Oxidation state of oxide supported nanometric gold

J. G. Wang and B. Hammer*

Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, University of Aarhus, DK 8000 Aarhus C, Denmark

We address the structure gap between surface science and catalysis studies of the activity of oxide supported Au clusters. Reviewing the recent literature we find that surface science investigations often deal with highly reduced systems that have anionic Au clusters and oxygen vacancies in the support. The catalysis studies on the other hand consistently report on oxidized samples with traces of cationic Au. Performing density functional theory calculations we show that the effect of oxidation of oxide supported Au clusters, Au₈/MgO, Au₇/TiO₂ and Au₁₀/TiO₂, is a strong increase in the Au/support adhesion energy and a great structural transformation of the clusters. Some of the Au atoms become positively charged (cationic) in the oxidation process as evidenced indirectly by calculated vibrational stretch frequency shifts of adsorbed CO.

KEY WORDS: gold nanoparticles; oxidation state; gold oxide; magnesium oxide; titanium dioxide; O₂ dissociation; CO adsorption; CO oxidation; CO stretch frequencies.

1. Introduction

Nanometric gold is known to exhibit catalytic activity for numerous reactions when supported on a range of oxide supports [1–4]. The physical origin of the catalytic behavior has developed into a controversial topic with many different explanations proposed. This diversity can partly be explained by considering that much different conditions have been assumed in the various studies. For experimental investigations, in particular the method by which the gold is deposited varies a lot. Examples are: (i) wet-chemistry methods involving precipitation of Au ion complexes [1] or ligand-protected Au clusters [5] from solution followed by calcination (heat treatment in air), (ii) deposition of size-selected Au clusters [6], and (iii) physical vapor deposition [7]. Since the latter two methods rely on ultra high vacuum conditions, the resulting model catalysts may be in reduced oxidation states. The wet-chemistry methods on the other hand provide a framework for making more realistic model catalysts, i.e. metallic or even oxidized Au clusters on fully oxidized supports [4]. The theoretical investigations of supported Au clusters have almost exclusively been carried out for small Au clusters on highly reduced oxide surfaces, an approach which has recently been challenged by us [8].

In the present paper, we shortly review the status of recent experimental and theoretical investigations. We then turn to consider the equilibrium oxidation state of the model systems of choice in the literature, i.e. Au₈/MgO, Au₇/TiO₂ and Au₁₀/TiO₂, by means of first principles thermodynamics considerations. Next, the adsorption properties of the clusters as a function of their oxidation state are discussed and it is argued that CO prefers adsorption sites far from the oxide support, while O₂ requires adsorption sites in which bonding to both cluster Au atoms and oxide support cations is achieved. Finally, we use CO vibrational stretch frequency analysis to analyze the oxidation state of the Au.

2. Previous studies

Some of the most well defined studies of oxide supported Au clusters involve the deposition of size-selected Au clusters. Using scanning tunneling microscopy (STM) Buratto et al. have characterized the appearance of Auₙ for n = 1–8 on rutile TiO₂(110) [9]. Studying Au₈ on rutile TiO₂(110) for n = 1–7, Anderson and coworkers concluded that Au₇ is the smallest cluster to show an appreciable activity towards CO₂ formation [10]. Heiz and coworkers studied a range of Au clusters on thin oxide films, mainly MgO, and found that certain Au cluster sizes, for instance Au₈, gave particularly high activities for CO oxidation by O₂ [6,11–13]. In this work, the pinning of the clusters by F-centers in the oxide surface was emphasized and the clusters were found to be negatively charged.

Valden, Lai and Goodman investigated with STM Au clusters and islands formed by physical vapor deposition onto rutile TiO₂(110) and found a maximum in the measured catalytic activity for 2 ML thick Au aggregates [7]. The declining activity for smaller Au systems was discussed in terms of the opening of a band gap as a result of finite size effects in such systems. Measured IR shifts for the vibrational stretch mode of adsorbed CO consistently indicated a negative charge state of the Au atoms and islands [14]. Theoretical work by Pacchioni et al. identified bridging oxygen vacancies on rutile TiO₂(110) and F-centers on MgO(100) as preferred Au atom adsorption sites and possible nucleation
centers for clusters grown by vapor deposition [14,15].

More recent work from the Goodman group has characterized Au aggregates grown on thin TiO₂ films supported by a Mo single crystal. In this work, evidence is given for single and double mono-layer thin films of Au with again the two ML films being the most reactive [16–18]. Most recently, Ricci et al. have demonstrated by theoretical means how metal supported thin films of MgO accommodate Au clusters with flat, 2-dimensional shapes at oxygen vacancy sites unlike the situation on the surface of bulky MgO crystallites [19].

Wahlström et al. conducted atomically resolved STM studies of Au islands formed by vapor deposition onto deliberately reduced rutile TiO₂(110) surfaces [20]. By counting the oxygen vacancies (later, these species have been reassigned to bridging hydroxyls [21]) it was concluded that upon Au cluster formation, one surface defect would disappear for every three Au atoms incorporated into a Au island. Subsequently, Remedia-

kis, Lopez and Nørskov conducted a comprehensive set of density functional theory investigations for a Au₁₀ cluster fulfilling this Au-to-surface-defect rule [22]. The Au₁₀ was adsorbed on a rutile TiO₂(110) surface with three bridging oxygen vacancies. Under these conditions, it was found that the Au₁₀ would bind O₂ even at the top of the Au cluster, i.e. far from the support and a “gold-only” route for CO oxidation, where the adsorbates only require low-coordinated Au atoms to react, was suggested. Low-coordinated Au atoms such as step atoms on extended Au surfaces have been shown by both experimental [23] and theoretical [24,25] means to lead stronger bonding of adsorbates and to the onset of activity for nanometric gold [24]. One virtue of the proposed Au-only mechanism is that it would explain the apparent absence of a dependence of the catalytic activity of nano-gold on the type of oxide support that has been reported in some experiments [26–28].

A number of calculational studies have emphasized the occurrence of Au/support interface perimeter sites, where oxygen may adopt an adsorption configuration in which it binds to both a cationic site of the support and to one or more Au atoms in the cluster [29–33]. In this model, the high activity of nanocrystalline Au comes about because of the higher abundance of interface perimeter sites per Au atom the smaller the Au particles are.

Some experimental and theoretical studies have dealt with crystalline Au surfaces, Au films or Au particles that are highly covered by atomic oxygen [34–38]. These investigations consistently show that atomic oxygen is highly reactive on the Au surface, thus identifying that the activation of the molecular oxygen is a step of key importance in oxidation reactions over Au.

Most of the experimental investigations mentioned this far [6,7,9–14,16–18,20,23,34–36] can be considered surface science type studies in which the model catalysts where first formed in UHV. Likewise, most of the theoretical approaches [6,11–15,19,22,24,25,29–33] neglected the possibility of modification of the oxidation state of the Au particles by surrounding gases. These surface science studies thus have reasonably well-defined model catalysts. Considering the vast literature on the activity of nanometric gold particles, most reports are, however, dealing with more realistic, but less well-defined model systems. In the catalysis literature, the Au particles are for instance most often produced by wet chemistry and characterized by in-situ or in-operando techniques. Consequently, research published in the catalysis literature is often reporting on gold particles that differ from those in the surface science literature. The most striking difference is that oxidized, i.e. cationic Au is a common finding in much of the catalysis lit-

erature.

For Au/ CeO₂ catalyst, the presence of cationic gold clusters has been observed by time-resolved XANES spectra [39], XPS analysis [40,41] and FTIR spectroscopy [42] methods. Both of the stable cationic gold species (Au⁺ and Au³⁺) are reported to be involved in catalytic CO oxidation [42]. For Au particles supported by several kinds of iron-oxide, traces of cationic gold in addition to metallic gold were found by a combination of EXAFS, in situ XANES, XPS, and Mössbauer spectroscopy studies to play a vital role in catalyzing CO oxidation [43–45]. For the popular Au/TiO₂ model catalyst an increasing number of reports identifying some cationic Au under operating conditions are emerging. These involve techniques such as time-of-flight SIMS [46], DRIFTS [47], and XPS [47,48]. On Al₂O₃ supports, Au has also been reported to be partly oxidized using a variety of experimental methods including SIMS [46], XRD and FTIR [49] and XANES [50]. Finally, Au clusters supported by MgO have also been found to be oxidized to some extent using EXAFS and XANES [51]. It is interesting to note that for mononuclear gold complexes in NaY-zeolites the Au atoms were reported to be exclusively in the Au⁺ and Au³⁺ oxidation states with the latter showing the highest activity [52,53].

Quite a number of different reasons have been given for the favorable involvement of cationic Au in activating Au particles. The increased Au/support interface strength prohibiting sintering of the Au clusters is highlighted by some researchers [5,47]. The occurrence of reactive ensembles involving both metallic and oxidized Au are pointed out by others [39,40,42–46,50,54,55] and yet others have proposed that the activity of nanoparticulate Au is exclusively due to the cationic gold sites [49,56]. The possible activity of gas phase cationic Au has very recently been demonstrated by theoretical means in a study of free, cationic Au clusters that were found to adsorb both CO and O₂ [57].

It should be mentioned that studies in which only metallic gold [58–64] or even reduced gold [65] are found are also numerous in the catalysis literature. It remains,