

# Structure of Electrode Surfaces in the Course of Electrocatalytic Reactions: Oxidation of CO, Glucose, and Formaldehyde on Reconstructed and Unreconstructed Au(100)

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Received March 30, 1995. In Final Form: September 27, 1995<sup>⊗</sup>

Grazing incident angle X-ray diffraction and linear sweep voltammetry were used to determine structure and reactivity of the Au(100) surface during the course of glucose, CO, and formaldehyde oxidations. The potential dependence of the diffracted intensity at the principal reconstruction peak was measured in HClO<sub>4</sub> (for CO and glucose) and NaOH (for formaldehyde) solutions in the absence and in the presence of adsorption and oxidation of organic molecules. The oxidation occurs before or at the onset of the lifting of the reconstruction. No significant change in the kinetics of the reconstruction lifting or recovering is caused by the adsorption and oxidation of the above organic molecules. The more negative current peak potentials and the larger values of heterogeneous rate constants for the unreconstructed Au(100) surface indicate that the unreconstructed Au(100) surface is more active than the hexagonally reconstructed Au(100) for all three reactions.

## Introduction

Atomic scale information on the structure of a catalytic surface during the course of reaction has been one of the major goals of surface science studies for many years.<sup>1</sup> Such information would be important for fundamental advances in catalytic and electrocatalytic fields. The atomic arrangements of the atoms on electrode surfaces, including effects of surface reconstruction and relaxation, are expected to affect the catalytic activity. Recently, *in situ* surface X-ray scattering (SXS) was used to investigate the structure of catalytically active metal monolayers during electrocatalytic reaction.<sup>2</sup> Here we apply *in situ* SXS to studies of the stability and activity of reconstructed surfaces in electrocatalytic reactions.

The studies of surface reconstruction of metal surfaces in vacuum have shown dramatic structural changes associated with the reconstruction, which exhibit a considerable influence on certain physical properties of these surfaces.<sup>3</sup> The reconstruction of electrode surfaces has also been well demonstrated during the last several years.<sup>4</sup> Information on the electrode surface reconstruction was obtained *ex situ* by low-energy electron diffraction (LEED)<sup>5</sup> and *in situ* by X-ray diffraction<sup>6,7</sup> and scanning tunneling microscopy (STM).<sup>8,9</sup> Particular attention has

been paid to the reconstruction of the Au(100) surface since upon reconstruction it undergoes a dramatic change associated with a large movement of the surface atoms. The Au(100) surface in the reconstructed state is hexagonally close-packed and contains about 25% more atoms than the unreconstructed (1 × 1) square lattice.<sup>6,8–11</sup> This reconstruction, which is now being referred to as “hex” reconstruction, is stable at negative potentials, but lifted at positive potentials due to adsorption of anions and/or charge effects.

In the presence of reactants and intermediates in electrocatalytic reactions, the stability of the reconstructed surfaces has not been studied thus far. The effect of the adsorbate on the reconstruction will depend on the strength of the adsorption bond, which in turn will depend on the nature of the reacting species and intermediates. It is also interesting to compare the catalytic activities of reconstructed and unreconstructed surfaces when the presence of adsorbed reactants and intermediates does not affect the surface reconstruction. In general, a difference in the activity can be expected since adsorption of the reactants and intermediates is likely to be weaker on the more densely packed reconstructed surfaces than on the more open unreconstructed ones. In addition, *in situ* structural information on the electrocatalytic activity of the reconstructed surfaces may also resolve ambiguities regarding the often observed difference in the activity of surfaces in the first and subsequent anodic potential sweeps. This is usually interpreted as a cleaning effect, which may not always be correct. It has been shown recently that the reconstruction affects the double-layer capacitance of the electrode surfaces<sup>12</sup> and, consequently, the kinetics of redox reactions.<sup>13</sup>

In this paper the potential dependence of the lifting and recovery of the reconstruction of the Au(100) surface

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1995.

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was measured by surface X-ray diffraction during the course of the oxidation of CO and D-glucose in acid and formaldehyde in alkaline solution. The electrocatalytic activities of the (1 × 1) and the "hex"-reconstructed Au(100) surface for these three reactions were also determined and apparent heterogeneous rate constants calculated. There is no data on the adsorption of these molecules on the reconstructed Au(100) in the gas phase. For CO, the adsorption would probably require low temperatures because of low reactivity of gold. The room temperature adsorption of CO may be, therefore, unique to the electrochemical system.

### Experimental Section

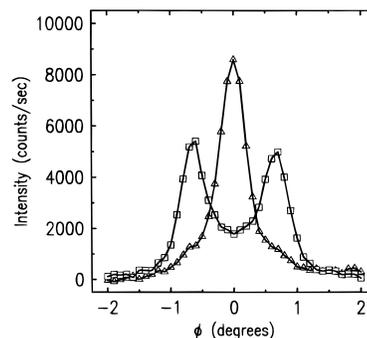
The Au(100) single crystals were oriented within 0.2° of its crystallographic plane and electrochemically polished in a cyanide-containing solution. After flame annealing, the sample was protected by pure water and transferred through air into an electrochemical X-ray scattering or electrochemical cell. The electrochemical X-ray scattering cell has been described elsewhere<sup>14</sup> and will be only briefly mentioned here. It was constructed from Kel-F and sealed using a 4- $\mu$ m-thick Prolene (polyethylene), Chemplex Inc. X-ray window film above the solution, which leaves about a 10–20- $\mu$ m-thick solution layer above the electrode. An outer cell was filled with flowing nitrogen gas to prevent oxygen from diffusing through the Prolene film during the measurements. The solutions were prepared from HClO<sub>4</sub> (Merck), NaOH (Fluka), paraformaldehyde and D-glucose (Aldrich), and Millipore QC-UV water (Millipore Inc.). A deoxygenation was carried out with nitrogen gas. A reversible hydrogen electrode (RHE) in 0.1 M HClO<sub>4</sub>, or 0.1 M NaOH separated by a fritted glass, was used as a reference electrode. The potentials are given with respect to a reversible hydrogen electrode.

In the experiments involving the oxidation of CO, CO-saturated solutions were used. In addition, CO was brought into the outer cell, from where it diffused into the solution through the thin Prolene film. In this way the depletion of CO in the thin-layer cell during the reaction was avoided. A large concentration of glucose and formaldehyde (0.5 M) was used in studies of the oxidation of these molecules, which ensured against their depletion during a single potential sweep.

SXS measurements at wavelength  $\lambda = 1.54 \text{ \AA}$  were carried out at beam line X22B of the National Synchrotron Light Source, Brookhaven National Laboratory. Grazing incident angle X-ray diffraction, as described in ref 6, was used to determine the in-plane structure of the Au(100) surface during the course of reactions. For in-plane diffraction measurements, the  $q$ -space resolution within the scattering plane was determined primarily by the Soller slits on the detector arm. This arrangement provides a  $2\theta$  resolution of 0.1° half-width at half-maximum (hwhm). The transverse in-plane resolution was limited by the mosaic spread of the gold crystal, which is about 0.07° (hwhm). A position in reciprocal space is given by  $(a^*, b^*, c^*)(H, K, L)$ , where  $a^* = b^* = c^* = 2\pi/a = 1.540 \text{ \AA}^{-1}$ , and  $a = 4.078 \text{ \AA}$ . The in-plane diffraction measurements were carried out in the  $(H, K)$  plane with  $L = 0.1$  corresponding to a grazing angle of 1.1°.

### Results and Discussion

**X-ray Diffraction Measurements.** The reconstruction of Au(100) gives rise to a hexagonal diffraction pattern in reciprocal space where one of the lowest order peaks is at (1.205, 1.205). This peak is consistent with the hexagonal pattern with  $\Delta = 1.205 \pm 0.002$ , where  $\sqrt{\Delta}a^*$  is the hexagonal wave vector along the (110) direction.<sup>6</sup> From the potential dependence of the diffracted intensity at the above position, the lifting and re-forming of the reconstruction can be monitored. A flame-annealed single



**Figure 1.** Two typical azimuthal scans near (1.206, 0, 0.1) from the reconstructed Au(100) surface at the aligned peak in 0.1 M HClO<sub>4</sub> at 0.05 V after flame annealing.

crystal, protected by a drop of ultrapure water, was transferred into the electrochemical cell and brought into contact with the solution phase at a potential of 0.05 V. In acid solutions containing anions which do not undergo specific adsorption, the Au(100) face remains reconstructed until the potentials reach approximately 0.6 V vs RHE.<sup>6,8</sup> Therefore, the reconstruction formed by flame annealing may be preserved at 0.05 V. Figure 1 shows two typical azimuthal rocking curves obtained from the in-plane diffraction measurements at 0.05 V in 0.1 M HClO<sub>4</sub>. A single peak aligned along the crystal axis indicates that the hexagonal reconstruction is aligned with the underlying (1 × 1) lattice, whereas split peaks indicate that the hexagonal lattice is rotated by about ±0.7°. Subtle differences in the annealing procedure seem to determine whether the reconstructed phase is rotated or aligned. In most cases a split peak was observed from annealed surfaces in acid solutions. From the present data, the alignment of the reconstructed layer does not appear to affect the kinetics of the reconstruction lifting and the catalytic properties. From the width (0.005  $\text{\AA}^{-1}$ ) of the diffraction peak along the radial direction, the estimated domain size of the reconstructed surfaces is at least 200  $\text{\AA}$ . This peak completely vanishes above 0.6 V, indicating that the reconstruction is lifted. The electrochemical reformation of the reconstruction (in the negative potential region) gives rise to the rotated structure and peaks which are broader than those shown in Figure 1 indicating smaller domains. This process is rather slow, as previously observed.<sup>4–8</sup>

In alkaline solutions a single peak was observed in majority of experiments, but some experiments showed the presence of the rotated structure evidenced by "shoulders", or a split peak at ±0.7° off the (110) direction for electrochemically grown reconstruction. Tidswell et al.<sup>7</sup> using X-ray diffraction observed only a single peak in alkaline solution and a rotated peak for the annealed surfaces in acid solutions.

**Surface Reconstruction during the Oxidation of Glucose, CO, and Formaldehyde.** The electrochemical oxidations of D-glucose,<sup>15</sup> formaldehyde,<sup>16</sup> and CO<sup>18</sup> on gold single-crystal electrodes are known as structure-sensitive reactions whose kinetics depend on the crystallographic orientation of the electrode surface. In these reactions the reactant adsorption is the first step which precedes

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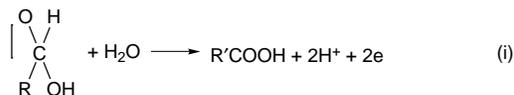
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the charge transfer. The rate-determining step in glucose oxidation on gold is bond breaking between a hydrogen atom and the C<sub>1</sub> carbon atom.<sup>17</sup>

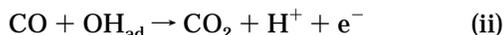
The overall reaction is the oxidation to gluconic acid, which can be written using the abbreviated notation for glucose in a cyclic form:



R and R' in eq i are alkyl groups representing the remainders of glucose and gluconic acid molecules, respectively. A previous study<sup>14</sup> found first-order kinetics with respect to glucose, and FTIR spectroscopy identified gluconolactone as the adsorbed intermediate:



The oxidation of CO on Au single-crystal electrodes with several orientations was reported by Chang et al.<sup>18</sup> A plausible formal mechanism involves an adsorption equilibrium of CO on Au before it reacts with OH<sub>ad</sub> to form CO<sub>2</sub>. It was, however, pointed out that the OH adsorbs on Au apparently only at potentials more positive than that of the onset of CO oxidation. Hence, the state of the oxygen-containing species participating in the oxidation of CO on Au(100) is still unresolved and alternative pathways, such as reaction of CO with the strongly adsorbed water in that potential region, are possible. There is, however, no electrochemical signature of this adsorbed water. The rate-determining step is charge transfer in the reaction of CO and oxygen-containing species such as OH<sub>ad</sub>,<sup>18</sup> viz.,

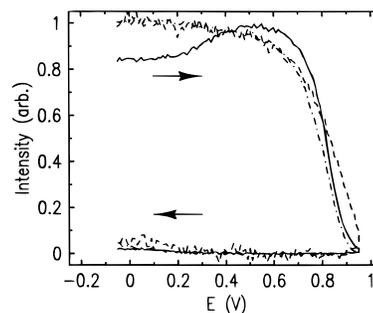


The oxidation of formaldehyde on gold in alkaline solutions is observed over a wide potential region, commencing at potentials slightly positive to the potential of the reversible hydrogen electrode (cf. Figure 6). Therefore, in a wide potential range the stability of the reconstructed surface overlaps with the formaldehyde oxidation. In alkaline solutions formaldehyde forms a *gem*-diol in a reversible nucleophilic addition of hydroxide to the carbonyl group. It is this form of formaldehyde which is oxidized to formate on gold in alkaline solutions. The corresponding reaction can be represented by

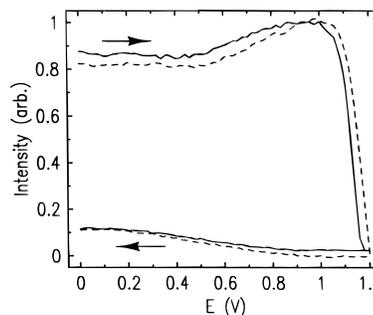


Both *gem*-diol and adsorbed formate were detected by electrochemically modulated infrared spectroscopy (EMIRS).<sup>19</sup>

The adsorption of D-glucose and CO in HClO<sub>4</sub> and formaldehyde in NaOH takes place upon their addition at 0.05 V, which can be inferred from their effect on the double-layer capacity of the gold electrode estimated from the voltammetry curves. X-ray diffraction measurements in the presence of these molecules show rocking curves similar to those in Figure 1. Hence, their adsorption does not significantly affect the reconstructed surface. The potential dependence of the intensity of the reconstruction peak at (1.205, 1.205, 0.1) in the absence and in the presence of the oxidation of organic molecules is shown



**Figure 2.** Diffracted intensity from the reconstructed surface (anodic sweep) as a function of potential in 0.1 M HClO<sub>4</sub> (solid line) and the curves in the presence of 0.5 M glucose (---) and solution saturated with CO (-·-). The cathodic sweeps were recorded after complete lifting of the reconstruction at 1 V where the sweeps were reversed. Sweep rate: 1 mV/s.

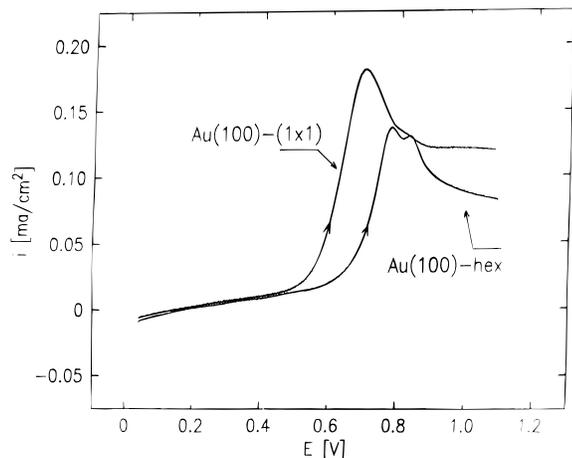


**Figure 3.** Diffracted intensity from the reconstructed surface (anodic sweep) as a function of potential in 0.1 M NaOH (—) and the curves in the presence of 0.5 M HCHO (---). The cathodic sweeps were obtained as for Figure 2. Sweep rate: 2 mV/s.

in Figures 2 and 3 for the experiments in HClO<sub>4</sub> and NaOH solutions, respectively. In the potential region from 0.05 to 0.6 V a strong reconstruction peak is observed. The small intensity increase may be due to enhanced order which accompanies the increased gold mobility at higher potentials. Above 0.6 V the intensity decreases rapidly, and at about 1 V the reconstruction is completely lifted. The sweep rate of 1 mV/s used in these measurements is too fast to provide equilibrium at the surface since the lifting of reconstruction is often kinetically hindered.<sup>8,9</sup> This can cause a small positive shift of the curves in Figures 2 and 3. The oxidation of these molecules occurs before or at the onset of the lifting of the reconstruction. No significant change in the kinetics of the reconstruction lifting or recovering is caused by the adsorption and oxidation of glucose, CO, and formaldehyde. Apparently, adsorption and oxidation of glucose and adsorption of gluconolactone do not affect the stability of the hex reconstruction significantly. The same is concluded for the adsorption and oxidation of CO in acid solutions, and oxidation of *gem*-diol and adsorption of formate in alkaline solutions.

The recovery of the reconstruction by the negatively charged electrode surface is a rather slow process,<sup>4-8</sup> as indicated by a slight increase in the diffraction intensity in the negative-going sweep in these experiments. The integrated intensity at the end of the first sweep in the negative direction is only a few percent of the intensity of the flame-annealed surface. Sweeping the potential for about 1 h in the range from 0.05 to 0.4 V at 1 mV/s promotes the electrochemically-induced reconstruction process.<sup>6</sup> In contrast to the reconstruction formed by annealing, the diffraction peaks observed after electrochemical formation in acid solution are always rotated by  $\pm 0.7^\circ$ . The slow recovery of the reconstruction allows us

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**Figure 4.** Anodic potential sweeps for the oxidation of D-glucose on Au(100)-(1 × 1) and on hexagonally reconstructed Au(100) in 0.1 M HClO<sub>4</sub> containing 0.1 M glucose. Sweep rate: 10 mV/s.

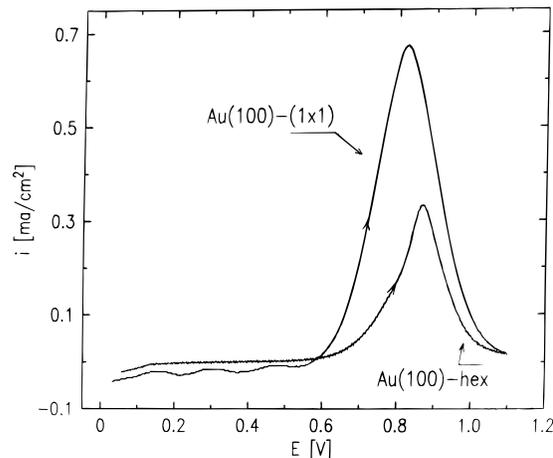
to measure the activity of both reconstructed and unreconstructed surfaces over the same potential range. It is interesting that the scanning tunneling microscopy data indicate that the CO adsorbate on Au(100) in alkaline solutions facilitates a faster recovery of reconstruction.<sup>20</sup>

The effects of adsorption on the stability of the Au(100)-hex have been reported for several organic molecules which do not undergo electrocatalytic reactions. For example, the adsorption of pyridine causes a lifting of the reconstruction of Au(100),<sup>21</sup> while the adsorption and phase transitions of uracil do not.<sup>22</sup>

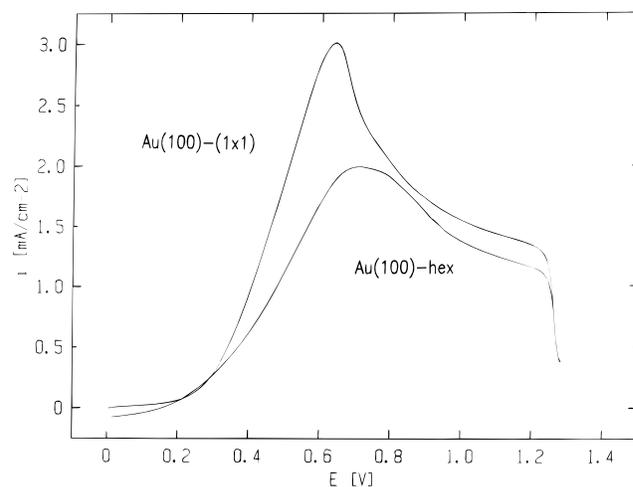
The X-ray diffraction data presented above show that the adsorption and oxidation of the three organic molecules investigated in this work do not affect the reconstruction lifting or formation of Au(100). This may indicate that the surface interaction of these species and intermediates in their reactions is relatively weak, and apparently they cannot lift the reconstruction of this surface.

**Electrocatalytic Activity.** The electrooxidations of the above three molecules are structure sensitive reactions. Thus, a distinct difference in the surface structure of the Au(100)-(1 × 1) and the reconstructed Au(100) is expected to produce an effect on their kinetics. Figures 4–6 show the first sweeps commencing at 0.05 V for the oxidation of glucose, CO, and formaldehyde on the Au(100)-(1 × 1) surface and on the reconstructed Au(100) surface. The Au(100)-(1 × 1) surface was obtained, from the reconstructed surface prepared by flame annealing, by sweeping the potential in a 0.1 M HClO<sub>4</sub> solution in a separate cell in the potential range from 0.05 to 1 V. The same potential regime was used to lift the reconstruction in the X-ray diffraction experiments shown in Figures 2 and 3. The electrode was removed from the cell at a controlled potential and, protected by a drop of solution, brought into contact with the solution containing the organic molecule at a potential of 0.05 V. In order to minimize the kinetic limited formation of the reconstruction which takes place at this potential, the measuring sweep was initiated immediately upon formation of the meniscus.

A general observation from the curves in Figures 4–6 is that the unreconstructed Au(100)-(1 × 1) surface is more active than the hexagonally reconstructed Au(100) for all three reactions. The oxidation of glucose on Au(100)-(1 × 1)



**Figure 5.** Anodic potential sweeps for the oxidation of CO on Au(100)-(1 × 1) and on hexagonally reconstructed Au(100) in CO-saturated 0.1 M HClO<sub>4</sub>. Sweep rate: 10 mV/s.



**Figure 6.** Anodic potential sweeps for the oxidation of HCHO on Au(100)-(1 × 1) and on hexagonally reconstructed Au(100) in 0.1 M HClO<sub>4</sub> containing 0.1 M HCHO. Sweep rate: 20 mV/s.

is shifted by approximately 50 mV to more negative potentials than the reaction on the Au(100)-hex, indicating faster kinetics on the Au(100)-(1 × 1) surface. In a similar way the oxidation of CO on the Au(100)-(1 × 1) surface is shifted by approximately 75 mV to more negative potentials in comparison with the Au(100)-hex surface. The curve for CO oxidation on the unreconstructed surface was obtained in a second sweep following the lifting of the reconstruction. Further cycling of potential did not show any significant change in the activity of the unreconstructed surface. This is in agreement with the X-ray diffraction data, which show that the reconstruction is completely lifted during the first potential sweep to 1 V and re-forms only slowly. The activity of the electrochemically-reconstructed surfaces, obtained by prolonged cycling between 0 and 0.4 V in solutions containing organic molecules, is remarkably close to the activity of surfaces reconstructed by flame annealing.

In order to quantify the difference in the catalytic activity of unreconstructed and reconstructed surfaces, the apparent (uncorrected for the double-layer effect) rate constants,  $k_{app}$  (cm s<sup>-1</sup>), were calculated from a single voltammogram by employing a modified version<sup>23</sup> of the conventional treatment of the irreversible reactions.<sup>24</sup>

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**Table 1. Electrochemical Kinetic Parameters for the Oxidation of CO and Glucose in HClO<sub>4</sub> Solution and Formaldehyde in NaOH Solution at 25 °C on Unreconstructed and Reconstructed Au(100) Surfaces**

molecule	surface	$E_{pzc}/V^a$	$E_p/V$	$\alpha$	$k_{app}/cm\ s^{-1}\ (0.6\ V)^a$
CO	(1 × 1)	0.270 <sup>b</sup>	0.715	0.68	$5 \times 10^{-4}$
	hex	0.480 <sup>c</sup>	0.810	0.65	$5 \times 10^{-5}$
glucose	(1 × 1)	0.270	0.800	0.53	$1 \times 10^{-4}$
	hex	0.480	0.860	0.44	$4.3 \times 10^{-5}$
formaldehyde	(1 × 1)	0.270	0.665	0.26	$1.1 \times 10^{-3}$
	hex	0.480	0.725	0.2	$6.6 \times 10^{-4}$

<sup>a</sup> Potential given vs RHE in the same solution. <sup>b</sup> Pzc value for Au(100)-(1 × 1) for 0.1 M perchlorate solutions with 10 mM HClO<sub>4</sub>.<sup>26</sup> <sup>c</sup> Pzc value for hex Au(100) in 0.01 M HClO<sub>4</sub>.<sup>3</sup>

Values of  $k_{app}$  were evaluated at the peak potential,  $E_p$ , and at potentials corresponding to one-half,  $E_{p/2}$ , and one-quarter,  $E_{p/4}$ , of the peak current, by using the relation

$$\log k_{app} = K + \log(\alpha_{app} \nu DF/RT)^{1/2} \quad (1)$$

where  $\nu$  is the sweep rate,  $D$  is the diffusion coefficient of the reacting species, and the constant  $K$  contains the dimensionless variable evaluated numerically which has the values 0.339, -0.469, or -0.851 at potentials corresponding to  $E_p$ ,  $E_{p/2}$ , and  $E_{p/4}$ , respectively. The values of the apparent transfer coefficient,  $\alpha_{app}$ , were obtained from 22

$$\alpha_{app} = 47.7\ mV/(E_p - E_{p/2}) \quad (2a)$$

or

$$\alpha_{app} = 22.6\ mV/(E_{p/2} - E_{p/4}) \quad (2b)$$

The analysis requires the first-order kinetics which was found for the oxidation of glucose<sup>17</sup> and formaldehyde<sup>19</sup> and estimated for CO.<sup>18</sup> Although the oxidations of glucose and CO are formally two-electron processes,  $\alpha_{app}$  will be used in the same manner as for a one-electron process.

Table 1 gives the summary of the  $k_{app}$  and  $\alpha_{app}$  values for the oxidation of glucose, CO, and formaldehyde on reconstructed and unreconstructed Au(100). The values of  $k_{app}$  were extrapolated at 0.6 V vs RHE from the log  $k_{app}$  vs  $E$  plots. Slower kinetics on the hexagonally reconstructed Au(100) for all three reactions is reflected in the measured and calculated parameters. In each case higher values of the apparent rate constants are obtained for the Au(100)-(1 × 1) surface. The calculated  $k_{app}$  values were reproducible to within 20%. The literature values for the potential of zero charge (pzc) are also listed in Table 1.

There are two possible origins of the observed difference in the activity of the reconstructed and unreconstructed Au(100) surfaces. First, the adsorption of these molecules can be considerably stronger on the open (100)-(1 × 1) compared to the hexagonal close-packed surface. In

addition, the pzc for the unreconstructed surface is more negative and therefore facilitates a maximum coverage of organic molecules at a more negative potential. This is likely to cause different reaction rates. Besides that, the adsorption of OH<sub>ad</sub> is also structure dependent and it appears to be more pronounced on Au(100) than on Au(111),<sup>15,23</sup> whose structure is similar to the Au(100)-hex surface. This can result in different oxidation rates of the above molecules since their oxidation is enhanced or facilitated by this adsorbate on Au. The oxidation of CO on Au occurs only in electrolytes with weakly-adsorbing anions.<sup>15</sup> In such solution a strong interaction of H<sub>2</sub>O and chemisorption of OH<sub>ad</sub> is possible at moderately positive potentials.<sup>25</sup> The origin of a higher activity of the unreconstructed surfaces, therefore, can be ascribed to the stronger adsorption of the reactants on this surface and to a stronger adsorption of OH or H<sub>2</sub>O species. Both reactions, OH adsorption<sup>23</sup> and CO oxidation,<sup>18</sup> occur at less positive potentials on the open Au(100)-(1 × 1) surface than on the close-packed Au(111) surface. The larger step density of the Au(100)-(1 × 1) surface resulting from the lifting of the reconstruction may contribute to its higher activity, although this effect is expected to be negligible.

### Conclusions

The present data demonstrate that *in situ* SXS technique can be successively used to monitor the state of the surface reconstruction during the course of the oxidation of several small organic molecules interesting for the electrochemical energy conversion. The same approach appears to be applicable to other electrocatalytic reactions on various electrode surfaces and can yield important results for the area of electrocatalysis. No significant change in the kinetics of the reconstruction lifting or recovering is caused by the adsorption and oxidation of glucose, CO, and formaldehyde. This indicates that the interaction of these species and their reaction intermediates with the reconstructed Au(100) surface is relatively weak. The unreconstructed Au(100)-(1 × 1) surface was found more active than the hexagonally reconstructed Au(100) for all three reactions. The difference of the apparent rate constants is about 1 order of magnitude. The more open structure of the Au(100)-(1 × 1) surface facilitates a stronger interaction of the reactants and surface gold atoms and a stronger adsorption of OH or H<sub>2</sub>O necessary for the oxidation of CO and glucose on gold.

**Acknowledgment.** This research was performed under the auspices of the U.S. Department of Energy, Divisions of Chemical and Material Sciences, Office of Basic Energy Sciences, under Contract No. DE-AC02-76CH00016.

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