

Novel Nanocatalysts for Water-Gas-Shift Reactions

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Introduction

The water-gas-shift (WGS) is an important reaction in the chemical industry, where CO and H₂O are converted into CO₂ and H₂. [1,2] It is primarily used to increase the H₂ content as well as reducing the CO concentration in synthesis of gas and is an essential part of a hydrogen plant. [2] More recently, the interest in the WGS reaction has increased due to its emerging application for onboard purification and production of H₂ for fuel cell vehicles. Cu-based catalysts are used for industrial operations of the WGS at relatively low temperature (470K-520K). [3] However, there are problems in using these systems for automotive applications, [4] which may result in condensation of water and subsequent deactivation of the catalysts. Hence, advanced WGS catalysts that include high activity and stability become a real need for the development of the fuel cell technology.

Recent experiments show that Au or Cu nanoparticles supported on the oxides, such as CeO₂ and TiO₂, display higher activity in the WGS reaction than the bulk materials and commercial catalysts. [5] However, the reaction mechanism and the origin of the high activity still remain elusive. To clarify the obscurity, we employ density functional theory (DFT) to investigate the WGS reaction on Au and Cu nanoparticles with a diameter of 1.2nm (Figure 1), which have been observed on CeO₂(111) with STM.

Materials and Methods

The DFT calculations were performed using DMol³. The ionic cores were described by effective core potentials (ECP). A numerical basis set was used with comparable accuracy to a Gaussian 6-31G (d) basis set. A local basis cutoff of 5.0 Å in real space was employed. The generalized gradient approximation (GGA) with PW91 functional was utilized in the present work. The adsorption of intermediates involved in the WGS reaction (CO, H₂O, OH, O, H, HCOO, HOCO and CO₂) was investigated. The transition state is calculated using a linear synchronous transit (LST). It was followed by repeated conjugate gradient minimizations and quadratic synchronous transit (QST) maximizations until a transition state has been located.

Results and Discussion

Our results show [6] that the WGS reaction follows redox mechanism on Cu(100), while the associative mechanism via a carboxyl intermediate is preferred for Au(100), Au₂₉ and Cu₂₉ (Figure 1). However, the rls step for all these systems is the same, water dissociation.

WGS activity was found to decrease in a sequence: Cu₂₉ > Cu(100) > Au₂₉ > Au(100), which is in good agreement with the experimental observations. Both nanoparticles are more active than their parent bulk surfaces. The nano-scale promotion on the WGS activity is associated with the corner of the edge sites, which are more active than those in the flat surfaces for O-H bond cleavage. A free Cu nanoparticle can catalyze the WGS reaction easily.

In contrast, on the extended Cu(100) surface the dissociation of water has a larger activation barrier. Neither Au₂₉ nor Au(100) is able to adsorb or dissociate the water molecule and catalyze the reaction. Although there is a significant improvement in chemical reactivity when going from Au(100) to Au₂₉, it is not enough for dissociating the water molecule (Figure 2). Charging of the Au nanoparticle to form either Au₂₉⁻ or Au₂₉⁺ also does not help (Figure 2). These results cannot explain the large catalytic activity observed experimentally for Au/CeO₂(111). Instead, they imply that CeO₂ should be directly involved to lower the barrier of water dissociation and facilitate the reaction substantially.

Significance

Our DFT studies make significant insight into the mechanism, the active sites, and the origin of the high activity of the WGS reaction on Cu and Au nanoparticles. This is of great importance for the further development of supported metal nanoparticles as WGS catalysts. From a fundamental point of view, this work also provides an insight towards how a metal nanoparticle catalyzes a reaction.

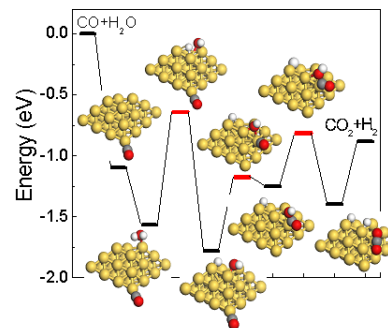


Figure 1. Reaction profile and structures for the WGS reaction on a Cu₂₉ nanoparticle. The red bars represent the transition state, and the black stand for reactants, intermediates or products. Yellow balls: Cu; red balls: O; grey balls: C; white balls: H.

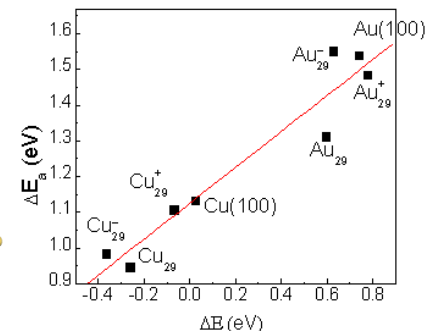


Figure 2. Correlation between the calculated barrier (ΔE_a) and the calculated reaction energy (ΔE) for water dissociation on several copper and gold systems

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