

Oxygen and hydrogen dissociation on gold clusters

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The specific role played by small gold clusters in the processes of catalytic oxidation and hydrogenation will be discussed. The unique catalytic activity of gold nanoparticles was discovered experimentally more than 20 years ago [1]. It was found that extraordinary catalytic properties of gold can be achieved by decreasing the size of the gold particles up to 1-5 nm, while larger particles and the bulk form of gold are catalytically inactive [2]. The origin of such size-dependent catalytic activity of gold remains highly debated. On one hand, the unusual catalytic properties of small gold clusters are determined by quantum size effects, resulting from the spatial confinement of the valence electrons in the cluster; on the other hand, in such clusters a dominant fraction of atoms are under-coordinated (in comparison with the bulk), hence they exhibit an enhanced chemical reactivity. Most experimental studies on the catalytic properties of gold clusters have been performed for clusters supported on the surfaces of metal oxides. It was demonstrated that the support material can play an important role in the catalytic process, thus considerably influencing the chemical reactivity of the supported cluster. Moreover, recent experiments by Haruta et al. demonstrate that the perimeter interface between the cluster and the support material can be the active site for hydrogen dissociation by gold nanoparticle on TiO₂ support [3]. However, a work by Turner et al. presents strong experimental evidence that small gold entities (~1.4 nm) deposited on an inert support can also be efficient and robust catalysts, hence catalytic activity is an intrinsic property of gold clusters [4].

In the present work, we demonstrate that catalytic reactivity of gold clusters can be sensitive not only to the interaction with the support material, but also to the presence of adsorbates on the cluster surface, including the reactant molecule itself. We report results of a theoretical investigation of the molecular and dissociative adsorption of O₂ on the pure odd-size Au_n (n=1, 3, 5, 7, 9) clusters and Au_n with a coadsorbed reactant – ethylene molecule [5-7]. It is demonstrated that catalytic activation of the adsorbed O₂ on the pure gold clusters in the considered size range cannot lead to O₂ dissociation. We find, however, that coadsorption of C₂H₄, involves an extra charge transfer from the gold cluster to O₂, energetically promoting oxygen dissociation [7]. The reaction barriers for O₂ dissociation on the pure Au_n clusters, and Au_n clusters with adsorbed C₂H₄ have been analyzed. Our finding indicates that adsorption of the reactant molecule on the surface of small neutral gold clusters can considerably influence the oxygen-gold interaction. It is necessary to take into account such an influence of the adsorbed reactant molecule on oxygen dissociation, even when there is no direct interaction between oxygen and the reactant [7]. Such a phenomenon can be particularly important for better understanding the mechanism of catalytic oxidation of ethylene and other hydrocarbons on gold clusters.

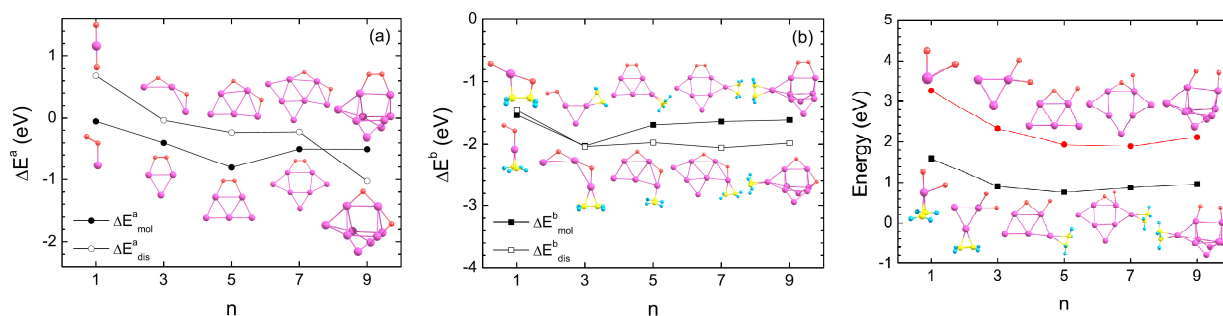


Figure 1: *Left:* energy change in the case of molecular (filled dots) and dissociative (open dots) adsorption of oxygen on the pure Au_n clusters, calculated relative to the energy of the non-interacting fragments, Au_n and O_2 ; *Middle:* energy change in the case of molecular (filled squares) and dissociative (open squares) adsorption of oxygen on Au_n clusters with coadsorbed reactant - ethylene molecule, calculated relative to the energy of the non-interacting fragments, Au_n , O_2 and C_2H_4 ; *Right:* energy of transitional states for O_2 dissociation in $\text{O}_2\text{-Au}_n$ (filled dots) and $\text{O}_2\text{-Au}_n\text{-C}_2\text{H}_4$ (filled squares) systems.

We also have studied molecular and dissociative adsorption of H_2 on small free gold clusters and gold clusters supported on the rutile TiO_2 (110) surface. It is demonstrated that active sites towards H_2 dissociation are located at corners and/or edges on the surface of gold cluster in agreement with previous theoretical studies [8]. Interaction with the TiO_2 (110) surface can alter the geometry structure of the supported cluster and promote hydrogen dissociation.

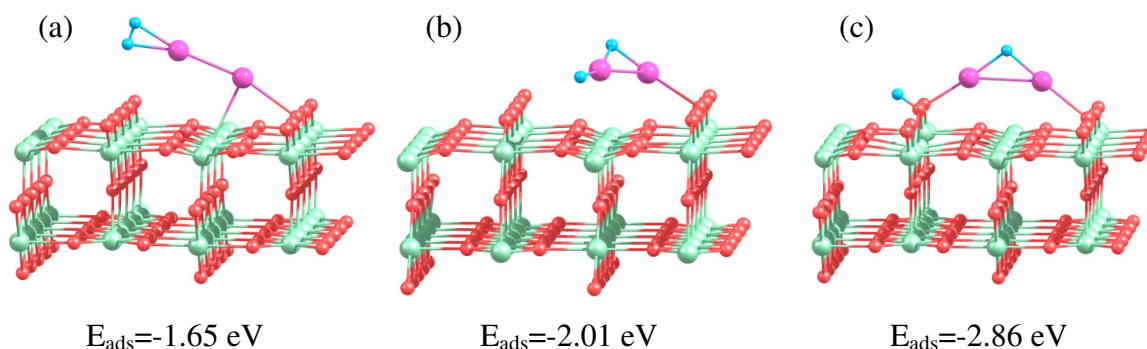


Figure 2: Optimized geometries in the case of molecular (a) and dissociative (b) and (c) adsorption of H_2 on Au_2 supported on the TiO_2 (110) surface.

References

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