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THE ADSORPTION SITE OF FORMATE (HCOO) ON COPPER SURFACES

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ROSSIS

Previous SEXAFS studies of the structure of formate on Cu(100) and Cu(110) have led to very different conclusions. In particular the Cu-O distance on Cu(100) was found to be very long (-2.3Å) and believed to be evidence for an 'anomalous' surface bond. Reanalysis of both sets of data using a multishell simulation shows that the structure is, in fact, very similar on both surfaces with a Cu-O nearest neighbour distance of about 1.97Å, similar to that in anhydrous copper formate. The previous assignment results from the failure of the Fourier filtering of the 'nearest neighbour contribution' to resolve the effects of two similar bondlengths to this shell. The problem arises because of the mismatch of the O-O distance in formate and the Cu-Cu distance on the surface which forces the oxygen atoms to adopt low symmetry adsorption sites.

1. Introduction

The great majority of structural studies of adsorbates on surfaces, both by surface EXAFS and by other methods, has been on atomic adsorbates. Of far greater general interest in relation to catalytic properties of surfaces, however, is the study of molecular adsorbate species. The recent application of SEXAFS and NEXAFS to the structure of a catalytic intermediate, formate (HCOO), on copper surfaces is therefore an important step in the study of adsorbate structures. The two independent studies performed, however, one on Cu(100)[1,2] and the other on Cu(110)[3,4] have led to markedly different conclusions. On Cu(110) the formate

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species is found to be positioned atop a top layer copper atom with a Cu-O nearest neighbour distance of approximately 1.97Å, essentially identical to that found in copper formates. The earlier study on Cu(100), however, concludes that on this surface the formate sits in a cross-bridge position with a Cu-O nearest neighbour distance of approximately 2.31Å. This very long Cu-O bondlength (-0.3Å longer than other known Cu-O nearest neighbour bondlengths) has been rationalised in terms of repulsive forces at the cross-bridged site[1,2,5] and was thought to be an example of a novel molecule-surface bond.

Here we show that by reanalysing the original data using a multishell simulation technique, rather than relying on nearest neighbour Fourier filtering, the discrepancy in conclusions for the two surfaces can be resolved. We conclude that both the adsorption site and bondlength for formate on Cu(100) are similar to that found on Cu(110). The difference in interpretation arises from the fact that the Fourier filtering approach fails to describe adequately the fact that there are two or more slightly different near neighbour atoms contributing to the "first" shell. This arises because the mismatch of the molecular O-O distance and the substrate Cu-Cu distance forces the oxygen atoms into low symmetry sites. Such problems are likely to be common in molecular adsorption systems but can be overcome by careful modelling calculations.

2. Computational Method

The main calculations presented here are based on the EXCURVE computer program[6,7] at the Science and Engineering Research Council's Daresbury Laboratory. The program allows the EXAFS to be calculated for a specified shell structure of scattering atoms using a 'curved wave' formulation. Its utility has been established in the study of a wide variety of bulk materials, and most recently for surface EXAFS. In addition to the structural parameters (bondlengths and number (or effective number) of atoms in each shell) a number of non-structural parameters are also involved; the vibrational amplitudes, inelastic scattering mean-free-path, energy zero for energy-photoelectron wavevector conversion, overall attenuation factor to account for many body effects and scattering phase shifts. In the present calculations we have attempted to fit as many of these non-structural parameters as possible by fitting to EXAFS data for a known Cu-O model compound, in this case Cu2O[8]. In particular we have fixed the scattering phase shifts and energy zero. Small changes in the energy zero, E0 of at most a few eV might be permitted to account for chemical differences[9] between the bulk oxide and surface formate but here we explore the consequences of no adjustment. The approach has therefore been to use these optimised non-structural parameters to compute the EXAFS for different possible copper surface/formate adsorption geometries, and compare these with the results of the previous experimental studies. These calculations have included not only the scattering from substrate copper atoms, but also scattering from the other oxygen atom in the surface formate. At low energies and in the appropriate polarisation geometry, this inclusion proves important. The precision of any deductions concerning O-O scattering is marred, however, by the fact that O-O scattering in the Cu2O model compound is likely to be influenced by linear chain multiple scattering so the O scattering phase shifts cannot be satisfactorily optimised.

3. Results and Discussion

Figs. 1 and 2 show comparisons of the experimental data for the Cu(110) and (100) adsorption systems, at normal and grazing incidence, compared with calculations based on the adsorption sites proposed in the original, single shell Fourier filtering, analyses. The (110) data have a rather short range due to experimental problems[3,4] but the comparisons of theory and experiment are generally satisfactory and appear to confirm the original analysis. By contrast, the comparisons of fig. 2 for the (100) surface show poor agreement. In particular, although the normal incidence (θ=90°) data are broadly in agreement, the grazing incidence data show peaks and valleys which are essentially completely
out of phase at the lower energies. Clearly this problem could only be resolved by the use of a different $E_0$ value for the two incidence directions. Reanalysis using a single shell filtering approach indicates that similar unphysical changes in $E_0$ (by $-10 - 15$eV) are needed in this method. We therefore believe the previously proposed structural model for formate on Cu(100) to be unsatisfactory and have tried a variety of sites and bondlengths to determine the best fit. This is found to involve the formate in an atop configuration but with the formate plane along a $<100>$ azimuth, with a Cu–O nearest neighbour distance of 1.99 Å. Fig. 3 shows the results of the calculation for this site. We see generally good agreement in absolute energy location and amplitudes of all features for both incidence angles using the same (previously fixed) $E_0$ value.

Inspection of the experimental data for the (100) surface (figs. 2 and 3), together with some simple considerations regarding the polarisation direction dependence of the EXAFS in different adsorption sites, allows us to understand why this site gives a generally superior fit to the data. Because of the mismatch of the O–O spacing in formate and the Cu–Cu spacing on Cu(100), adsorption of formate in any high symmetry site leaves the O atoms in low symmetry sites. There will therefore always be at least two similar Cu–O bondlengths contributing to the 'nearest neighbour' scattering shell. The experimental data show clear differences in the EXAFS recorded at the two different incidence angles which clearly indicate that these different contributions to the near neighbour shell have different relative importance as the polarisation direction changes. This, in turn, implies that the two (or more) near neighbour bonds have significantly different angles, $\beta$, relative to the surface normal. Such a situation occurs in the 'diagonal atop
site' (fig. 3) but not the cross-bridged site (fig. 2) or indeed any other site which we have investigated. For example the ratio of the effective coordination numbers of the true nearest and second nearest Cu-O distances for the cross-bridged site at 15° and 90° grazing incidence respectively are 1.13 and 0.94 while for the diagonal atop sites these ratios are 0.79 and 0.28. In such a situation the 'first shell' EXAFS clearly does not provide a measure of the 'average nearest-neighbour' Cu-O bondlength. Of course, one effect of two similar bondlengths is that amplitude modulations of the EXAFS will result. Because no modulation minimum is evident in the data Outka et al[2] deduced that the first modulation minimum lies above the experimental data range indicating the difference in these bondlengths, $\Delta R < 0.15\AA$. This is compatible with the cross-bridged site. Our model, on the other hand, has $\Delta R \approx 0.5\AA$, which corresponds to a first modulation minimum at the beginning of the experimental data range, and the second minimum at the end. Note that this appears only in the Cu backscattering. The simulations in fig. 3 show strong EXAFS at the low energy end of the data range due to O scattering; the Cu scattering contributions at these energies is, indeed, small.

In summary, therefore, the multishell simulation approach allows us to resolve the apparent discrepancy between the two copper/formate SEXAFS studies. In both cases formate is found to be atop a copper atom with a Cu-O nearest neighbour distance in the same range as for bulk copper formate. Specifically, we find best fits for the (110) surface at 1.94$\AA$ and for the (100) surface at 1.99$\AA$. The precision, however, is only in the range 0.05-0.10$\AA$ due to the difficulty of finding a unique combination of first and second neighbour distances and nonstructural parameters (especially $E_0$). We also highlight the potential difficulties of using the simple Fourier filtering method of analysis to SEXAFS studies of adsorbed molecules due to low symmetry adsorption sites and short data ranges. By contrast we find that the multishell simulation approach is more successful but may nevertheless lead to bondlength precision considerably worse than that expected for high symmetry adsorption site data.

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