Methoxy Species on Cu(110): Understanding the Local Structure of a Key Catalytic Reaction Intermediate

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Partial oxidation of methanol to formaldehyde over Cu(110) is one of the most studied catalytic reactions in surface science, yet the local site of the reaction intermediate, methoxy, remains unknown. Using a combination of experimental scanned-energy mode photoelectron diffraction, and density functional theory, a consistent structural solution is presented in which all methoxy species occupy twofold coordinated "short-bridge" adsorption sites. The results are consistent with previously-published scanning tunnelling microscopy images and theoretical calculations of the reaction mechanism.

A major goal of modern surface science has been to gain an understanding of fundamental processes in heterogeneous catalysis through the study of model reactions on well-characterized surfaces in ultrahigh vacuum [1]. One of the most studied such systems is the partial oxidation of methanol (CH_3OH) over Cu(110) to produce formaldehyde (H_2CO). However, while the key surface intermediate in this reaction was identified to be the methoxy species, CH_3O, more than 30 years ago [2], the local adsorption site and associated structure of this species remain undetermined, and this missing structural information is crucial in gaining a molecular-scale understanding of the reaction. Here we show, through the combination of experimental scanned-energy mode photoelectron diffraction (PhD) [3], and density functional theory (DFT) calculations, that only local high-symmetry "short-bridge" sites are occupied. These sites have been implicated in theoretical investigations of the atomic-scale reaction mechanism [4,5], but are inconsistent with previous interpretations of experimental data taken to infer occupation of a multiplicity of low-symmetry sites [6–8]. We show that this single local site can be reconciled with all previous experimental data, but also identify the involvement of Cu adatoms that may play a hitherto unconsidered role in the surface reaction mechanism.

The surface methoxy species is formed by reaction of methanol with preadsorbed atomic oxygen ($2CH_3OH + O_a \rightarrow 2CH_3O_a + H_2O$), the oxygen being accommodated on the surface in a (2×1) added-row reconstruction comprising alternate [001] Cu adatom rows with O atoms in the long-bridge sites (Fig. 1) to form Cu-O-Cu-O chains. Subsequent heating leads to dissociation of the methoxy and desorption of formaldehyde and hydrogen ($2CH_3O_a \rightarrow 2CH_2O + H_2$). Scanning tunnelling microscopy (STM), together with qualitative low energy electron diffraction (LEED), has shown that an ordered (5×2) pg structure is formed by the adsorbed methoxy, and it is believed that this phase incorporates 4 or 6 Cu adatoms per unit mesh

coming from the initial (2×1)-O added row [8,9]. Guided by earlier indications from x-ray photoelectron diffraction (XPD) [6] that there may be two distinct methoxy species on the surface, with their O-C molecular axes tilted in the two orthogonal principal azimuthal directions ([001] and [1$\bar{1}$0]—see Fig. 1), structural models were proposed based on coadsorption in several distinct sites, mainly of low symmetry [7,10]. A recent DFT study [4] has concluded that one of these complex models has a relatively low total energy, yet investigation of the methanol-oxygen reaction mechanism in this same theoretical investigation favors initial adsorption of the methoxy in simple short-bridge (SB) sites on an unreconstructed surface. Our new results show that such SB sites are, indeed, occupied, and that published data from the adatom-(5×2) phase can be reconciled with occupation of only this type of site, including adatom-short-bridge (AdSB) sites (Fig. 1).

The experiments reported here were conducted in an ultrahigh vacuum surface science end-station installed on the UE56/2-PGM-2 beam line of BESSY II, which com-
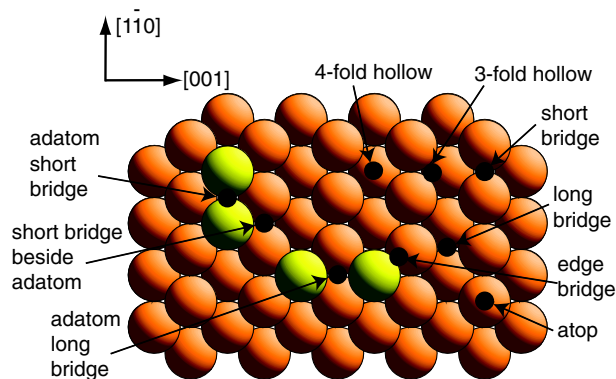

FIG. 1 (color online).   Plan view of a Cu(110) surface with four Cu adatoms showing the two principal azimuths and some local adsorption sites.

prises a 56 mm period undulator followed by a plane grating monochromator [11]. Different electron emission directions can be detected by rotating the sample about its surface normal (to change the azimuthal angle) and about a vertical axis (to change the polar angle). Sample characterization *in situ* was achieved by LEED and by soft-x-ray photoelectron spectroscopy (SXPS), executed using an Omicron EA-125HR hemispherical electrostatic analyzer, mounted at a fixed angle of 60° to the incident x radiation in the same horizontal plane as that of the polarization vector of the radiation. The Cu(110) surface was prepared by the usual combination of Ar^+ ion bombardment and annealing to produce a well-ordered and clean surface as monitored by LEED and SXPS. This surface was exposed at room temperature to 1.5 L (1 L = 1 langmuir = 10^{-6} Torr s) of oxygen to produce a nominal 0.25 monolayer (ML) coverage of atomic oxygen; LEED showed a (2×1) pattern characteristic of ordered domains of the oxygen added-row structure. The methanol reaction was effected by dosing 5.0 L of methanol on the surface at 140 K, followed by heating briefly to 240 K to remove excess methanol and create the methoxy species. Care was taken not to expose the surface at room temperature to the synchrotron radiation beam, having observed significant radiation damage occurred under these conditions. Similar caution was applied to the use of the LEED electron gun, but checks on the LEED pattern after measurements of the PhD data from these surfaces revealed no long-range ordered adsorbate structure. O $1s$ and C $1s$ SXPS confirmed that the resulting surface species was methoxy, with only very small amounts of coadsorbed atomic oxygen and formate (HCOO) produced by reaction of methoxy with atomic oxygen.

The PhD technique [3] is able to provide element-specific and chemical-state-specific local structural information for adsorbates on surfaces, through the coherent interference of the directly emitted photoelectron wave field from an adsorbate atom core level, and components of the same wave field elastically scattered by surrounding (substrate) atoms. PhD modulation spectra were obtained by recording a sequence of photoelectron energy distribution curves (EDCs) around the O $1s$ peaks at 4 eV steps in photon energy in the photoelectron kinetic energy range of approximately 60–300 eV at a range of polar emission angles in both the $[1\bar{1}0]$ and $[001]$ azimuths. A set of three such PhD spectra from the methoxy O $1s$ peak, one recorded at normal emission, the other two at 30° and 40° polar emission angle in the $[1\bar{1}0]$ azimuth (these being the two that showed the strongest modulations), was used for the structural analysis. In most other directions modulations were very weak ($< \sim 10\%$) and thus substantially less reliable. Multiple scattering simulations were performed using computer codes developed by Fritzsche [12–14], the fit between the experimental spectra and the theoretical simulations for a series of model structures being optimized with the aid of a reliability factor or R factor, based on a normalized sum of mean-square deviations [3]; the

final structural precision was defined by a variance as described elsewhere [15].

Simulations were performed for several different adsorption sites shown in Fig. 1, each for a range of different Cu-O bond lengths. The best fits ($R = 0.24$—see Fig. 2) were found for adsorption in either of the two short-bridge sites of Fig. 1, namely, the SB site on the unreconstructed surface and the AdSB site above a pair of adjacent adatoms aligned along $[1\bar{1}0]$; in both cases the optimal Cu-O bond-length, $d_{\text{Cu-O}}$, was 1.97 Å. The next lowest R factor, for any structure with a similar, physically meaningful, Cu-O bond length, was for the long-bridge site, but with a much higher value of $R \approx 0.7$. These results clearly indicate that the only acceptable single-site model is methoxy occupation of short-bridge sites. While the quality of experiment-theory fit for the short-bridge site (Fig. 2) is good for the off-normal emission data, that for the normal emission spectrum is significantly worse. In view of previous suggestions of two (or more) co-occupied adsorption sites, exploration of models based on equal occupation of two different local geometries was therefore undertaken. The one model of this type that led to a significant improvement in experiment-theory agreement ($R = 0.15$) has co-occupation of the AdSB site and the SB site on the underlying surface at slightly different Cu-O bond lengths (Fig. 1). The results for this model are discussed further below in the context of the DFT results.

In order to understand this result in the context of previous studies, both experimental and theoretical, and particularly those on the ordered (5×2) phase, new DFT calculations were performed using the CASTEP pseudopotential plane wave [16] code. The Revised Perdew-Burke-Ernzerhof edition of the Generalized Gradient Approximation (GGA-RPBE) exchange-correlation functional was used, with ultrasoft pseudopotentials. A plane
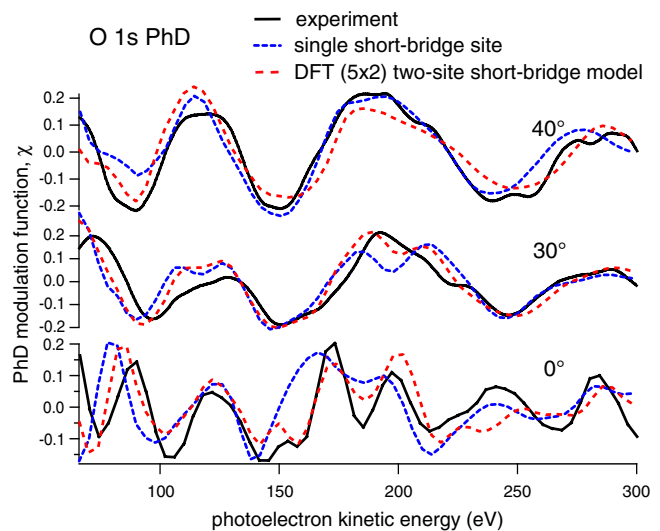

FIG. 2 (color online). Comparison of the experimental O $1s$ PhD spectra recorded at three different emission angles in the $[1\bar{1}0]$ azimuth with theoretical simulations for two different model structures.

wave cutoff energy of 380 eV was found to provide adequate convergence. Seven-layer slabs were used to represent the Cu(110) substrate with a lateral periodicity defined by the calculated bulk Cu fcc lattice constant with a supercell height of 20 Å, sufficient to leave a vacuum gap of at least 7.5 Å in all the adsorbate phases; tests using a larger 25 Å height led to energy differences of only ~1 meV. The positions of Cu atoms in the top three substrate layers, as well as any Cu adatoms, were allowed to relax, while those in the bottom two layers were fixed in bulk positions. Initial calculations were conducted using a (2×2) mesh with 5×7 Monkhorst-Pack k-point sampling (18 inequivalent points). For structures involving a single methoxy species on an unreconstructed surface in this (2×2) mesh the lowest-energy configuration corresponded to adsorption in SB sites with an O-C tilt in [001] of 36°. This conclusion, and the associated adsorbate geometry, are essentially identical to those of previous DFT calculations [4,5,17]. Also consistent with this previous work is our result that increasing the coverage to two methoxy species per (2×2) mesh [in a $c(2 \times 2)$ structure] leads to a slightly more strongly-bound methoxy (by 41 meV) in the SB sites. We also find that adsorption of one methoxy per (2×2) mesh onto the AdSB sites of a (1×2) $[1\bar{1}0]$ added-row structure leads to even stronger bonding. However, to compare adsorption energies on reconstructed and nonreconstructed surfaces we must correct for the energy cost of the reconstruction. To do this we use the bulk energy per Cu atom, allowing us to compare the results of the calculations for supercells containing different numbers of Cu atoms. For the $[1\bar{1}0]$ added-row structure we find an energy cost of 82 meV per unit mesh, reducing the energy advantage for this AdSB site to 55 meV/methoxy (Table I). By comparison, the energy cost per adatom for the same coverage of adatoms in a $c(2 \times 2)$ "checkerboard" arrangement is 350 meV per adatom, while for [001] added rows it is 315 meV per adatom. This result suggests that $[1\bar{1}0]$ pairs of nearest-neighbor adatoms are likely to be favored over more isolated adatoms in any model of the (5×2) structure that includes Cu adatoms.

Calculations were then extended to different models of an ordered (5×2) phase, with reduced (3×5) k-point sampling in the smaller associated Brillouin zone. Two main models were explored. The first was that identified in previous DFT calculations [4] as the most favorable

optimization of all the models previously proposed in the STM studies [8,10]; this contains 6 Cu adatoms and 4 methoxy species per unit mesh, with two methoxy species in long-bridge sites, one in a threefold hollow adjacent to adatoms, and one in an edge-bridge site. The adsorption energy per methoxy species on this reconstructed surface is slightly less favorable than the short-bridge site on the unreconstructed surface (Table I), as reported previously [4]. However, including the energy cost of this adatom structure makes the adsorption energy per methoxy much less favorable than the simple SB site by 415 meV. The alternative models tested, consistent with the PhD results, were based on a mixture of SB and AdSB sites. Figure 3 shows the energetically favored model, with a (5×2) unit mesh containing 4 Cu adatoms and 4 methoxy species. The average adsorption energy per methoxy species in this model is actually 50 meV more favorable than in the simple (2×2) SB site model, but accounting for the energy cost of the adatom structure renders the energy less favorable by 120 meV per methoxy. However, this model structure is strongly favored (by almost 300 meV/methoxy) over the previously-proposed model. PhD simulations based on this model, allowing small changes in methoxy-Cu bond lengths, yield a much improved fit to experiment (Fig. 2) with $R = 0.14$, with a particularly large improvement for the normal emission spectrum. This best-fit PhD structure has slightly different Cu-O bond lengths for the adatom-bridge and surface-bridge sites of 1.98 ± 0.03 Å and 1.90 ± 0.03 Å, to be compared with the DFT value of 1.98 Å for both sites.

Further support for this model is presented in Fig. 3 which shows that a simulation of the expected STM image for this structure, based on the Tersoff-Hamman approximation [18], reproduces the main features of the experimental image [9]. Also shown in Fig. 3 are the structural

TABLE I. Relative adsorption energies, ΔE, per methoxy species, referenced to the value for the SB site in a (2×2) phase at a coverage of 0.25 ML. Positive values correspond to stronger adsorption. ΔE_a values take no account of the energy cost of any surface reconstruction; ΔE_a^* values include this energy cost.

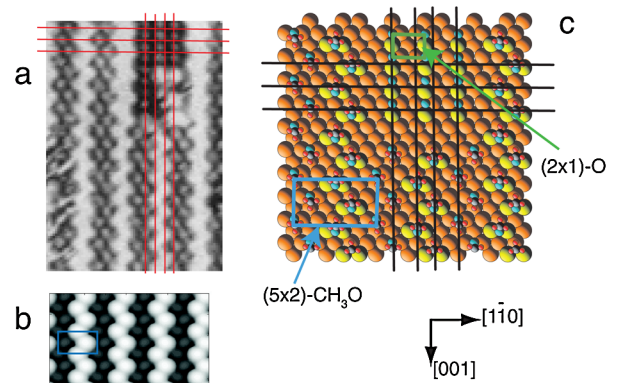| structure	ΔE_a (meV)	ΔE_a^*
AdSB on $[1\bar{1}0]$ added rows	+137	+55
(5×2) mixed site model [4]	−90	−415
(5×2) SB + AdSB (Fig. 3)	+50	−120

FIG. 3 (color online). Comparison of (a) an experimental STM image (reprinted with permission from Fig. 2c of Ref. [9]; copyright (1994) by the American Physical Society) showing coexistent (2×1)-O and (5×2)-methoxy regions with (c) a model of a similar region of the surface, and (b) a simulated STM image of the (5×2)-methoxy region. The simulated image is based on the structure shown in (c) that is the result of the DFT and PhD calculations described in the text.

model and an experimental image, showing the juxtaposition of STM protrusions and associated features in the (5×2)-methoxy and (2×1)-O regions. In the [001] direction the relative registry, shown by the superimposed lines, is in excellent agreement. In the $[1\bar{1}0]$ direction the situation is more ambiguous; our model with alternately tilted methoxy species means the imaged methyl end-groups are aligned midway between the Cu and O atoms of the Cu-O added rows of the (2×1)-O phase. The STM protrusions in the (2×1)-O region are believed to correspond to the Cu adatoms [8], but it is not really clear whether the methoxy protrusions are aligned exactly midway between these protrusions, or offset by $\frac{1}{4}$ of the spacing as required by our structural model. However, bearing in mind the image resolution and possible artefacts resulting from the imaging process, there is certainly no major inconsistency between the image and the associated model and most aspects are clearly in excellent agreement.

These results provide a structural model of the $\text{Cu}(110)(5 \times 2)$-methoxy phase that is consistent with the PhD data and the STM images, and that has a significantly lower energy than the previously-proposed model. Nevertheless, we may note that the surfaces studied by PhD failed to show a long-range ordered (5×2) phase, and that we find the total energy of this (5×2) adatom structure is less favorable than that of a simple $c(2 \times 2)$ arrangement of methoxy species on an unreconstructed surface. The reason for the existence of the adatom (5×2) structure, in the face of these energetic considerations, must be attributed to the release of Cu adatoms from the initial (2×1)-O added-row structure. In the absence of any convenient sink for these excess atoms, there is no simple alternative to accommodating them into the methoxy structure. As such, the (5×2) phase may be viewed as a kinetically-limited metastable phase. We note that in several of the published STM images [8,9,19], particularly in regions close to surface steps that provide a convenient sink for excess adatoms, a $c(2 \times 2)$ ordering is seen. Indeed in some images $(n \times 2)$ regions, with $n > 5$, are seen, the bright zig-zag rows we attribute to adatom-bridging methoxy species being separated by narrow regions of $c(2 \times 2)$ regions. Some images also show lines and disordered regions of bright protrusions that may be attributable to isolated adatom-bridging methoxy species. This local variability in ordering, coupled with the fact that the best-fit single geometry for the PhD data is a short-bridge site, also provides a rational for the good fit of the simulations for the (5×2) structure to the experimental data, despite our failure to observe (5×2) long-range ordering. The key structural ingredients of all these structures—the short-bridge sites—are the same, but the fractional occupation of adatom short-bridge sites will vary. This has, however, only a second-order effect on the PhD data. Finally, we note that the O-C axes tilt of approximately 36° in [001] for the $c(2 \times 2)$ and (5×2) DFT optimized structures is consistent with this aspect of the

earlier XPD results [6,7]. The angular peak in O $1s$ emission in the $[1\bar{1}0]$ azimuth, also reported in the XPD study, cannot be attributed to zero-order scattering in a similarly tilted O-C axis on the basis of our structure, but simple calculations indicate it may be due to first-order scattering of the single [001]-tilted species; this explanation is qualitatively similar to the alternative interpretation to two different tilted species offered in the original XPD study [7].

In conclusion, our combined PhD and DFT investigation provides a consistent picture of the local geometry of methoxy on Cu(110). The local short-bridge site is the one that has been preferred in theoretical modeling of the methanol-oxygen reaction that underpins the formaldehyde production mechanism, but previous experiments have led to a belief that other sites are occupied. We show that short-bridge sites *are*, indeed, the *only* sites that are occupied, but the release of Cu adatoms from the initial chemisorbed oxygen phase leads to the formation of a more complex ordered phase that includes methoxy species in adatom short-bridge sites. These conclusions also raise an important question: Do Cu adatoms play a hitherto unconsidered role in this (and other) surface reaction mechanism(s)?

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