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Atomic and molecular adsorption on Au(111)

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ABSTRACT

Periodic self-consistent density functional theory (DFT-GGA) calculations were used to study the adsorption of several atomic species, molecular species and molecular fragments on the Au(111) surface with a coverage of 1/4 monolayer (ML). Binding geometries, binding energies, and diffusion barriers were calculated for 27 species. Furthermore, we calculated the surface deformation energy associated with the binding events. The binding strength for all the analyzed species can be ordered as follows: $NH_3 < NO < CO < CH_3 < HCO < NH_2 < COOH < OH < HCOO < CNH_2 < H < N < NH < NOH < COH < Cl < HCO_3 < CH_2 < CN < HNO < O < F < S < C < CH$. Although the atomic species preferred to bind at the three-fold fcc site, no tendency was observed in site preference for the molecular species and fragments. The intramolecular and adsorbate-surface vibrational frequencies were calculated for all the adsorbates on their most energetically stable adsorption site. Most of the theoretical binding energies and frequencies agreed with experimental values reported in the literature. In general, the values obtained with the PW91 functional are more accurate than RPBE in reproducing these experimental binding energies. The energies of the adsorbed species were used to calculate the thermochemical potential energy surfaces for decomposition of CO, NO, N_2, NH_3 and CH_4, oxidation of CO, and hydrogenation of CO, CO_2 and NO, giving insight into the thermochemistry of these reactions on gold nanoparticles. These potential energy surfaces demonstrated that: the decomposition of species is not energetically favorable on Au(111); the desorption of NH_3, NO and CO are more favorable than their decomposition; the oxidation of CO and hydrogenation of CO and NO on Au(111) to form HCO and HNO, respectively, are also thermodynamically favorable.

1. Introduction

Interest in the catalytic properties of gold nanoparticles emerged in the late 1980s, when Haruta and coworkers reported that these particles are effective catalysts for the oxidation of CO at low temperature [1,2]. In the same decade, another key discovery was made by Hutchings, when he reported that gold nanoparticles are very selective catalysts for the hydrochlorination of acetylene [3]. However, the commercialization of gold catalysts did not start until a decade later, c.a. 1992, when they were proven to decompose ammonia and trimethylamine at room temperature, and were used mainly to decompose odors [4]. A particular feature that made these catalysts so effective for this application is that moisture enhances their catalytic activity. Since this commercialization, gold nanoparticles have also showed high activities and selectivities for many other reactions, in particular for selective oxidation and hydrogenation reactions. Some of the reactions in which gold catalysts have been proven useful include: propylene epoxidation [5,6], oxidation of glycerol [7–9], oxidation of ethylene glycol [10], direct synthesis of hydrogen peroxide from hydrogen and oxygen [11–13], hydrogenation of acetylene to ethylene [14] and reduction of NO by H_2[15]. Reviews by Hashmi and Hutchings [16], Corma and Garcia [17], Pina et al. [18] and Wittstock and Bäumer [19] provide comprehensive summaries of gold catalyzed reactions.

Many adsorbates and reactions have been studied on gold surfaces using a variety of experimental and theoretical methods. Because the main applications of gold catalysts are related to the oxidation of CO and hydrogenation of CO, CO_2[20–25] and NO [20,26], the species involved in those reaction systems have been extensively studied on gold surfaces. Several experimental surface science techniques have been used to study the adsorption of O_2 and/or O on Au(111), such as: temperature-programmed desorption (TPD) [20,27–32], high-resolution electron energy loss spectroscopy (HREELS) [28,32], He diffraction [33], scanning tunneling microscopy (STM) [34], low-energy electron diffraction (LEED) [31,32], X-ray photoelectron spectroscopy (XPS) [32,34] and Auger electron spectroscopy (AES) [32]. The adsorption of atomic and molecular oxygen has been widely analyzed with density functional theory (DFT) calculations [27,28,35–37]. Oxygen does not chemisorb, molecularly or dissociatively, on clean gold surfaces under ultrahigh-vacuum (UHV) conditions, nor at elevated temperature and pressure [20,27]. To study the interaction between oxygen and gold surfaces, different approaches have been developed such as: thermal dissociation of gaseous O_2 on hot filaments, ozone decomposition, coadsorption of NO_2 and H_2O, O^+ sputtering, electron-

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induced adsorption of oxygen, and electron bombardment of condensed NO_2[27]. Also, the oxidation of CO by gold catalysts has motivated a number of reaction studies and fundamental surface science investigations into the relevant intermediates. Stolcic et al. showed evidence of CO oxidation on small Au particles proceeding via molecular oxygen rather than atomic oxygen when O_2 is absorbed on free Au_2^- and Au_4^- particles at room temperature [38]. Moreover, an $^{18}O_2$ isotope study performed by Stiehl and coworkers with nanoparticles of Au supported on TiO_2 demonstrated a reaction pathway that does not require the dissociation of molecular oxygen, such that O_2 can react directly with CO to form CO_2[39]. These results were further substantiated with DFT calculations by Molina and coworkers showing that O_2 can react with CO adsorbed at the edge sites of Au particles leading to the formation of CO_2 with a low energy barrier of ~0.15 eV [40]. Among the experimental methods that have been employed for studying CO on Au(111) are: TPD [20,41], infrared reflection absorption spectroscopy (IRAS) [41,42], Fourier transform infrared spectroscopy (FTIR) [20,43], ^{129}Xenon nuclear magnetic resonance (^{129}Xe NMR) spectroscopy [20], diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) [20], and STM [42]. Fourier transform ion cyclotron resonance (FT-ICR) mass spectroscopy has been applied to study the co-adsorption of oxygen and CO on anionic gold clusters [44]. Several DFT studies have been performed for the adsorption of CO and the co-adsorption of CO with O or O_2 on Au(111) [45–48].

The chemisorption of molecular hydrogen on gold has been achieved on unsintered thin gold films at low temperature [49,50]. For supported gold particles, the chemisorption of H_2 molecule has been reported, but amounts are small [20,51]. H_2 dissociation is favorable on supported surfaces as proved by Fujitani and coworkers, and the active sites for H_2 dissociation on gold catalysts are thought to be at the interface between gold and the metal oxide support [52]. Despite the limited circumstances under which gold surfaces are found to chemisorb molecular hydrogen, the literature reveals a number of observations in which hydrogen molecules or atoms participate in reactions on gold. Some of these reactions include the hydrogenation of hydrocarbons (e.g. alkenes [53–55], alkadienes [56,57] and alkynes [57]), both saturated and unsaturated ketones [57,58] and carbon oxides [22,57], hydrogenolysis [59,60], dehydrogenation [61,62] and water–gas shift (WGS) reaction [16]. Furthermore, Azar and coworkers demonstrated with TPD experiments that hydrogen can regenerate their Au catalyst through the removal of the poisoning carbonate-like species produced during CO oxidation [63]. Sugawara et al. studied the reactions of cationic gold clusters Au_n^+ ($n = 1$–12) with H_2 using FT-ICR mass spectrometry [64]. Pessoa et al. analyzed the adsorption of several ionic and non-ionic species, among which is H, on the low-index gold surfaces Au(100), Au(110) and Au(111) using DFT calculations (B3LYP and GGA-PW91) [35]. Many other DFT studies of hydrogen adsorption on gold clusters have been performed [65–68].

It has been suggested that hydroxyl groups present on the surface of gold in aqueous solution promote reactions such as the oxidation of CO and glycerol [69–72]. Sanchez-Castillo and coworkers observed CO oxidation by O_2 at room temperature on gold nanotubes in polycarbonate membranes without the presence of a catalyst support, finding that the activity can be enhanced by performing the reaction in the aqueous phase, increasing the pH of the solution and using H_2O_2 as the oxidizing agent [73]. Ketchie et al. investigated the promotional effect of OH on the oxidation of both CO and glycerol in the aqueous phase, as a function of pH, over Au/C and Au/TiO_2 using transmission electron microscopy (TEM), near-edge X-ray absorption fine structure (NEXAFS) and X-ray absorption near edge structure (XANES) spectroscopy, high performance liquid chromatography (HPLC) and ultraviolet–visible (UV–VIS) spectroscopy [71]. They concluded that the hydroxyl groups adsorbed on the Au surface increase CO oxidation rates by facilitating the adsorption and activation of O_2 on the Au surface. Similarly, OH groups are necessary in order to activate glycerol by deprotonation of the primary alcohol group prior to the selective oxidization to glyceric acid over both gold catalysts. The adsorption of the OH ion on Au(100), Au(110) and Au(111) was also analyzed by Pessoa and coworkers using DFT calculations [35].

For many reactions involving CO, CO_2, H_2 and water (e.g. WGS reaction), reaction intermediates such as formyl (HCO), COH, formate (HCOO), carboxyl (COOH) and bicarbonate (HCO_3) have been proposed as relevant species [69]. For that reason, Senanakaye and coworkers have investigated the role of formate, carbonate, and carboxyl as possible intermediates in the WGS reaction through the interaction of CO with OH ($OH_{ads} + CO_{gas} \rightarrow CO_{2,gas} + 0.5H_{2,gas}$) on Au(111) and O/Au(111) using synchrotron-based core level photoemission, NEXAFS, infrared absorption spectroscopy (IR) and DFT calculations [74]. Their results indicate that formate is not a key intermediate at low temperatures because HCOO is stable on Au(111) up to temperatures near 350 K. In fact, they suggest that the formation of this species could provoke surface poisoning. Moreover, the results of IR spectroscopy and photoemission spectroscopy point to HO–CO interactions, which are consistent with the formation of a COOH intermediate with a short lifetime on the gold surface [74]. On the other hand, Bond and Thompson, based on a reaction mechanism developed by Costello and coworkers [72], proposed a mechanism for CO oxidation on Au/Al_2O_3 where a bicarbonate species is involved. In this mechanism, an Au–OH species reacts with a CO molecule adsorbed on an under-coordinated gold atom to form a carboxyl species, which is then oxidized to bicarbonate. They suggest that the decomposition of bicarbonate would yield CO_2, and in the presence of water, COOH is formed. Thus, water and OH groups play an important role on this mechanism to facilitate CO oxidation through the formation of COOH [69].

Gold catalysts are very susceptible to poisoning, particularly with chloride ions. Supported Au catalysts are often prepared using $HAuCl_4$ as a precursor. Yang and coworkers have demonstrated using X-ray fluorescence (XRF), NEXAFS, XANES and high-resolution scanning transmission electron microscopy (STEM) that residual chloride can cause agglomeration of Au particles during heat treatment and suppresses its catalytic activity by poisoning active sites [75,76]. On the other hand, the adsorption of chloride on gold can be advantageous for various applications in homogeneous and heterogeneous catalysis. Mercury can be removed from coal-fired boiler gas effluents by oxidizing it to $HgCl_2$ with chlorinating reagents over a gold catalyst [77] and chlorine also increases the selectivity of styrene epoxidation on Au(111) [78]. These potential applications of Cl on catalytic systems motivated Baker and coworkers to perform first-principles DFT calculations to study the nature of the interaction between Cl and the Au(111) surface, and they have reported evidence that this bonding is primarily of covalent character [79]. Lemoine and coworkers also studied the Eley–Rideal type reaction of Cl adsorbed on Au (111) with gas-phase H atoms using DFT [80]. The adsorption of chlorine on Au (111) has also been studied by various experimental (e.g. AES, XPS and UV photoelectron spectroscopy (UPS), LEED, TPD [81] and STM [82]) and theoretical techniques [82].

Although the catalytic properties of nanoscale gold have been extensively studied, the intrinsic mechanism of the heterogeneous catalysis at the atomic and molecular level has not been fully clarified. DFT studies can provide further insight into the fundamental surface science of gold catalysis. Similar to previous works on Pt(111) [83], Rh(111) [84], Ir(111) [85], Pd(111) [86], Ru(0001) [87] and Re(0001) [88] this work aims at performing a systematic study of the chemisorption of several atomic and molecular species, and molecular fragments involved in gold catalyzed reactions. We study the adsorption of these species on the Au(111) facet, which is the thermodynamically most stable and prevalent configuration of supported gold nanoparticles [27]. While it has been observed that this surface reconstructs to the characteristic herringbone structure [89,90] with an additional 4% of Au atoms incorporated into the surface layer, our calculations only account for reactions on the unreconstructed Au(111) surface. For this analysis, we have used periodic self-consistent DFT calculations to determine