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Theoretical study of CO adsorption on Au catalysts under environmental catalytic conditions

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ABSTRACT

Density Functional Theory calculations with both standard GGA and hybrid functionals are performed on Au adatoms, steps, and low index surfaces with coordination numbers (CNs) varying from 3 to 9. The results are used to study adsorption thermodynamics and reactivity of CO on Au nanoparticles. We find that the hybrid functional improves calculated site preferences and predicts CO top site adsorption, regardless of the Au CN, in good agreement with experiments. The calculated adsorption energies vary monotonically with respect to Au CNs, and the results from the hybrid functional are around 20% smaller than the corresponding values from the GGA–PBE functional. A comparison with experimental adsorption energies suggests that these functionals may bound the true CO–Au interaction strength, and seven-coordinated Au atoms may be the active low-coordinated sites on many Au single crystal surfaces. However, thermodynamic analysis on Wulff-like Au particles at ambient temperatures shows that, even though the number of 6-coordinated corner Au atoms is much less than the number of 7-coordinated edge Au atoms and of higher-coordinated Au atoms, they are the dominant sites for CO adsorption on Au nanoparticles with sizes up to 10 nm. In addition, we find that CO adsorption is not influenced by the shape of Au nanoparticles, but the CO oxidation reaction may be.

1. Introduction

CO oxidation on oxide-supported Au catalysts is a classic model reaction in heterogeneous nanocatalysis, and the chemistry is also relevant to environmental catalysis, generally taking place at room temperature and low CO concentrations [1]. Experiments have shown that reactions on Au nanoparticles (NPs), with diameters of around 3 nm, may exhibit very high turn-over frequencies (TOF) [2]. The reaction mechanism has been widely studied, and it has been found that reaction barriers are very low (~0.2 eV) and that the mechanism involves formation of CO–O_2 complex at perimeter sites [3–5]. As part of this complex formation, it has been generally accepted that O_2 is stabilized at the Au–oxide interface [3–5]. However, there is still no consensus concerning the mode of CO adsorption; even though it is thought to be adsorbed on defect sites or low-coordinated Au atoms under real catalytic conditions, the exact coordination of these active Au atoms is still unclear. Indeed, the proposed coordination numbers of potentially active Au atoms vary from 3 to 7 in the literature [3,4,6–10], and their dependence on the size and the shape of Au catalyst particles is unknown.

CO adsorption sites on Au low-index and stepped single crystal surfaces have been studied extensively with both calculations [6,11–17] and experiments [11,13,15,18–22]. Experiments uniformly show top site adsorption. For example, based on infrared reflection absorption spectroscopy (IRAS), CO top site adsorption was proposed on Au(111) [13,22], Au(100) [22], Au(211) [19], Au(311) [22], and Au(332) [20] surfaces. Density functional theory (DFT) calculations, however, have shown that bridge site adsorption is more favorable on Au(100), Au(211) and Au(221) surfaces, while there is no clear site preference on the Au(111) surface [6,16,17]. We note that local and semi-local functionals are well known to incorrectly predict CO adsorption sites on Pt, Rh, Cu, Ag, and some other transition metal surfaces, leading to challenges in the interpretation of these theoretical studies [23].

DFT calculations have also shown that binding energies are generally enhanced with reduction of the coordination number (CN) of Au atoms [6,16,17,20,24]. The trend is consistent with experiments on Au NPs, in which higher desorption temperatures have been reported for CO adsorption on lower coordinated Au atoms or smaller clusters [25]. This behavior is also well known for other adsorbates on metal substrates and has been attributed to the change in the electronic structure of metal atoms with different CN's [26]. Surface science experiments on Au single crystal surfaces, however, have revealed some trends that are difficult to interpret within this simple coordination paradigm. For example, it was reported that the high temperature desorption peaks on (111) vicinal surfaces (e.g. Au(211) and Au(332)) [18,19] and (100) vicinal surfaces (e.g. Au(310) and Au(321)) [21] are very close in temperature, implying an approximately constant CO desorption/adsorption energy, even though the coordination numbers of the two types of surfaces are not identical. These results suggest that, even though the CO binding strength has been studied extensively, careful benchmarking

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of coordination trends with high accuracy calculations can contribute to the general understanding of these relationships.

To address some of the above questions, we have performed a series of benchmark calculations, with both standard GGA and hybrid functionals, for CO adsorption on Au(111) and Au(100) low index surfaces, Au(211) and Au(310) stepped surfaces, and Au adatoms on Au(111), Au(100) and Au(211) substrates (see Fig. 1). The results are used to clarify both the site preferences for CO adsorption on various structural features of Au and the relationship between the CO adsorption energy and the local coordination number. A Wulff construction, combined with both simple geometric assumptions about the particle shapes near the metal/oxide interfaces and a basic thermodynamic analysis, is then used to determine the CO coverage and the contribution of different sites to the average adsorption properties of CO on the particles.

2. Methods

Self-consistent total energy calculations are performed based on the all-electron projector augmented wave (PAW) method [27] with the generalized gradient approximation (GGA-PBE) [28] and HSE06 hybrid functionals [29], as implemented in the Vienna Ab-initio Simulation Package (VASP) [30]. Additional computational details can be found in the supporting information.

3. Results and discussion

3.1. CO adsorption sites

Average CO adsorption energies are calculated and given in Table 1, together with the CO–CO lateral distance and the CN of the Au atoms on which the CO is adsorbed.

For CO adsorption on terrace adatoms of Au(111)-(2 × 2) and Au(100)-(2 × 2), with CNs of 3 and 4, respectively, the only local energy minimum is the top site. The most favorable adsorption site on step adatoms of Au(211)-(2 × 1) and on Au(310) steps with CNs of 5 and 6, respectively, is also the top site, with adsorption preferred by at least 0.23 eV compared to adsorption on the second most stable site. The above site preferences are in good agreement with both previous calculations [13,16,20] and available experimental results [13,19–22].

The site preferences on Au(111) (CN = 9), Au(100) (CN = 8), and Au(211) (CN = 7) surfaces, however, are more complex than the corresponding preferences on the adatoms. The GGA calculations indicate that, at low coverage, CO prefers bridge sites on the (211) and (100) surfaces, respectively, while there is no clear site preference on Au(111). Even though these site preferences, and associated adsorption energies, are consistent with previous calculations [6,11,12,15–17], they are contrary to experimental results [19,22] in which only top site adsorption was reported. On the other hand, the HSE06 calculations at the PBE optimized geometries predict a site preference consistent with experiments; the top site is the most favorable adsorption site on all three of the surfaces (Table 1).

Table 1
CO average adsorption energy (E_{ad} in eV) on Au surfaces with PBE and hybrid HSE06 functionals. CNs are the coordination numbers of Au atoms that bind with CO. The most favorable adsorption sites are indicated in bold font. For surfaces where PBE correctly predicts the generally accepted experimental site preference (top), we report only top sites binding energies in the HSE06 calculations.

Surface	Supercell	d_{CO-CO}	Site	CNs	E_{ad}^{PBE}	E_{ad}^{HSE06}
(111)	(2 × 2)	$\sqrt{2}a_0$	fcc	(9,9,9)	**−0.29**	−0.02
			Bridge	(9,9)	−0.27	−0.06
			Top	9	−0.21	**−0.17**
	$(\sqrt{3} \times \sqrt{3})$	$\sqrt{6}/2a_0$	fcc	(9,9,9)	−0.26	
			Bridge	(9,9)	**−0.28**	
			Top	9	−0.23	
	(1 × 1)	$\sqrt{2}/2a_0$	fcc	(9,9,9)	0.52	
			Bridge	(9,9)	0.39	
			Top	9	**0.06**	
(100)	(2 × 2)	$\sqrt{2}a_0$	Bridge	(8,8)	**−0.50**	−0.25
			Top	8	−0.40	**−0.32**
	c(2 × 2)	a_0	Bridge	(8,8)	**−0.45**	
			Top	8	−0.37	
	(1 × 1)	$\sqrt{2}/2a_0$	Bridge	(8,8)	−0.12	
			Top	8	**−0.16**	
(211)	(2 × 1)	$\sqrt{2}a_0$	Step bridge	(7,7)	**−0.60**	−0.29
			Step top	7	−0.57	**−0.47**
	(1 × 1)	$\sqrt{2}/2a_0$	Step bridge	(7,7)	−0.34	
			Step top	7	**−0.44**	
(310)	(2 × 1)	$2a_0$	Step bridge	(6,6)	−0.42	
			Step top	6	**−0.77**	**−0.63**
	(1 × 1)	$\sqrt{2}a_0$	Step bridge	(6,6)	−0.47	
			Step top	6	**−0.75**	
Adatom/(211)	(2 × 1)	$\sqrt{2}a_0$	fcc	(5,8,8)	−0.39	
			Bridge	(5,8)	−0.60	
			Top	5	**−0.83**	**−0.68**
Adatom/(100)	(2 × 2)	$\sqrt{2}a_0$	Top	4	**−0.90**	**−0.72**
Adatom/(111)	(2 × 2)	$\sqrt{2}a_0$	Top	3	**−1.08**	**−0.87**

The improved site prediction for the hybrid functional is consistent with trends reported for CO adsorption on other transition metals [23]. It should be noted, however, that the hybrid functional calculations in the present study give weaker adsorption energies than GGA calculations. This is consistent with previous calculations for CO adsorption on Ag surfaces but is opposite to the trend on platinum group metal surfaces [23]. The trends in CO adsorption energies on Ag and Au seem to follow classic arguments: increases in the CO HOMO–LUMO gap (e.g. from 6.9 eV to 9.1 eV in the present study) with hybrid functionals

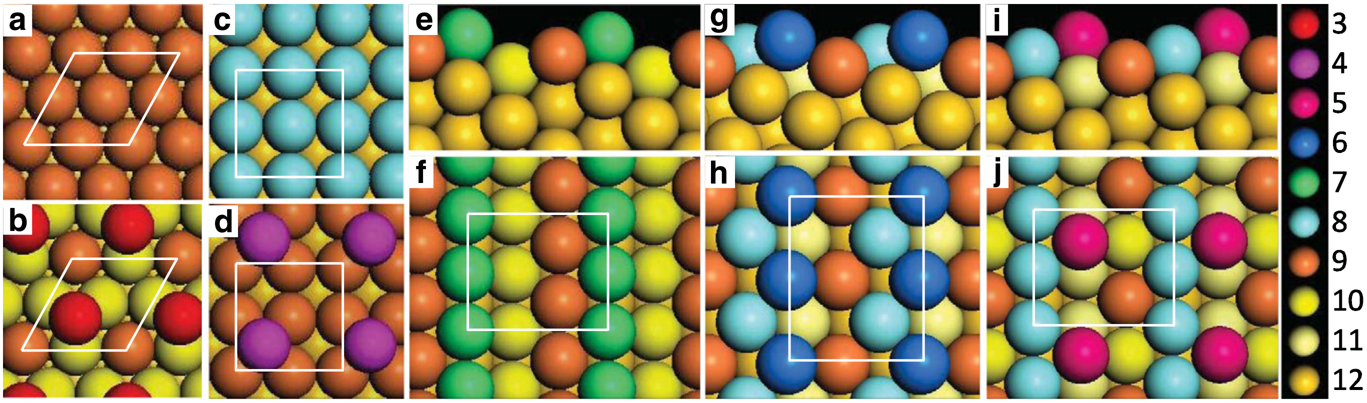

Fig. 1. Au surfaces and adatoms with different coordination numbers. Au(111) surface with (2 × 2) supercell (a) and Au adatom on it (b); Au(100) surface with (2 × 2) supercell (c) and Au adatom on it (d); side (e) and top (f) view of Au(211) surface with (2 × 1) supercell; side (g) and top (h) view of Au(310) surface with (2 × 1) supercell; side (i) and top (j) view of Au adatom on (2 × 1) Au(211) surface. The color scheme for Au atoms with different coordination numbers is given at the far right.