Carbonate formation on $p(4 \times 4)$-O/Ag(111)

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High-resolution core-level spectroscopy and density-functional theory calculations have been used to investigate CO adsorption on the $p(4 \times 4)$ structure of oxidized Ag(111). CO adsorption with subsequent carbonate formation was observed at 100 K. The experimental results are consistent with calculations that reveal low activation barriers to form CO_2 and CO_3^{2-} from adsorbed CO. On the basis of a good match between calculated and experimental shifts in the Ag 3d and O 1s core-level binding energies, a model for a monolayer of carbonates on $p(4 \times 4)$-O/Ag(111) is proposed.

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I. INTRODUCTION

One way to reduce fuel consumption and CO_2 emissions is to operate engines at a high air-to-fuel ratio. This method is used in modern diesel and lean burn vehicles. However, under oxidizing conditions, the traditional three-way catalyst (TWC) is unable to efficiently reduce nitrogen oxide (NO_x) species. The main routes for NO_x reduction in oxygen excess are NO_x storage and reduction (NSR)[1] and selective catalytic reduction (SCR)[2] with either ammonia (or urea) or hydrocarbons (HC's) as a reducing agent. For HC assisted SCR, an Ag/Al_2O_3 catalyst has recently shown promising results.[3] Although many aspects of this catalyst have been clarified,[3] detailed structural information about the catalyst is missing. For example, the oxidation state of Ag in the alumina matrix is unclear. As the catalysts operates under oxidizing conditions, it is, however, probable that silver is in an oxidized state. It is clear that an increased understanding of adsorption and reaction properties of exhaust gases on oxidized Ag surfaces is required to unravel the active phase of the Ag/Al_2O_3 catalyst.

The Ag(111) surface is the low-energy orientation of silver, and is consequently expected to be dominant on silver crystallites.[4] A number of different oxygen-induced surface reconstructions have been identified on Ag(111), and the corresponding structural models have been established.[5–7] The adsorption properties of these structures are, however, virtually unexplored. In this contribution, we focus on the CO-induced surface reconstruction of the well-known $p(4 \times 4)$-O/Ag(111) structure.[6,7] State-of-the-art high-resolution core-level spectroscopy (HRCLS) measurements are presented in combination with *ab initio* density-functional theory (DFT) calculations. It is demonstrated that carbonate (CO_3^{2-}) species are formed upon CO adsorption at 100 K on the $p(4 \times 4)$-O/Ag(111) structure. The experimental results are consistent with the theoretical prediction of low activation energies to form CO_3^{2-} from CO. On the basis of a good match between calculated and measured shifts in the Ag 3d and O 1s core-level binding energies, a model for a monolayer of carbonates on Ag(111) is proposed. The structure implies a significant rearrangement of the original $p(4 \times 4)$-O/Ag(111) structure and suggests that the ability of oxygen to reconstruct the Ag(111) surface leads to the formation of Ag vacancies favorable for carbonate adsorption.

II. METHODS

A. Experimental

The HRCLS experiments were carried out at Beamline I311[8] at the Swedish synchrotron radiation facility MAX-Lab in Lund, Sweden. All spectra were collected in normal emission with photon energies of 380 eV (140 meV experimental resolution) for C 1s, 650 eV (160 meV experimental resolution) for O 1s, and 430 eV (90 meV experimental resolution) for Ag 3d. The spectra were normalized to the background and the binding energies were calibrated to the Fermi edge. The sample was mounted on a tungsten wire through which it could be heated with an electric current. The temperature was measured by a Chromel-Alumel thermocouple spot-welded on the back side of the crystal. The Ag(111) crystal was cleaned by sputtering and annealing at 850 K and the cleanliness was checked with x-ray photoelectron spectroscopy (XPS) prior to each experiment. As the sticking probability of molecular oxygen on Ag(111) is extremely low, $\sim 5 \times 10^{-6}$,[9] we used atomic oxygen[5,7] produced with a commercial thermal gas cracker. The $p(4 \times 4)$-O/Ag(111) structure was grown by adjusting the exposure of atomic oxygen until an Ag $3d_{5/2}$ spectrum was obtained, which resembled the known spectrum reported in the literature[6]. Low-energy electron diffraction (LEED) characterization was not performed as it is known[5] that exposure of Ag(111) to atomic oxygen leads to patches of coexisting structures [$p(4 \times 4)$-O/Ag(111), $p(4 \times 5\sqrt{3})$rect-O/Ag(111), and $c(3 \times 5\sqrt{3})$rect-O/Ag(111)] that obscure the LEED pattern.

B. Computational

The DFT[10,11] was used in an implementation with plane waves and pseudopotentials. In particular, the CASTEP code was used.[12] The exchange correlation functional was approximated with the form proposed by Perdew, Burke, and Ernzerhof.[13] The interaction between valence electrons and the core was described by ultrasoft scalar relativistic pseudopotentials.[14] The considered elements were treated with 4 (C), 6 (O), and 11 (Ag) valence electrons, respectively. A plane-wave kinetic energy cutoff of 380 eV was used to expand the Kohn-Sham orbitals, which was sufficient for convergence in energy differences. All surface calculations were performed in

a $p(4 \times 4)$ surface cell and repeated slabs were separated by at least 15 Å vacuum. Calculations of reaction barriers were done with a four-layer slab, whereas seven layers were used for evaluation of core-level shifts. Reciprocal space integration over the Brillouin zone was approximated by summation over eight unique k points. Structural optimization and transition state searches were performed with the two bottom layers constrained to bulk positions. (All configurations were reoptimized without structural constraints with the seven-layer slab for calculations of core-level shifts.) Adsorption potential energies for the adsorbates (X) were calculated according to

$$E_b(X) = E_{X/MO} - E_{MO} - E_X, \qquad (1)$$

where $E_{X/MO}$ is the total energy of the combined system (adsorbate and oxidized silver surface), E_{MO} is the energy of the oxidized silver surface, and E_X is the total energy of the gas phase adsorbate. In order to evaluate activation energies for carbonate formation, a transition state search was performed. The activation barrier was estimated with a linear synchronous transit and quadratic synchronous transit (LST/QST) method.[15] The surface core-level shifts (SCLS's) were calculated by use of a pseudopotential generated with an electron hole in the Ag $3d$ and O $1s$ shells, respectively. As an Ag bulk reference, an Ag $3d$ core hole in the center of the slab was used, whereas the O $1s$ shifts were calculated with respect to the average O $1s$ binding energy in $p(4 \times 4)$-O/Ag(111). The present procedure was tested for clean Ag(111) and found to be in good agreement with previous calculations and experiments.[16] Here, the shifts for the first and second atomic layers of the clean Ag(111) surface were calculated to be -0.19 and 0.0 eV, respectively.

III. RESULTS AND DISCUSSION

The $p(4 \times 4)$-O/Ag(111) structure has previously been characterized experimentally with photoemission spectroscopy,[6] scanning tunneling microscopy,[5–7] surface x-ray diffraction,[6] and low-energy electron diffraction,[17] and the structure has been determined by comparisons to first-principles calculations.[5–7] In summary, the structure consists of a stoichiometric $Ag_{12}O_6$ overlayer structure attached to the Ag(111) registry [Fig. 1(b)]. The overlayer unit cell consists of two planar Ag_6 triangles placed in fcc and hcp sites, respectively, and rotated $60°$ with respect to each other. The furrow formed between the triangles provides two adsorption sites for O atoms. One O atom is adsorbed slightly subsurface with respect to the Ag_6 clusters and is calculated to be 2.16 Å above the unreconstructed Ag(111) layer, whereas the second atom is positioned 3.05 Å above Ag(111) in a fourfold-like site between the two clusters.

In this work, the $p(4 \times 4)$-O/Ag(111) [hereafter denoted $p(4 \times 4)$] has been included as a reference and the Ag $3d_{5/2}$ photoemission result is shown in Fig. 1(a). This spectrum was recorded after oxidation of the Ag(111) surface with atomic O at 470 K. When atomic O is used to oxidize Ag(111), it is difficult to avoid the formation of patches with coexisting structures of similar stability. In addition to $p(4 \times 4)$-O/Ag(111), two related triangular structures are often formed, namely $p(4 \times 5\sqrt{3})$rect-O/Ag(111) and $c(3 \times 5\sqrt{3})$rect-O/Ag(111).[5] As the stoichiometry, stability, and
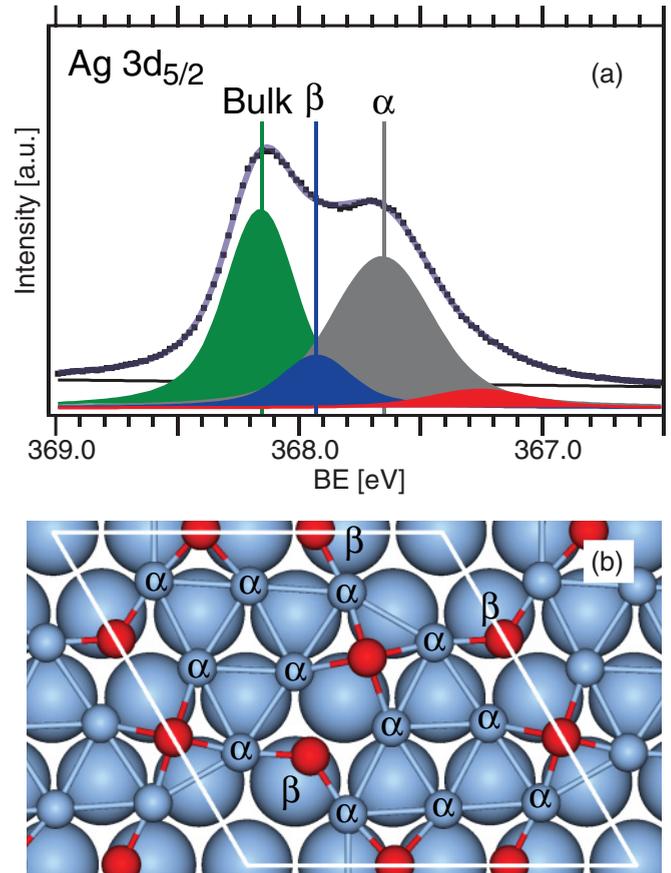
FIG. 1. (Color online) (a) Ag $3d_{5/2}$ photoemission spectrum recorded in normal emission with $h\nu = 430$ eV. (b) Stick-and-ball model of $p(4 \times 4)$-O/Ag(111). O (Ag) atoms are colored red (blue). Ag atoms in the oxide overlayer are represented by small spheres, whereas Ag atoms in the topmost Ag(111) layer are represented by large spheres. Ag atoms assigned to the α and β components in (a) are indicated.

local geometry of these three different structures are similar, it can be assumed that their chemical properties are comparable. Consequently, we restrict the analysis of the XPS results and the DFT calculations to the $p(4 \times 4)$ structure. Deconvolution of the recorded spectrum resulted in four different peaks, which are assigned to bulk atoms (368.16 eV), atoms in the Ag_6 triangles (-0.50 eV with respect to the bulk component), atoms in the furrow (-0.23 eV), and one additional peak at -0.90 eV.

The SCLS's of $p(4 \times 4)$ were also investigated computationally. Shifts were calculated for all atoms in the Ag_6 units and the first unreconstructed Ag(111) layer, Fig. 1(b). The Ag $3d$ (Ref. 18) shifts of the 12 Ag atoms (α) in the two Ag_6 triangles were calculated to be -0.60 ± 0.03 eV, whereas the Ag atoms located in the furrows between the Ag_6 clusters (β) were shifted by -0.30 eV. The remaining atoms in the topmost Ag(111) layer were calculated to be shifted by less than -0.13 eV with respect to the bulk reference. With a common 0.1 eV difference between the experimental and calculated Ag $3d$ CLS's, the agreement between DFT and experiment is good. The measured weak feature at -0.90 eV is not present in the calculations of the $p(4 \times 4)$-O/Ag(111) structure and
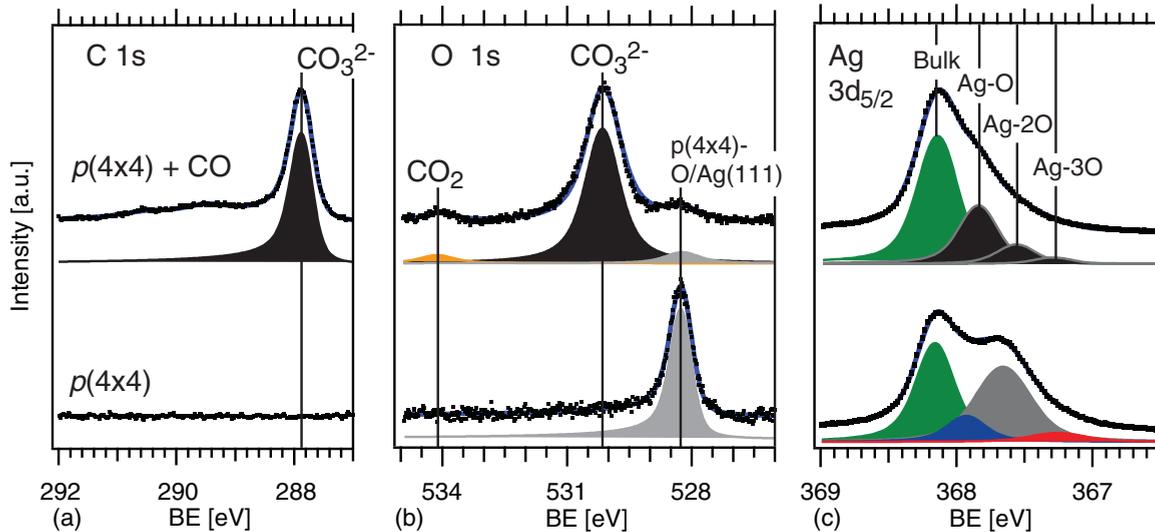
FIG. 2. (Color online) (a)–(c) Photoemission spectra of the $p(4 \times 4)$ (bottom) and the $p(4 \times 4)$ structure when exposed to 100 L CO at 100 K (top).

could be ascribed to small amounts of either impurities[6] or coexisting structures with higher oxygen content.[19]

Also the O 1s photoemission spectrum provides a sensitive signature of $p(4 \times 4)$-O/Ag(111). The recorded O 1s spectrum shows a single component located at 528.23 eV [Fig. 2(b), bottom] in good agreement with previously reported values for this surface.[5,9] The calculated CLS of the three O atoms adsorbed slightly subsurface are all within 0.01 eV, whereas the three O atoms adsorbed in the fourfold position have an average shift of -0.13 eV. Overall, the calculated O 1s shifts cover an interval of 0.13 eV, which is consistent with the observation of a single O 1s peak taking into account a full width at half-maximum of (0.14 eV) associated with the lifetime of the core hole and the experimental resolution (0.16 eV).

After the $p(4 \times 4)$ reference system has been established, the chemistry of CO adsorption onto this surface was investigated. When CO was dosed onto $p(4 \times 4)$ at room temperature (300 K), we observed that the O 1s peak at 528.23 eV, assigned to bare $p(4 \times 4)$, gradually disappeared (not shown). However, there was no evidence for carbon on the surface; the C 1s signal remained close to zero. This result clearly shows that CO reacted with oxygen and formed CO_2, which immediately desorbed from the surface. The observed room-temperature CO-induced removal of oxygen atoms from the $p(4 \times 4)$ surface is in agreement with previous studies of Ag(111),[9] as well as more recent results reported for the $p(4 \times 4)$ structure.[4]

Lowering the exposure temperature to 100 K significantly changes the chemistry of CO adsorption. In Figs. 2(a)–2(c), the C 1s, O 1s, and Ag $3d_{5/2}$ spectra are presented, before and after exposure to 100 L of CO at 100 K. In the C 1s spectrum [Fig. 2(a)], a single peak is observed at 287.85 eV. In the O 1s spectrum [Fig. 2(b)], the peak at 528.23 eV, assigned to the bare $p(4 \times 4)$, is significantly reduced and two new components are observed at 530.15 and 534.12 eV, respectively. Finally, the Ag $3d_{5/2}$ α component previously assigned to Ag_6 triangles in $p(4 \times 4)$ completely disappears upon CO exposure, and

overall we observe a CLS toward the binding-energy position of Ag bulk.

Previous XPS measurements of polycrystalline Ag exposed to CO/O mixtures indicate carbonate (CO_3^{2-}) formation.[20] Moreover, the formation of CO_3^{2-} has been reported on single crystals.[21,22] In Ref. 21, carbonates were observed on Ag(110) after reaction of CO_2 with preadsorbed atomic oxygen, and in Ref. 22, carbonates were formed upon CO dosage onto an oxygen precovered Ag(111) surface at 90 K. The C 1s and O 1s binding energies in these studies were 287.7–289.0 and 529.9–530.3 eV, respectively. Both the C 1s peak at 287.85 eV and the O 1s main peak at 530.15 eV in Figs. 2(a) and 2(b) agree well with the signatures of carbonates reported in the literature. It can, therefore, be concluded that the majority of the observed intensities in both the C 1s region and in the O 1s region are due to carbonate formation. The weak feature at ~ 534 eV in the O 1s spectrum has previously been assigned to physisorbed CO_2.[22] Adsorbed CO_2 has a corresponding C 1s peak at ~ 291.5 eV.[22] The CO_2 peak is, however, too weak to be observed in the experimental C 1s spectrum in Fig. 2(a).

In order to further elucidate the experimentally observed low-temperature carbonate formation, DFT calculations were performed for CO adsorption and carbonate formation on $p(4 \times 4)$. As the room-temperature experiments indicated CO_2 formation, this was considered to be an intermediate step in the full reaction pathway:

$$CO(g) + O(ads) \Rightarrow CO_2(ads),$$
$$CO_2(ads) + O(ads) \Rightarrow CO_3^{2-}(ads).$$
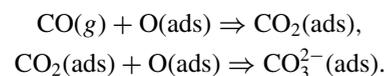
The optimized structures for CO, CO_2, and CO_3^{2-} adsorbed on $p(4 \times 4)$ are presented in Figs. 3(a)–3(c). We find that CO adsorbs weakly ($E_b = -0.23$ eV) in an atop position on one of the side Ag atoms in the Ag_6 triangle [Fig. 3(a)]. This site is preferred by 0.16 eV over adsorption at the Ag corner atom. In the stable structure, the Ag-C (C-O) bond length is calculated to be 2.45 (1.15) Å and the Ag-C-O angle is 159°.
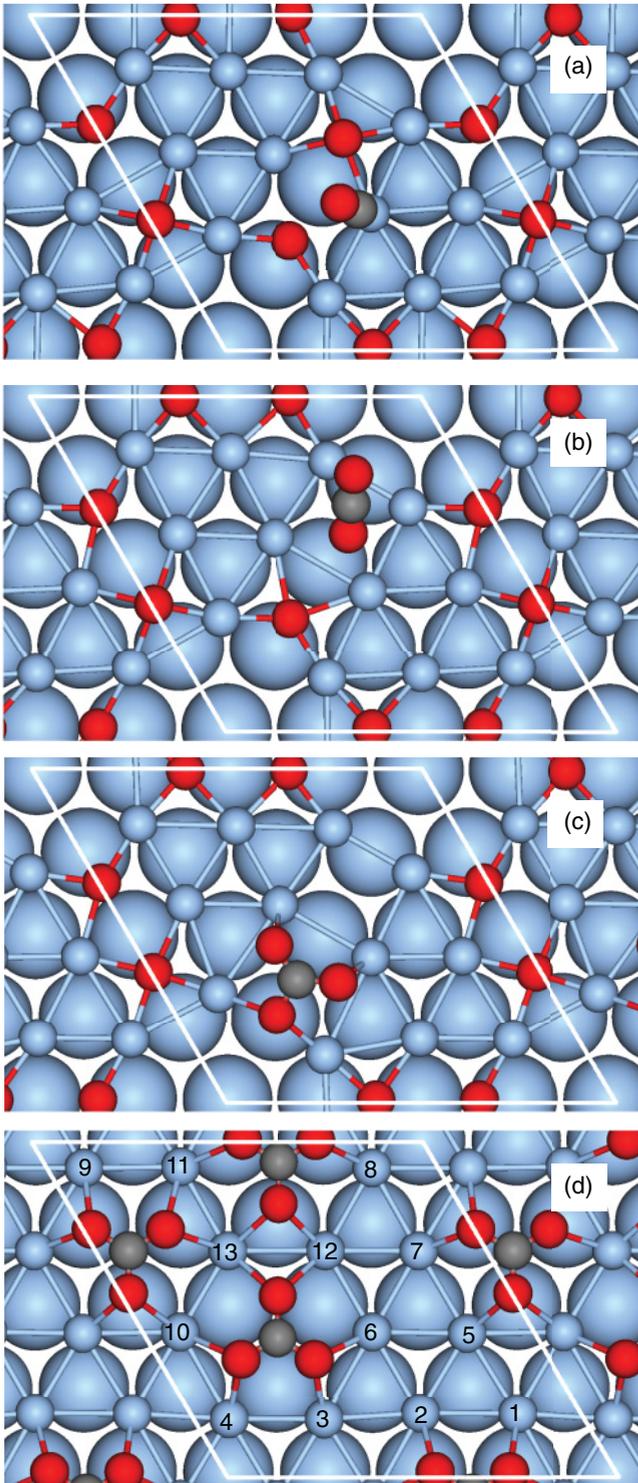
FIG. 3. (Color online) Low-energy structures with CO (a), CO_2 (b), and CO_3^{2-} (c) adsorbed on $p(4 \times 4)$-O/Ag(111). (d) Proposed structural model of the carbonate structure with one monolayer of CO_3^{2-}. Color code: C, gray; O, red; Ag, blue.

The C-O bond length is identical to the bond length in the CO gas-phase molecule. As a reference, we also considered CO adsorption on a clean Ag(111) surface. In this case, CO is adsorbed in the atop site in a linear configuration with $E_b = -0.25$ eV. The calculated CO adsorption energy on clean Ag(111) agrees well with an experimental value of -0.28 eV

found from isotherms derived from both surface potential and Auger electron spectroscopy measurements.[23]

As already mentioned, the $p(4 \times 4)$ structure contains six O atoms per unit cell with two distinctly different adsorption positions. CO_2 formation is calculated to be facile via reaction between adsorbed CO molecules and the fourfold positioned O atoms with a 0.25 eV reaction barrier. The barrier can be related to the cleavage of the O-Ag bonds. In the calculated transition state structure, the CO molecule is located 1.89 Å from the reacting O atom and has a C-O bond length of 1.17 Å. CO_2 formation is clearly exothermic and a -2.02 eV gain is calculated with respect to CO adsorbed on the surface.

CO_2 is physisorbed on the slightly reduced $p(4 \times 4)$ structure, and the adsorption energy with respect to CO_2 in the gas phase is only -0.10 eV. This low adsorption energy explains the experimentally observed CO_2 desorption at room temperature. The relaxed structure is shown in Fig. 3(b) with the CO_2 molecule located in the preferred fourfold position previously occupied by the reacting surface O atom. The four distances between Ag atoms and the closest oxygen atom in CO_2 are calculated to be 3.73, 3.77, 3.95, and 3.97 Å, and the Ag-O-(CO) angle is $\sim 130°$. The adsorbed CO_2 molecule has a linear configuration and a C-O bond length of 1.18 Å. The molecular geometry is identical to the calculated gas phase structure of CO_2.

In Fig. 3(c), the stable structure of one carbonate species adsorbed on the $p(4 \times 4)$ surface is presented. CO_3^{2-} occupies the preferred adsorption geometry site in the furrow between the two Ag_6 structures. In agreement with previous photo-electron diffraction (PD) studies,[24] near-edge x-ray absorption fine-structure studies,[25] and DFT calculations[26] on Ag(110), we find that CO_3^{2-} is preferably adsorbed close to parallel to the surface; the molecular plane has an angle of 21° to the surface and the C-O bond lengths are all calculated to be ~ 1.30 Å. The Ag-O distances for the O atom in a bridge configuration are calculated to be 2.16 Å, whereas the Ag-O distances for the singly coordinated O atoms are calculated to be 2.27 Å. The internal carbonate structure on the surface is found to be close (within 0.04 Å) to the calculated structure of a hypothetical gas phase CO_3^{2-}. Previous DFT calculations and PD experiments on the Ag(110) surface have observed an adsorption geometry of CO_3^{2-} with one O atom in the bridge position next to the Ag add-row, whereas the other two O atoms are near-atop Ag atoms of the underlying substrate surface.[24,26]

The overall reaction from adsorbed CO to adsorbed CO_3^{2-} is calculated to be exothermic by -2.63 eV. The barrier for carbonate formation from CO_2 is calculated to be 0.11 eV, where the transition state is related to rotation of the CO_2 molecule and breaking of the O-Ag bonds. In the transition state, the CO_2 molecule is parallel to the surface, with an 179° O-C-O bond angle. The distance between the O surface atom and the C atom is calculated to be 3.72 Å.

The O 1s feature assigned to CO_3^{2-} in Fig. 2(b) corresponds to $\sim 90\%$ of the total intensity in the spectrum. Assuming that 100 K is too low for CO_2 desorption, this observation suggests that most O atoms on the surface are bound in carbonates. It can, thus, be assumed that the six O atoms in the original $p(4 \times 4)$ structure have reacted with three CO molecules to form three carbonates in each surface unit cell. This assumption is further justified by an experimental $\sim 1.4{:}1$ O 1s intensity ratio

between the CO_3^{2-} peak and the original $p(4 \times 4)$ peak before CO exposure, which is very close to the expected 1.5:1 O $1s$ intensity ratio as each CO molecule reacts with two surface oxygen atoms.

Figure 3(d) shows the relaxed structure of the $p(4 \times 4)$ cell with full carbonate coverage. As the number of Ag atoms in the first metal layer is unknown for the carbonate monolayer, this number has been allowed to vary by using bulk Ag as a reservoir. The preferred structure contains 13 Ag atoms in the first layer. This structure is calculated to be exothermic by -0.63 eV with respect to one with 12 atoms, the number in the $p(4 \times 4)$ structure. The geometry in Fig. 3(d) can be described as an Ag(111) surface with three vacancies where CO_3^{2-} is adsorbed. All Ag atoms in the overlayer are located in fcc hollow sites. This situation is preferred by 0.13 eV with respect to a configuration with all atoms in hcp positions. Note that both fcc and hcp sites are occupied in the $p(4 \times 4)$ structure. In the vacancies, the carbonate ions are adsorbed in a near planar geometry parallel to the surface. Similar to the structure in Fig. 3(c), each carbonate ion in Fig. 3(d) is bonded to the substrate with three O atoms, which each form a bond with two Ag-add atoms. Our adsorption geometry with all O atoms in bridge positions, therefore, suggests that the carbonate ion prefers a tridentate bonding with all three O atoms bonded to two Ag atoms when this is possible. The average Ag-O bond length is 2.32 ± 0.05 Å. Previous theoretical studies of carbonates on Ag(110)[26] and on Ag(100)[27] also found a planar geometry near-parallel to the surface, suggesting that this adsorption geometry is generally preferred on all the low-index surfaces of silver. The Ag-O distances in Ref. 26 were calculated to be in the range 2.27–2.33 Å, in good agreement with our calculations.

The calculated average SCLS's for O and Ag in the carbonate monolayer [Fig. 3(d)] are collected in Table I. The calculated Ag $3d$ shifts can be divided into three groups that correlate with the number of O-Ag bonds: -0.41 ± 0.02 eV (O-Ag), -0.68 ± 0.02 eV (2O-Ag), and -0.95 eV (3O-Ag). The shifts for the Ag atoms in the second layer were calculated to be close to 0.0 eV. The calculated SCLS's were used as an initial guess in the curve-fitting procedure of the experimental Ag $3d_{5/2}$ spectrum [Fig. 2(c)]. Deconvolution of the experimental spectrum revealed three peaks located at -0.30, -0.58, and -0.85 eV with respect to the Ag bulk component. Inspection of the structure in Fig. 3(d) reveals that the unit cell contains nine Ag atoms coordinated to one O atom, three Ag atoms coordinated to two O atoms, and

one Ag atom coordinated to three O atoms. The relative intensities of the peaks were, therefore, fixed to the expected value of 9:3:1 during the fitting procedure. The calculated SCLS's were slightly larger (~ 0.1 eV) as compared to the experimental shifts. As a similar discrepancy in the Ag $3d$ shifts was calculated for $p(4 \times 4)$, it can be concluded that the experimental Ag $3d_{5/2}$ shifts for the carbonate monolayer strongly support the proposed the structure in Fig. 3(d).

Also the calculated O $1s$ shifts are in good agreement with the experiments [Fig. 2(b)]. The shifts are 1.75 ± 0.1 eV with respect to O atoms in the $p(4 \times 4)$ structure. This should be compared with an experimental shift of 1.90 eV. Looking at the proposed structure in Fig. 3(d) we notice that the O atoms are chemical equivalent, as they all are bound to two Ag adatoms and one C atom if bonds to the underlying Ag(111) surface are neglected. Chemical equivalent O atoms agree well with the experimental observation of one single O $1s$ peak assigned to carbonates.

The proposed model of the carbonate monolayer with carbonates adsorbed in vacancies suggests that undercoordinated Ag-add atoms are essential for stabilizing the carbonate ion. Previous studies of carbonate formation on the Ag(110) suggested that a (1×2) reconstruction structure forms with carbonate ions stabilizing rows of added Ag atoms.[28] Reconstruction and bonding to undercoordinated Ag atoms thus seem to be a general phenomenon when carbonates are formed on oxygen-covered silver surfaces.

In contrast to the carbonate formation observed upon CO exposure at 100 K, we already mentioned that room-temperature exposure leads to titration of surface oxygen in the $p(4 \times 4)$ structure due to the formation of CO_2, which directly desorbs to the gas phase. Low temperatures and close to UHV conditions are thermodynamically equivalent to working at high temperatures near atmospheric pressure, provided that kinetic effects are negligible. The proposed atomic-scale structure of carbonates formed on the $p(4 \times 4)$ structure could therefore be relevant for oxidized silver surfaces exposed to CO near atmospheric pressure.

IV. SUMMARY

With the use of HRCLS, we have shown that carbonates are formed when a $p(4 \times 4)$-O/Ag(111) structure is exposed to CO at 100 K. Exposure at room temperature instead leads to CO_2 formation and titration of surface oxygen atoms. On the basis of DFT calculations, we have suggested that the low-temperature structure consists of carbonates adsorbed parallel to the surface in silver vacancy sites. The proposed model is supported by calculated Ag $3d$ and O $1s$ core-level shifts, which agreed well with the experimentally observed features.

TABLE I. Calculated and measured core levels for Ag and O atoms in Fig. 3(d). Ag $3d$ core-level shifts are given with respect to Ag bulk atoms and the O $1s$ with respect to O atoms in the $p(4 \times 4)$-O/Ag(111) structure.

	Theoretical CLS (eV)	Experimental CLS (eV)
Ag_{1-9}	-0.41 ± 0.02	-0.30
Ag_{10-12}	-0.68 ± 0.01	-0.58
Ag_{13}	-0.95	-0.85
Ag_{sub}	~ 0.0	
O_{1-9}	1.75 ± 0.10	1.90

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[1] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, and K. Kasahara, Catal. Today **27**, 63 (1996).

[2] V. I. Parvulescu, P. Grange, and B. Delmon, Catal. Today **46**, 233 (1998).

[3] R. Burch, Catal. Rev. **46**, 271 (2004).

[4] A. Klust and R. J. Madix, J. Chem. Phys. **126**, 084707 (2007).

[5] J. Schnadt, J. Knudsen, X. L. Hu, A. Michaelides, R. T. Vang, K. Reuter, Z. S. Li, E. Lægsgaard, M. Scheffler, and F. Besenbacher, Phys. Rev. B **80**, 075424 (2009).

[6] M. Schmid *et al.*, Phys. Rev. Lett. **96**, 146102 (2006).

[7] J. Schnadt, A. Michaelides, J. Knudsen, R. T. Vang, K. Reuter, E. Lægsgaard, M. Scheffler, and F. Besenbacher, Phys. Rev. Lett. **96**, 146101 (2006).

[8] R. Nyholm, J. N. Andersen, U. Johansson, B. N. Jensen, and I. Lindau, Nucl. Instrum. Methods Phys. Res., Sect. A **467**, 520 (2001).

[9] C. T. Campbell, Surf. Sci. **157**, 43 (1985).

[10] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[11] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[12] S. J Clark *et al.*, Z. Kristallogr. **220**, 567 (2005).

[13] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[14] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[15] T. A. Halgren and W. N. Lipscomb, Chem. Phys. Lett. **49**, 225 (1977).

[16] J. N. Andersen, D. Hennig, E. Lundgren, M. Methfessel, R. Nyholm and M. Scheffler, Phys. Rev. B **50**, 17525 (1994).

[17] R. Reichelt, S. Günther, J. Wintterlin, W. Moritz, L. Aballe, and T. O. Mentes, J. Chem. Phys. **127**, 134706 (2007).

[18] Spin-orbit coupling was not considered in the calculations.

[19] This subject will be discussed in a forthcoming publication.

[20] V. I. Bukhtiyarov, V. A. Kondratenko, and A. I. Boronin, Surf. Sci. **293**, L826 (1993).

[21] M. A. Barteau and R. J. Madix, J. Electron Spectrosc. Relat. Phenom. **31**, 101 (1983).

[22] T. E. Felter, W. H. Weinberg, G. Y. Lastushkina, A. I. Boronin, P. A. Zhdan, G. K. Boreskov, and J. Hrbek, Surf. Sci. **118**, 369 (1982).

[23] G. M. Elhiney, H. Papp, and J. Pritchard, Surf. Sci. **54**, 617 (1976).

[24] M. Kittel, D. I. Sayago, J. T. Hoeft, M. Polcik, M. Pascal, C. L. A. Lamont, R. L. Toomes, and D. P. Woodruff, Surf. Sci. **512**, 237 (2002).

[25] R. J. Madix, J. L. Solomon, and J. Stöhr, Surf. Sci. **197**, L253 (1988).

[26] J. Robinson and D. P. Woodruff, Surf. Sci. **556**, 193 (2004).

[27] T. Y. Soo and C. Quin, J. Quantum Chem. **110**, 946952 (2009).

[28] X.-C. Guo and R. J. Madix, Surf. Sci. **489**, 37 (2001).