



Full Length Article

Theoretical insights into acetylene adsorption on nanoporous gold surfaces: Role of residual silver



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ABSTRACT

Unveiling the acetylene adsorption is crucial for designing novel and highly active catalyst for the semi-hydrogenation of alkyne. In order to achieve this goal, we have studied C₂H₂ adsorption on the various nanoporous gold models in detail, including the Au(100), Au(111) and Au(321) slab models. The calculated results indicate that the C atoms of C₂H₂ experience rehybridization from sp toward sp²/sp³ when the adsorption occurs on bridge and hollow sites, which can be illustrated via the projected density of state (PDOS) and crystal orbital Hamilton population (COHP). Meanwhile, the formation of σ(Au–C) bond is beneficial for facilitating acetylene adsorption and the kink Au atom plays an important role for the C₂H₂ adsorption. In addition, for C₂H₂ adsorption on the Ag doped nanoporous gold, the configurations strongly depend on the position of superficial unsubstituted Au atoms. Further, the inversely relationship has been found between the adsorption energies and number of the Ag substituents, demonstrating that the superficial Ag substituents are harmful for C₂H₂ adsorption and activation.

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1. Introduction

Unsupported nanoporous gold (NPG) materials, as catalysts, have aroused extensive attention due to the excellent virtues, including high surface area, high stability for versatile chemicals, high reusability, no toxic nature and green [1–8]. Moreover, the unique structural features of NPG, such as tree-dimensional (3D) bicontinuous open network structure and high surface-to-volume ratio, make it become an attractive candidate for heterogeneous catalysis [9], electrocatalysis [5,10,11], sensors [12] and optics [13]. NPG catalyst has exhibited excellent activity for the selective oxidation reactions, for example, the CO oxidation, alcohols oxidation in liquid-phase, the electrochemical oxidation of MeOH, and so on [6,8,14–16].

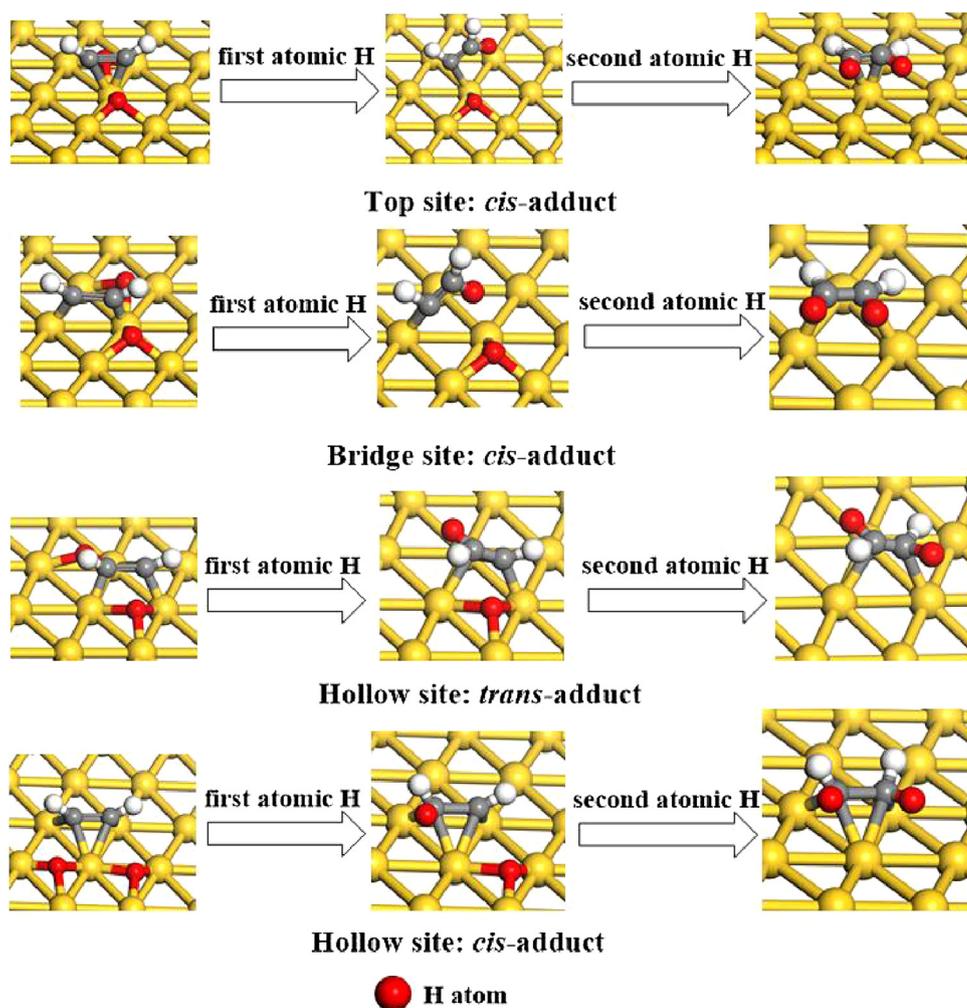
However, NPG catalyst used for selective hydrogenation is few reported owing to the limited ability of gold for H₂ dissociation. Recently, Yamamoto and co-workers have found that unsupported NPG catalyst possesses highly reactivity for selective hydrogenation of alkynes and organosilanes with water as the hydrogen source [17]. Apart from the hydrogen source, inevitably, the

adsorption of alkyne on the unsupported NPG surfaces is another pivotal step for the semihydrogenation of alkyne because the activation of alkyne is closely related with the continued reaction processes [18,19]. Moreover, the conformation of the partial hydrogenation product, namely *cis*- and *trans*-adducts, deeply depends on the adsorption configuration of alkyne and the corresponding relationship is shown in the Scheme 1. It is found that the diboration of alkynes over the nanoporous gold can form the adducts predominantly and in some cases the formation of small amounts of the *trans*-adduct, which is described in the review reported by Yamamoto and co-workers [20]. Therefore, the investigation of alkyne adsorption on the nanoporous gold is necessary and valuable. In addition, according to the SEM and TEM characterization [17], the atomic steps and kinks on the ligament surface have a high concentration of low-coordinated Au atoms, indicating that they should be the important origins of catalytic activity. Understanding the active site for the important elementary steps is crucial for reasonably designing the catalyst. Therefore, unveiling the active site for alkyne adsorption on the NPG should be also inestimable for designing the high-performance semihydrogenation catalyst.

In addition, for the NPG, the catalytic activity can be tremendously perturbed by the Ag impurities. In general, the NPG is composed of two different components, Au and Ag, while the Au is the predominated component. Based on the wide explorations [21–23], the Ag impurities play a crucial role in the catalytic activity

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Scheme 1. The relationship between the adsorption configuration of C_2H_2 and the corresponding *cis*- or *trans*- adduct.

of NPG. For instance, the NPG without residual Ag is nearly inactive for the CO oxidation [22]. The higher content of impurity Ag atoms can cause high catalytic activities in CO oxidation and O_2 dissociation [24,25].

Although the previous works have proved that the impurity Ag atom can play an important role in the CO oxidation and O_2 dissociation, the nature of active site and the role of impurity Ag atom remain unknown in the adsorption of alkyne on NPG. Which site is preferred for alkyne adsorption? How does the residual Ag affect the alkyne adsorption, a small amount of Ag or a large concentration of Ag can cause outstanding effect? Here, the present work systematically investigated the adsorption of acetylene on the NPG surfaces using density functional theory (DFT) calculations. Moreover, in order to unveil the role of residual Ag atoms, the adsorption of acetylene on the silver-doped NPG was also taken into account.

2. Computational models and methods

In this paper, three Au-slab models (Scheme 2) were constructed to unveil the acetylene adsorption on NPG. As Scheme 2 shown, the flat Au(111) and Au(100) slabs were constructed using (4×8) surface unit cells and consisted of six atomic layers. On the basis of constructed Au(111) and Au(100) slabs, the Au(100)-np and Au(111)-np slab models are obtained via removing the top-layer and second-layer Au atoms, resulting in the formation of step and kink Au sites. For the kinked Au(321) surfaces, (4×4) surface unit

cells are employed with 12 layers. Herein, the high density of low-coordinated Au atoms with coordination numbers 6 and 8 along zigzag-shaped steps can be regarded as a reasonable first approach to represent terrace and step or kink sites. The 6-fold coordinated Au atoms along the step are served as the kinks, see Scheme 2. In order to elucidate the role of the residual Ag atoms, we conducted the adsorption reaction of acetylene on the different superficial and sub-superficial silver-doped Au-slab models. These models can be representative of most probable facets that may be present in nanoporous gold catalysts [21,26]. For each model, most favorable types of atoms for acetylene adsorption were identified.

All DFT calculations were performed using Dmol³ software [27,28] with the generalized-gradient approximation (GGA) in the form of the PBE functional. The real-space global cutoff radius was set to be 4.5 Å. The structural optimizations were performed with a $2 \times 1 \times 1$ k-point grid for (111) and (100) and Gamma point for (321). The double numerical plus p polarization (DNP) basis set and semicore pseudopotential were used to treat atomic orbitals and core electron of Ag and Au, respectively. The all-electron basis sets were used for other atoms (C and H). The van der Waals interactions were taken into consideration by adding a pairwise interatomic term E_{disp} to the Kohn–Sham DFT energies, which was evaluated using the Tkatchenko–Scheffler (TS) scheme by Tkatchenko and Scheffler [28]. The convergence criteria for the geometrical optimization are 1.0×10^{-5} hartree for energy change, 2.0×10^{-3} hartree for the gradient and 5.0×10^{-3} hartree for the displacement.

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