Reactivity study of CO on the surface of nanosized gold cluster

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1 Introduction

Carbon monoxide (CO) is one of the main air pollutants originating from motor vehicles and stationary combustion plants. There are many innovative technologies to reduce drastically the CO emissions, e.g., automotive catalysators have been widely used over twenty years. There Pd and Pt based three-way catalyst are normally used but they need over +200ºC to oxidize CO to CO_2. However, most of the CO emission from traffic is emitted during the first five minutes after start up. For this reason, it is important to develop more active and selective heterogeneous catalyst to these devices. In this kind of effort, computational methods gives support to experimental study, by giving tools not only to understand catalysts at atomic scale but also to engineer the materials from knowledge of its electronic structure (Nørskov, 2009).

M. Haruta et al. discovered that supported gold nanoparticles (AuNPs) can oxidise CO in very mild conditions, even below room temperature (Haruta, 1987). Despite of more than two decades of research the catalytic mechanism of AuNP catalysis is still not well understood. The aim of this study is to use computational tool to study CO oxidation on 1.4 nm gold nanoparticles. Experimentally, a nanoparticle of this size has been found to be very selective and effective catalyst to oxidize various compounds (Turner, 2008).

2 Objectives of the research

Instead of using support material, reactivity of CO (i.e. adsorption and dissociation, oxidation) has been studied on an isolated icosahedral Au_{55} nanoparticle's surface. The calculations have been done using the density functional theory (DFT) and super-computers of the Finnish IT centre for sciences (CSC). The full relaxed stable adsorption geometries were calculated using the GPAW code (Mortensen, 2005) with the general gradient correction approximation (rPBE-functional) and dissociation reactions were calculated with nudged elastic band theory (NEB (Henkelman, 2000)).

3 Results

3.1 CO adsorption

First, the adsorption of the CO molecule was studied. The bridge sites were found to be the most stable ones and, during the geometry optimization, the CO molecule spontaneously moved from the hollow (A) site to the bridge ones whereas top site (D) and hollow site (E) were unfavourable ones.

Table 1 *CO adsorption*

Initial geometry	Final geometry	B.E. [eV]
A	B	-0.41
B	B	-0.34
C	C	-0.26
D	-	-
E	-	-
F	F	-0.34

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3.2 CO dissociation

CO dissociation is one of the most important reactions in industrial chemistry and it has also served as a test reaction in the recent exploration of the catalytic activity of Au nanoparticles. In this study, a dissociation of CO, kinetic barriers for the reaction were calculated on the step and on the facet of the cluster. The edge site was found to be slightly less efficient than the flat site for the CO's bond breaking (Figures 1 & 2.). Still, the barrier is very high and the CO molecule will much more likely fly off from the cluster than dissociate.

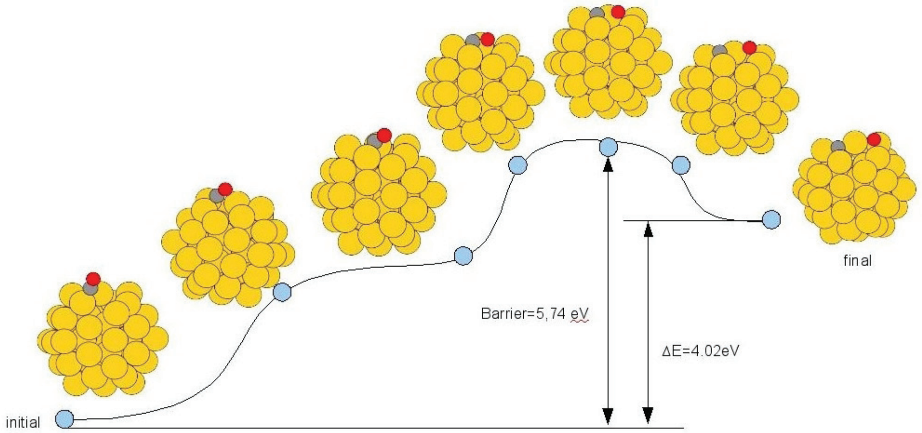

Figure 1 *CO dissociation on the same facet.*

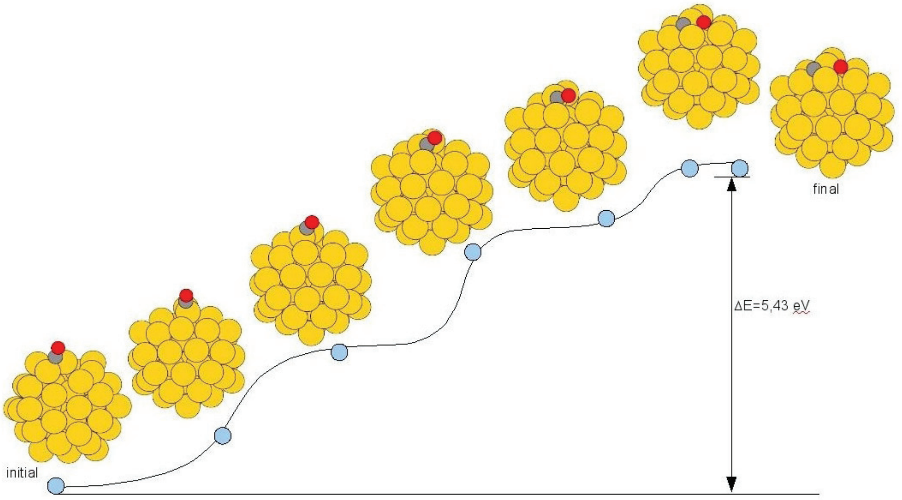

Figure 2 *CO dissociation on the different facet.*

3.3 O_2 dissociation

In the literature, the dioxygen dissociation is found to occur more feasible than CO. Turner et al. showed experimentally that there is a strong size threshold of gold particle's size to dissociation molecular oxygen (Turner, 2008). This is also observed computationally by Roldán et al. (Roldan, 2009), they found a barrier to be 0,47 eV on surface on Au_{38} with RevPBE exchange-correlation functional. In the present study, atomic oxygen has been found to be stable (figure3). When the atomic oxygen exists, the oxidation is possible to take place.

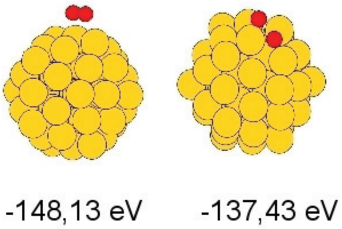

Figure 3 *Molecular oxygen (left) and atomic oxygen adsorbed on the surface (right).*

3.4 CO_2 forming

The oxidation of CO was modelled in situation when both CO and atomic oxygen are initially adsorbed in the most favourable positions; CO in the bridge site on the triangular facet, whereas oxygen in hollow site. From this starting geometry, the CO_2 formation was spontaneous (Figure 4).

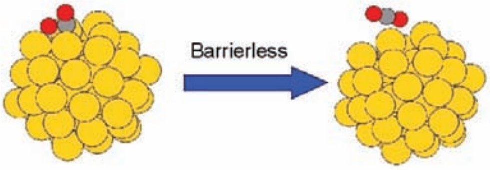

Figure 4 *Formation of CO_2 on the surface of Au_{55}.*

4 Relevance of the research

In this study, an adsorption of CO on the surface of Au_{55} has been showed to favour bridge sites. CO dissociation has been found to be infeasible to get atomic oxygen on the cluster. This is due to the very high reaction barrier. Due to the fact that atomic oxygen was found to be stable on the surface of gold cluster and of evidence of dissociative adsorption of molecular oxygen from literature, the oxidation of CO has been modelled. Much more studies are still needed but gold is a very attractive material and understanding its catalytic behaviour helps us for developing future's catalyst materials and devices to reduce carbon emissions.

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