Angewandte Chemie

Gold Electrochemistry

DOI: 10.1002/anie.200905387

Carbon Monoxide as a Promoter for its own Oxidation on a Gold Electrode**

*Paramaconi Rodríguez, Andrey A. Koverga, and Marc T. M. Koper**

The catalytic activity of gold towards the oxidation of carbon monoxide in the gas phase, the liquid phase, and electrochemically, has attracted substantial interest.[1–12] The mechanism for the remarkable activity of gold in CO oxidation, especially when dispersed as nanoparticles on an oxidic support, is still a subject of much debate. The high activity of gold for the oxidation of CO in the aqueous phase, and particularly in alkaline media,[4] was originally reported in the electrochemistry literature.[5,6] Gold is the most active electrode material for oxidizing CO dissolved in an aqueous solution, and is superior to, for example, platinum.[6]

We have previously reported that CO may be adsorbed irreversibly on single-crystalline gold electrodes in alkaline media; on Au(111) and Au(100)-(5 × 20) surfaces, the CO adsorption was accompanied by an unusual reversible peak in the cyclic voltammogram at circa 0.4 V versus RHE (RHE = reversible hydrogen electrode).[12] We ascribed this peak to the enhanced co-adsorption of OH onto the CO-covered gold surface. Such an enhancement of OH adsorption onto the gold surface by adsorbed CO would still be advantageous for the oxidation of CO in solution, even if the irreversibly adsorbed CO may only be oxidized off the surface at relatively high potentials (circa 0.8 V). Indeed, the CO-promoted adsorption of OH may lead to the oxidation of CO in solution. For such a model, a simplified rate equation for the CO oxidation current on a gold surface would be:

$$j = 2\,F\,k\,\theta_{\mathrm{CO}*}\,\theta_{\mathrm{OH}} \tag{1}$$

where two electrons are transferred when CO is oxidized to CO_2, F is the Faraday constant, k is the oxidation rate constant, $\theta_{\mathrm{CO}*}$ is the coverage of oxidizable CO* molecules adsorbed on the surface when CO is in solution (as opposed to, and in addition to, the more strongly irreversibly adsorbed CO molecules that are oxidized at higher potential when there is no CO in solution), and θ_{OH} is the OH coverage on the surface, all at a fixed applied potential. If the OH adsorption energy is enhanced by the presence of CO on the surface by a linear dependence on the CO coverage, θ_{OH} could be expressed as:

$$\theta_{\mathrm{OH}} = \theta^{0}_{\mathrm{OH}}\exp(\gamma\theta_{\mathrm{CO}}) \tag{2}$$

where θ_{CO} is now the total CO coverage, although we do not really know how to distinguish in this model between strongly (irreversibly) and weakly adsorbed CO molecules (only when CO is in solution). If both $\theta_{\mathrm{CO}*}$ and θ_{CO} depend on the concentration of CO in solution (c_{CO}), then it is straightforward to show that the reaction order r in c_{CO} is given by:

$$r = \mathrm{d}\ln j/d\ln c_{\mathrm{CO}} = 1 + \gamma\theta_{\mathrm{CO}} \tag{3}$$

Therefore, this model predicts a reaction order in c_{CO} of $r > 1$ if $\gamma > 0$; $\gamma > 0$ expresses the idea that CO promotes the adsorption of its own oxidant (OH), and thereby possibly enhancing its own oxidation.

Herein, we provide support for this self-promotion mechanism using DFT calculations and the experimental determination of the reaction order in CO. The binding energies of OH and CO on a clean Au(111) surface in a 3 × 3 unit cell (0.11 monolayer) are given in Table 1. The binding energy for OH "atop" (−2.32 eV) is presented for comparison with the co-adsorption results, although OH has a slight preference for the "bridge" geometry on the Au(111) surface over the atop geometry by about 0.14 eV.[13] The atop binding energy of CO to Au(111) is low: about −0.13 eV in the 3 × 3

Table 1: DFT-computed binding characteristics of CO and OH adsorption and co-adsorption on a Au(111) surface.

Adsorbate system[a]	Binding energy [eV]	Adsorbate charge/e_0	Geometry
OH–Au(111)	−2.32	−0.43	atop
CO–Au(111)	−0.13	+0.02	atop
Nearest-neighbor OH binding to CO–Au(111)	−2.70	−0.58	
Nearest-neighbor CO binding to OH–Au(111)	−0.52	+0.15	
Next-nearest-neighbor OH binding to CO–Au(111)	−2.37	−0.43	
Next-nearest-neighbor CO binding to OH–Au(111)	−0.11	+0.02	

[a] All calculations were carried out in a (3 × 3) unit cell with one adsorbate of each kind per nine gold surface atoms.

---

[*] Dr. P. Rodríguez, A. A. Koverga, Prof. Dr. M. T. M. Koper
Leiden Institute of Chemistry, Leiden University
PO Box 9502, 2300 RA Leiden (The Netherlands)
Fax: (+31) 71-527-4451
E-mail: m.koper@chem.leidenuniv.nl
Homepage: http://casc.lic.leidenuniv.nl/

[**] We acknowledge financial support from the Netherlands Organization for Scientific Research (NWO), the National Computer Facilities (NCF) for computing resources, and the European Commission (FP7 Initial Training Network "ELCAT", Grant Agreement No. 214936-2).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905387.

unit cell. Also included in Table 1 are the binding energies of OH on the CO–Au(111) surface that has pre-adsorbed CO, the binding energies of CO on the OH–Au(111) surface, and the final geometries of chemisorbed CO and OH. In the 3 × 3 unit cell, OH is adsorbed on the gold atom neighboring the gold atom binding CO, and on the next-neighboring gold atom (with a Au–Au distance of circa 5.0 Å). Whereas CO and OH binding in the latter geometry does not afford an enhanced binding energy, OH and CO co-adsorption on neighboring gold atoms on the CO–Au(111) and OH–Au(111) surface, respectively, leads to enhanced binding energies in both cases. Note also that when CO and OH bind to neighboring gold atoms, the distance between the carbon monoxide carbon atom and the hydroxy oxygen atom is too large for the formation of a COOH species (2.70 Å; in formic acid, the CO(H) distance is 1.34 Å).

To understand the quantum-chemical origin of this mutual enhancement of the bonding of CO and OH to the Au(111) surface, we carried out a charge analysis. The charges corresponding to the adsorbates were calculated using a Bader charge analysis (Table 1).[14] The Bader analysis shows that CO binds to the Au(111) surface in an almost neutral state ($+0.02\,e_0$), and that OH binds essentially as an anion (Bader charge $= -0.43\,e_0$). However, in close proximity to one another on the Au(111) surface, CO acquires a more positive charge ($+0.15\,e_0$), and OH a more negative charge ($-0.58\,e_0$), with the changes in their adsorbate charges compensating each other almost exactly; this implies that in the case of nearest-neighbor co-adsorption, electrons flow from CO to OH without any significant electronic charge being stored in the gold surface. This effect is absent if CO and OH are adsorbed on next-nearest-neighboring gold atoms. The weak bonding between CO and the gold surface is accompanied by donation of the 5σ electrons from the CO to the gold d_{z^2} orbital,[15] whereas OH typically binds to metals by accepting electrons from the metal into its 1π* orbital.[16] Therefore, we suggest that the mutual enhancement may be understood as a gold-mediated charge flow from CO to OH to create a stronger bonding to the gold surface for both molecules.

An alternative way of looking at this effect is to notice that CO adsorbed on the Au(111) surface lowers the work function of the Au(111) (in our DFT calculation from 5.14 to 4.57 eV). A lower work function would facilitate the flow of electrons into an electronegative adsorbate such as OH.

Reaction order measurements were performed using bead-type Au(111), Au(100), and Au(110) single crystal electrodes in a hanging meniscus rotating disk electrode (HMRDE) configuration.[17] The 0.1 M NaOH aqueous solution was purged with a mixture of CO/Ar, the mixing ratio of which was controlled using a gas splitter. Rather than measuring the concentration of CO in the solution directly, the concentration was inferred from the mass-transport-limited current at 1.0 V versus RHE (see Figure 1 a). The reaction order may then be obtained by plotting the logarithm of the kinetically limited current at some low potential ($E = 0.2, 0.25, 0.3, 0.35$ V vs. RHE) versus the logarithm of the mass-transport-limited current at 1.0 V, for a varying ratio of CO/Ar and a fixed electrode rotation rate of 1100 rpm (Figure 1 b). The slope was calculated to be significantly larger than 1; that is, 1.2 ± 0.05, 1.12 ± 0.05, 1.19 ± 0.05, and 1.14 ± 0.05 for the four potentials, respectively. These values are in good agreement with other reaction order values larger than 1 for CO oxidation on polycrystalline gold in alkaline media reported in the literature,[5,6] although those values were obtained using different electrochemical methods, without discussion and without error bars. On the other hand, Weaver et al. reported that the reaction order for CO oxidation on gold at various pH values is approximately 1.[7] We also found reaction orders $r > 1$ for Au(100) and Au(110) electrodes in alkaline media (see the Supporting Information, Figure S1), which will be discussed in detail in a forthcoming publication.[18] These values of $r > 1$ confirm the self-promoting role of CO in its own oxidation on a gold electrode.

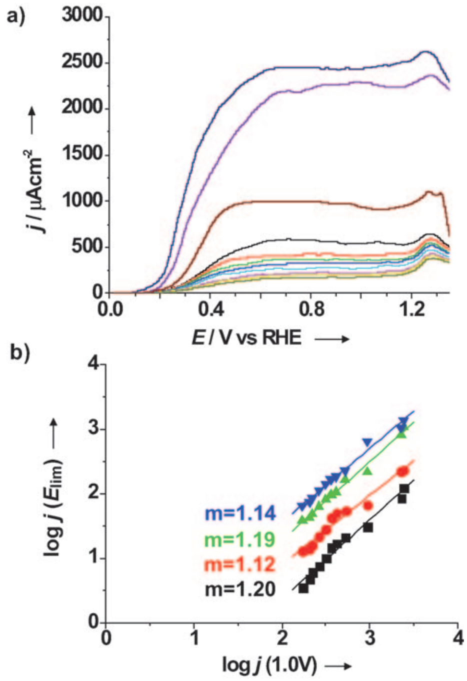

Figure 1. a) HMRDE voltammograms of Au(111) in 0.1 M NaOH in the presence of CO at different CO partial pressures; $\upsilon = 50\ \text{mV}\,\text{s}^{-1}$; rotation rate 1100 rpm. b) Reaction order plots of the logarithm of the kinetic current density at different potentials versus the logarithm of the mass-transport-limited current density at 1.0 V: (■) 0.2 V, (●) 0.25 V, (▲) 0.30 V, (▼) 0.35 V. m = slope.

We stress that the above model is oversimplified, as we do not take into account that the adsorbed CO itself is not oxidized by adsorbed OH at these low potentials. CO only oxidizes at such low potentials in the presence of CO in solution. In fact, this difference between the oxidation of adsorbed CO and CO in solution can only be explained by a reaction order larger than 1. Interestingly, it is exactly opposite to the trend observed for platinum, where adsorbed CO is more easily oxidized than dissolved CO, which is in agreement with a reaction order $r < 0$.[19]

In acidic media, $r < 1$ on the Au(111) surface.[18] CO oxidation on gold in acidic media takes place at a substantially more positive potential[6] (on the RHE scale), which we believe is due to the fact that CO binds more strongly to gold in alkaline media than in acidic media. In alkaline media, CO adsorption is studied at more negative potentials (vs. SHE) than in acidic media, even if the CV (cyclic voltammetry) is plotted on the reversible hydrogen electrode scale, which may lead to stronger chemisorption bonding.[9,12]

In summary, we have presented a model for CO oxidation on gold electrodes in alkaline media that assumes that CO enhances the adsorption of its own oxidant. This model explains both the reaction order, which is larger than 1, and the fact that dissolved CO is easier to oxidize than adsorbed CO. DFT calculations provide evidence for this mechanism by confirming that on the Au(111) surface, CO and OH enhance each other's binding through what appears to be a local gold-mediated electron-transfer mechanism that is driven by a change in the local electrostatics. Although this mechanism may be specific to CO oxidation on single-crystalline gold electrodes in alkaline media, we believe that it may be worthwhile to explore its applicability to other gold-based CO oxidation catalysts.

Experimental Section

Bead-type single-crystals of gold were flame annealed and cooled down according to well-known procedures.[20] CO oxidation experiments have been performed in the HMRDE configuration.[17] Full experimental details can be found in our previous publication [12] and in the Supporting Information.

DFT calculations were performed using the Vienna Ab-initio Simulation Package (see the Supporting Information).[21] The Au(111) surface was represented as a six-layer slab in a (3 × 3) supercell, and the Perdew–Burke–Ernzerhof approximation to the exchange correlation energy was used.[22] Bader charges on atoms and molecules were calculated using the method suggested by Henkelman et al.[23]

Received: September 25, 2009

Keywords: carbon monoxide · density functional calculations · electrochemistry · gold · oxidation

---

[1] a) M. Haruta, N. Yamada, T. Kobayashi, S. Ijima, *J. Catal.* **1989**, *115*, 301; b) M. Haruta, *Catal. Today* **1997**, *36*, 153.

[2] a) R. J. Davis, *Science* **2003**, *301*, 926; b) A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon, G. J. Hutchings, *Science* **2008**, *321*, 1331.

[3] a) R. Grisel, K. J. Weststrate, A. Gluhoi, B. E. Nieuwenhuys, *Gold Bull.* **2002**, *35*, 39; b) H. Falsig, B. Hvolbaek, I. S. Kristensen, T. Jiang, T. Bliggaard, C. H. Chrsitensen, J. K. Nørskov, *Angew. Chem.* **2008**, *120*, 4913; *Angew. Chem. Int. Ed.* **2008**, *47*, 4835.

[4] W. Ketchie, Y.-L. Fang, M. Wong, M. Murayama, R. J. Davis, *J. Catal.* **2007**, *250*, 94.

[5] a) J. L. Roberts, Jr., D. T. Sawyer, *J. Electroanal. Chem.* **1964**, *7*, 315; b) J. L. Roberts, Jr., D. T. Sawyer, *Electrochim. Acta* **1965**, *10*, 989.

[6] a) H. Kita, H. Nakajima, K. Hayashi, *J. Electroanal. Chem.* **1985**, *190*, 141; b) H. Nakajima, H. Kita, K. Kunimatsu, A. Aramata, *J. Electroanal. Chem.* **1986**, *201*, 175; c) K. Kunimatsu, A. Aramata, H. Nakajima, H. Kita, *J. Electroanal. Chem.* **1986**, *207*, 293.

[7] G. J. Edens, A. Hamelin, M. J. Weaver, *J. Phys. Chem.* **1996**, *100*, 2322.

[8] B. B. Blizanac, M. A. Arenz, P. N. Ross, N. M. Markovic, *J. Am. Chem. Soc.* **2004**, *126*, 10130.

[9] A. Cuesta, N. López, C. Gutiérrez, *Electrochim. Acta* **2003**, *48*, 2949.

[10] G. L. Beltramo, T. E. Shubina, M. T. M. Koper, *ChemPhysChem* **2005**, *6*, 2597.

[11] a) B. E. Hayden, D. Pletcher, M. Rendall, J.-P. Suchsland, *J. Phys. Chem. C* **2007**, *111*, 17044; b) B. E. Hayden, D. Pletcher, J.-P. Suchsland, *Angew. Chem.* **2007**, *119*, 3600; *Angew. Chem. Int. Ed.* **2007**, *46*, 3530.

[12] P. Rodriguez, J. M. Feliu, M. T. M. Koper, *Electrochem. Commun.* **2009**, *11*, 1105.

[13] P. Vassilev, M. T. M. Koper, *J. Phys. Chem. C* **2007**, *111*, 2607.

[14] R. F. W. Bader, *Atoms in Molecules—A Quantum Theory*, Oxford University Press, New York, **1990**.

[15] M. Gajdoš, A. Eichler, J. Hafner, *J. Phys. Condens. Matter* **2004**, *16*, 1141.

[16] M. T. M. Koper, R. A. van Santen, *J. Electroanal. Chem.* **1999**, *472*, 126.

[17] a) B. D. Cahan, H. M. Villullas, *J. Electroanal. Chem.* **1991**, *307*, 263; b) M. D. Macia, J. M. Campiña, E. Herrero, J. M. Feliu, *J. Electroanal. Chem.* **2004**, *564*, 141.

[18] P. Rodriguez, N. Garcia-Araez, M. T. M. Koper, *Phys. Chem. Chem. Phys.*, submitted.

[19] N. M. Markovic, P. N. Ross, *Surf. Sci. Rep.* **2002**, *45*, 117.

[20] a) J. Clavilier, D. Armand, S. G. Sun, M. Petit, *J. Electroanal. Chem.* **1986**, *205*, 267; b) A. Rodes, E. Herrero, J. M. Feliu, A. Aldaz, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3769.

[21] a) G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558; b) G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251; c) G. Kresse, J. Furthmüller, *Comp. Mater. Sci.* **1996**, *6*, 15; d) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.

[22] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

[23] G. Henkelman, A. Arnaldsson, H. Jónsson, *Comput. Mater. Sci.* **2006**, *36*, 354.