The reaction of formic acid with Raney™ copper

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Abstract

The interaction of formic acid with Raney™ Cu proves to be complex. Rather than the expected generation of a monolayer of bidentate formate, we find the formation of a Cu(II) compound. This process occurs by direct reaction of copper and formic acid; in contrast, previous methods are by reaction in aqueous solution. This is a rare example of formic acid acting as an oxidant rather than, as more commonly found, a reductant. The combination of diffraction, spectroscopic and computational methods has allowed this unexpected process to be characterised.

Introduction

The industrial production of methanol from a mixture of CO, CO_2 and H_2 over a $Cu/ZnO/Al_2O_3$ catalyst is a major industrial[1] process: worldwide ~6.5×10^7 tonnes per annum are used. The mechanism of methanol synthesis has been vigorously debated, however, the consensus[2] is that CO_2 is the main carbon source for methanol. Experimental studies demonstrate formate is present as a surface species[3] and computational studies[4,5] show that the process proceeds by reaction of CO_2 with a surface hydroxyl to generate formate which is then sequentially hydrogenated to methoxy and then to methanol.

The key intermediate, formate, is readily generated on model single crystal surfaces by exposure to formic acid vapour and has been extensively studied by both spectroscopic[6,7] and structural methods.[8] These conclude that formate is present in a bidentate coordination mode with the oxygen atoms bonded to adjacent copper atoms along the rows, Fig 1. This conclusion is strongly supported by a comprehensive DFT study of formate adsorption on a variety of copper surfaces.[9]
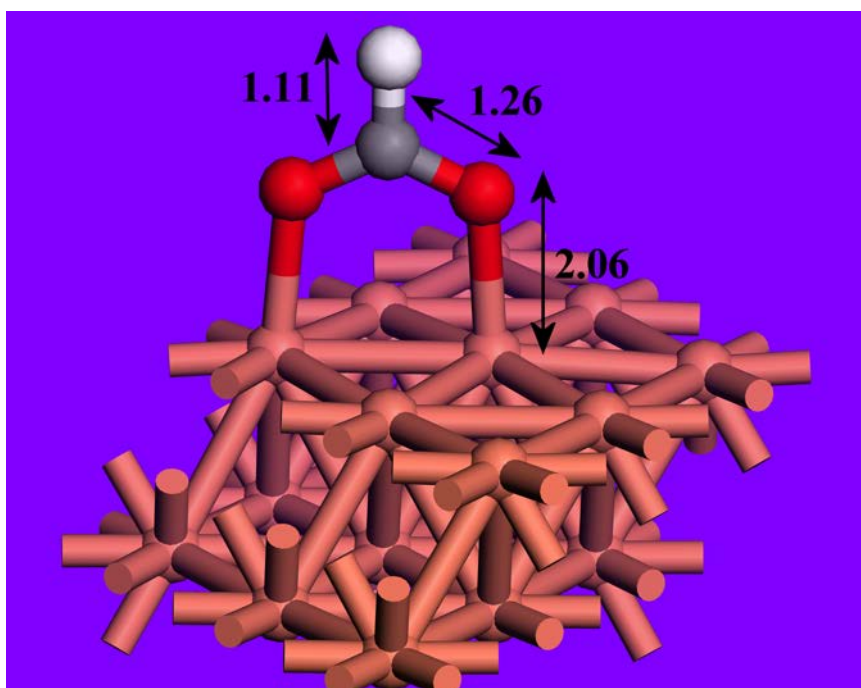
Figure 1 The structure of formate on Cu(111).[8] Bond distances in Å.

However, all of the structural characterisation has been on model single crystal surfaces. We have recently shown that it is possible to obtain structural information about adsorbates on real catalysts at ambient temperature and pressure by total scattering neutron diffraction.[10] The aim of this paper was to obtain a structural characterisation of formate bonded to a real catalyst surface by chemisorption of formic acid on Raney™ Cu. As we will show, the reaction proceeded much further than simple adsorbed formate.

Experimental

Raney™ Cu (Aldrich) was supplied as a 50% slurry in water. *Ca*. 40 g was dried on a Buchner filter under a nitrogen blanket and then transferred to an Inconel™ cell installed on a gas rig designed to handle the large samples required for neutron scattering.[11] The catalyst was then dried overnight in flowing helium (0.6 l min^{-1}) at 100 °C. The catalyst was then heated to 300 °C under $H_2(10\%)$/He (0.6 l min^{-1}) at 1 °C min^{-1}. It was maintained under the $H_2(10\%)$/He for 2.5 h, the feed was then switched to pure He and the sample allowed to cool under flowing He. This process resulted in a 48% weight loss, due to evaporation of water and reduction of the surface. The sample was then transferred to a flow-through quartz cell in an argon-filled glovebox. The total scattering neutron diffraction pattern was then measured at room temperature using the SANDALS[12] diffractometer at the ISIS Pulsed Neutron and Muon Facility[13] (Chilton, UK). The sample was then dosed *in situ* for 30 minutes with formic acid (Aldrich, >96%) by entrapment of the vapour by flowing He through a Dreschel bottle filled with formic acid. The sample was then measured again. Data reduction was carried out with the Gudrun package.[14] After the SANDALS measurements, the sample was transferred in an argon-filled glovebox to a thin-walled, indium-sealed aluminium cell and the sample measured on the broadband, high resolution neutron vibrational spectroscopy (INS) spectrometer TOSCA[15] at ISIS.

Computational studies

Periodic density functional theory calculations (periodic-DFT) calculations were carried out using a plane wave basis-set and pseudopotentials as implemented in the CASTEP code.[16,17] Initial input structures were obtained from the Cambridge Structural Database (CSD).[18] All calculations were carried out with spin polarisation. The generalised gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional was used in conjunction with optimised norm-conserving pseudopotentials with a plane-wave cut-off energy of 880 eV and a 6×6×4 Monkhorst-Pack k-point grid. Phonon modes were calculated using density-functional perturbation-theory.[19] As a prerequisite to any lattice dynamics calculation a full geometry optimization of the internal atomic co-ordinates was performed, the residual forces were |0.0025| eV Å^{-1}. The output of the phonon calculation includes the atomic displacements of the atoms in the mode, which were used for animations of the modes in Jmol[20] and to generate the INS spectra with ACLIMAX.[21] The transition energies have *not* been scaled.

Results and Discussion

Fig. 2 compares the difference radial distribution of formate on Raney™ Cu ([Cu + formic acid] – [clean Cu]) obtained experimentally and that calculated for bidentate formate on Cu(111),[9] the model used for the latter is shown in Fig. 1. It can be seen that there is almost no agreement between the two. A comparison of the experimental INS spectrum with that generated from the model shows equally poor agreement, Fig. 3. We conclude that the model of isolated formate on a copper surface is not correct.
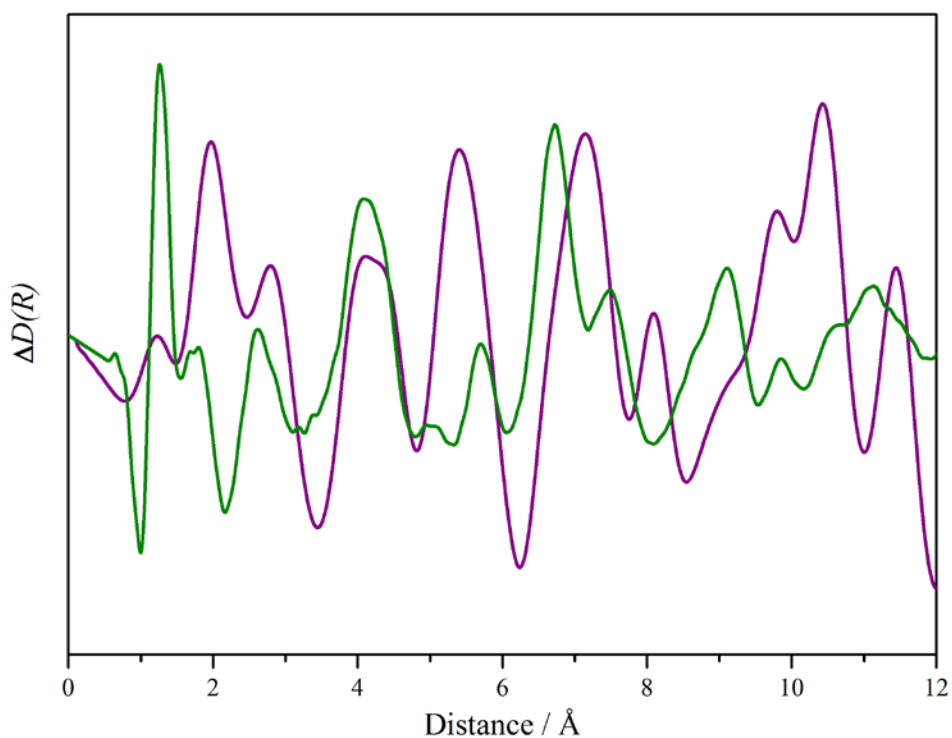
Figure 2 Comparison of the difference radial distribution of formate on Raney™ Cu (olive) and that calculated for formate on Cu(111)[9] (purple).
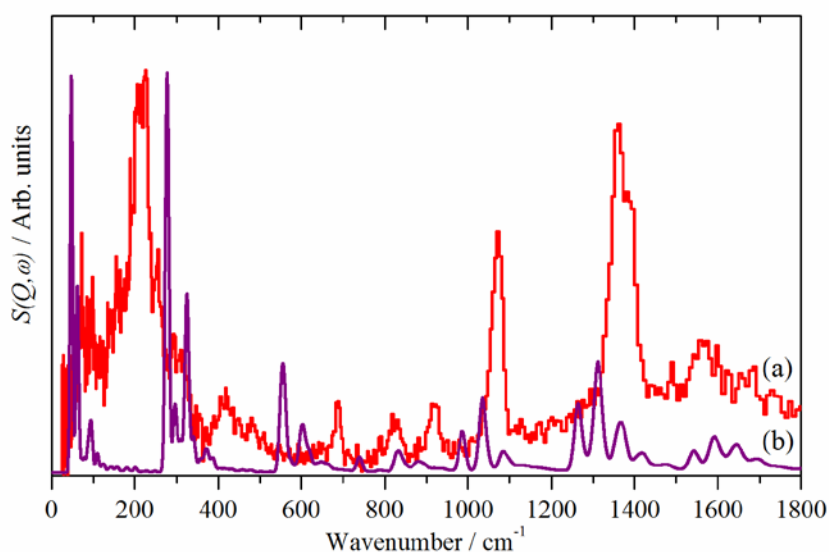

Figure 3 Comparison of the INS spectra of: (a) formate on Raney™ Cu and (b) that calculated for formate on Cu(111).[8]

However, while the overall agreement for both the structural and INS data is poor there are a few similarities. For the structural data the first two peaks in the experimental data occur at 1.02 and 1.26 Å. These are close to those expected for the C–H and C–O distances in formate, Fig. 1. The major peaks in the experimental INS data are at 220, 1070 and 1365 cm^{-1} as found for adsorbed formate[22] and model compounds containing formate.[23] Thus the data

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suggests the presence of formate, but in a more complicated state than an isolated bidentate species, which is supported by inspection of the diffraction data shown in Fig. 4. In addition to the copper peaks at ≥ 3 Å^{-1}, there are a series of peaks in the range 0.5 – 3 Å^{-1}, which suggest a structure with long range order. (The data are on the same ordinate scale, the offset is due to the incoherent scattering of hydrogen and demonstrates the presence of a hydrogenous material).
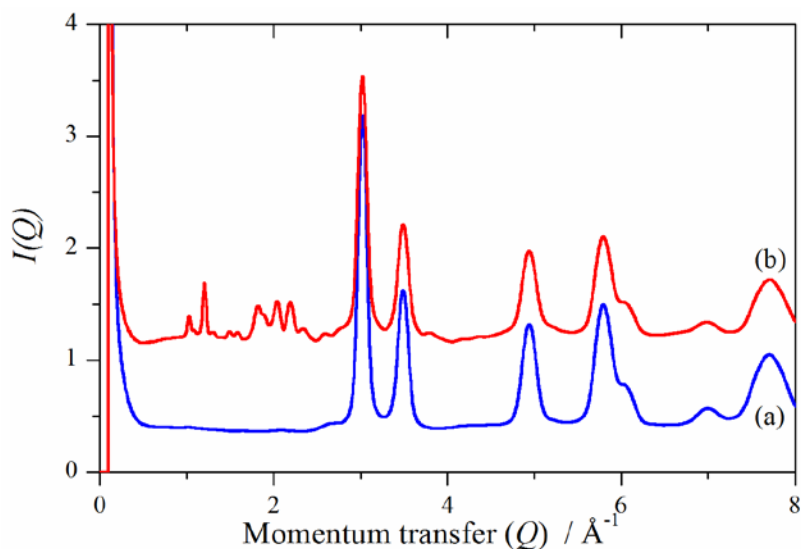

Figure 4 Comparison of the neutron diffraction patterns of: (a) clean Raney™ Cu and (b) formate on Raney™ Cu.

A search of the Cambridge Structural Database[18] for formate and copper containing structures found 20 hits comprising eight distinct structures. (The different numbers of hits and structures is because there are multiple determinations of some of them and others exhibit polymorphism). Of these, one of them (CSD refcode: DOKPOI01): catena-(*bis*(µ2-formato-*O,O'*)-bis(formic acid-*O*)-copper(II)),[25] Fig. 5, (hereafter: DOKPOI01) exhibits a diffraction pattern that is very similar to that found experimentally, Fig. 6. (Figs. 5 – 8 are for data generated after geometry optimisation of the structure because the X-ray structure determination[24] resulted in the usual under-determination of the C–H and O–H bond distances). Assuming the space group of DOKPOI01 (*P*bca), the unit cell derived from the experimental data is: $a = 7.8804$, $b = 8.4578$, $c = 12.1898$ Å at 300 K, in good agreement with the literature[25] $a = 7.8773(17)$, $b = 8.4775(2)$ and $c = 12.1423(3)$ at 150 K. The local structure seen in the radial distribution function, Fig. 7 is fairly well reproduced and the calculated INS spectrum, Fig. 8, shows reasonable agreement with the experimental data.

There is little doubt that the material generated by the reaction of formic acid and Raney™ Cu is very similar to the bulk material DOKPOI01, albeit with some disorder present. There are minor differences between the experimental data and that generated for this literature, which are probably ascribable to the unusual method of synthesis. For Raney™ Cu, the predominant facet will be (111) since this is the lowest energy surface for an fcc metal such as copper. Thus it is likely that growth of DOKPOI01 will be highly anisotropic and the resulting material is probably strongly textured, which will both affect the diffraction data and the INS spectrum. The latter has two possible mechanisms; to be observed in the INS

spectrum a mode must have a component of motion parallel to the momentum transfer vector Q, which in a partially oriented sample is not guaranteed. The second possibility is *via* the Debye-Waller factor. ACLIMAX[21] assumes an isotropic Debye-Waller factor and this condition is probably not fulfilled in the present case.
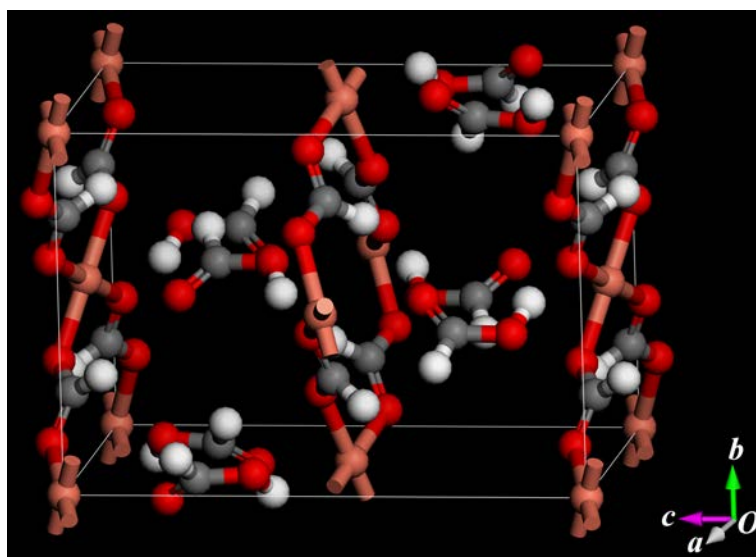

Figure 5   Structure of catena-(*bis*(μ2-formato-*O,O'*)-bis(formic acid-*O*)-copper(II))[24] (CSD refcode: DOKPOI01) after geometry optimisation.

We have investigated whether the data could be accounted for simplified versions of DOKPOI01. Thus, we considered a single layer of the structure that included only formate and also a structure that did not include the interlayer formic acid molecules. Neither of these could reproduce the diffraction data. There is also a monoclinic polymorph of DOKPOI01 (CSD refcode DOKPOI[25]), which is made by a solution reaction of a Cu(II) salt. The calculated diffraction and INS spectra did not agree with the experimental results.

The creation of DOKPOI01 at the surface of Raney™ Cu is surprising. The literature[24] synthesis is by reaction of copper(II) formate tetrahydrate with formic acid at 80 °C. After a week to crystallise, the resulting crystals are reported to be very unstable when taken from the mother liquor. In contrast, here, the reaction has occurred at room temperature in less than hour, as a heterogeneous reaction. This is a rare example of formic acid acting as an oxidant rather than, as more commonly found, as a reductant. Formally, it is the proton that is released as formate is formed that is the oxidant. Hydrogen is not stable on copper at room temperature, so desorbs and is not seen in any of the data.

$$4n \, HCOOH + nCu \rightarrow [Cu(HCOO)(HCOOH)]_n + nH_2 \qquad (1)$$
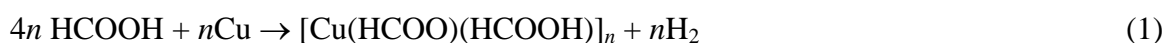
The direct reaction of copper with formic acid in humid atmospheres has been studied on several occasions[26-29] in order to help understand corrosion mechanisms. A mixture of products is typically found: Cu_2O, $Cu(OH)_2.H_2O$ and $Cu(HCO_2)_2.4H_2O$. A study looking at sublimation of copper[30] from a powdered copper catalyst in the presence of formic acid found that it behaved in the same way as copper (II) formate, suggesting that this was an intermediate, although it was not detected directly. However, the reaction was carried out at

Summary and Conclusions

The interaction of formic acid with Raney™ Cu has proven more complex than expected. Rather than formation of a monolayer of bidentate formate, we find the formation of a compound. This occurs by direct reaction of copper and formic acid, in contrast to the previously reported solution reaction. The combination of diffraction, spectroscopic and computational methods has allowed an unexpected process to be characterised.
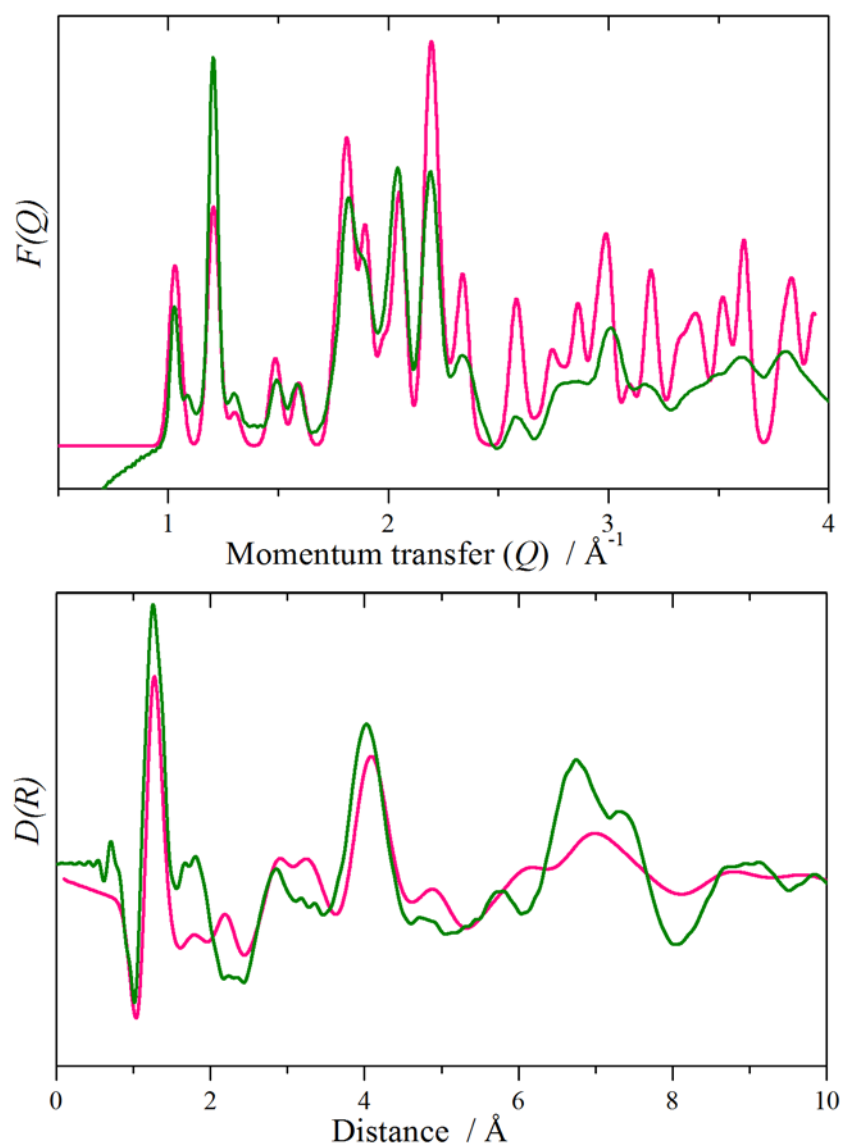

Figure 6 Comparison of the difference neutron diffraction pattern of formate on Raney™ Cu (olive) and that calculated for DOKPOI01 after geometry optimisation (pink) for reciprocal space (top) and real space (bottom).
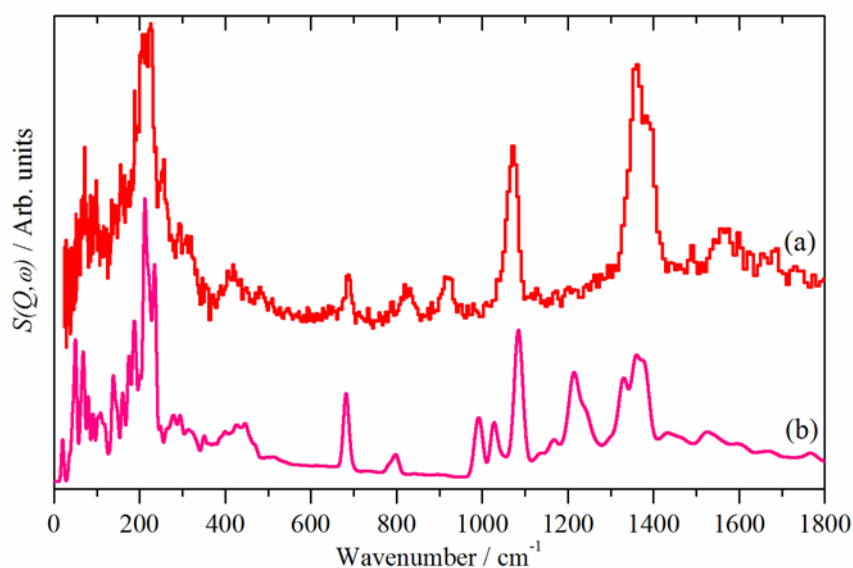
Figure 7 Comparison of the INS spectra of: (a) formate on Raney™ Cu and (b) that calculated for DOKPOI01.[24]

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