoretical investigation of the structural and electronic properties of Au and $Au_2$ deposited on the regular h-BN surface, as well as on the h-BN surface with B and N vacancy and impurity defects. Adsorption, catalytic activation of $O_2$ as well as catalytic oxidation of CO by $O_2$ on Au/h-BN and $Au_2$/h-BN are studied with the aim to understand the specific role played by the h-BN support in the catalytic processes on gold clusters.

The unique catalytic activity of gold nanoparticles in oxidation reactions by molecular oxygen was discovered experimentally more than 20 years ago [1]. It was shown that the so-called "active" supports, such as metal oxides, considerably influencing the catalytic activity of gold clusters [2,3]. Some adsorbates, including reactant molecule itself can also promote catalytic activity of the gold clusters [4,5,6]. On the other hand it is commonly accepted that "inert" supports, such as, for example hexagonal boron nitride (h-BN) do not affect the electronic and geometry structure of the supported clusters, and hence such clusters can be considered as pseudo–free. This suggestion is widely used to study intrinsic properties of metal clusters that are free from the support effects [7]. Thus, it has been demonstrated experimentally that small gold clusters deposited on h-BN support are efficient and robust catalysts [7]. However, the origin of catalytic activity of gold clusters supported on h-BN has yet to be fully understood. The present work aimed to clarify whether the catalytic activity of $Au_n$/h-BN is the intrinsic property of gold clusters or h-BN support is not inert for gold.

## II. Computational methods

The calculations are carried out using density-functional theory (DFT) with the generalized gradient-corrected exchange-correlation functional of Wu and Cohen as implemented in the SIESTA code. Double-$\zeta$ plus polarization function (DZP) basis sets are used to treat the $2s^2 2p^1$, $2s^2 2p^3$, $2s^2 2p^4$ and $5d^{10} 6s^1$ valence electrons of B, N, O and Au, respectively. The remaining core electrons are represented by the Troullier-Martins norm-conserving pseudopotentials in the Kleinman-Bylander factorized form. Relativistic effects are taken into account for Au. The atoms in molecules method of Bader (AIM) has been used to calculate charge distribution in the considered systems.

## III. Results and discussion

In the present work we demonstrate that catalytic activity of gold clusters can be sensitive not only to the interaction with the active support materials, such as metal oxides, but also to the interaction with the inert supports, such as h-BN. It is shown that vacancy defects on the h-BN surface can promote the catalytic activity of the supported Au clusters. It is demonstrated that Au and $Au_2$ interact weakly with the regular h-BN surface; however they can effectively be trapped by vacancy

defects. We found that Au and $Au_2$ adsorb most strongly on the vacancy of B atom. Strong adsorption on the surface defects is accompanied by the charge transfer to/from the adsorbate. The value and the sign of the charge accumulated on the adsorbate depend on the adsorption sites. The excess of the positive or negative charge on the supported gold clusters can considerably promote their catalytic properties and enhance activation of the adsorbed $O_2$ (Fig. 1).
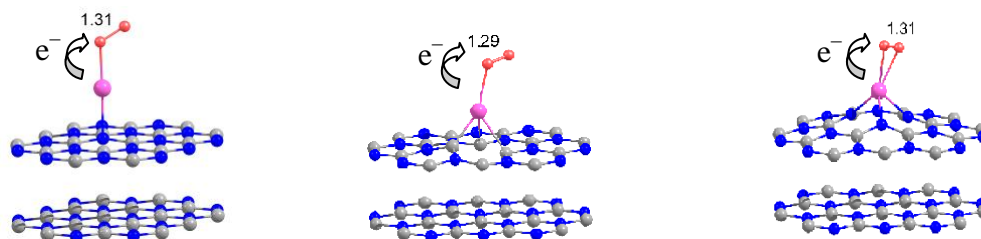


**Figure 1**. Optimized geometries of $O_2$ on the Au atom supported on the pristine h-BN surface (left); h-BN surface with the N vacancy (middle) and h-BN surface with the B vacancy (right).

We demonstrate that interaction of Au with the defect-free h-BN surface also leads to the strong promotion of binding and catalytic activation of the adsorbed $O_2$. Hybridization of the 5d states of the supported Au with N-$p_z$ states results in a strong modification of the Au-5d states, which in turn strongly influence the adsorption of $O_2$ on the supported Au (Fig. 2).
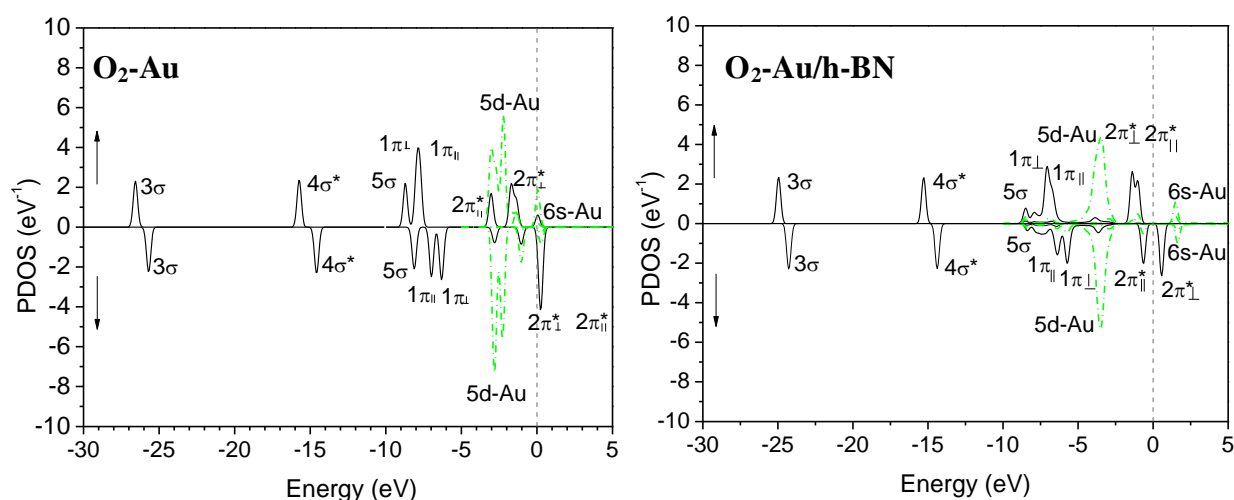


**Figure 2.** Partial density of electronic states (PDOS) projected on the $O_2$ molecule (solid line) and Au atom (dashed line) calculated for $O_2$ adsorbed on the free (left) and h-BN supported (right) Au.

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