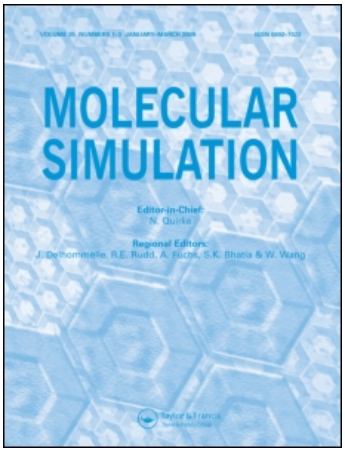

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Sulphur poisoning of water-gas shift catalysts: site blocking and electronic structure modification

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Sulphur poisoning of water-gas shift catalysts: site blocking and electronic structure modification

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Density-functional theory calculations were used to study sulphur poisoning of low Miller index surfaces of Cu(111), (100) and (110). The adsorption properties of S on the studied facets were investigated in different adsorption sites and at coverages between 0.25 and 1 ML. The comparison of adsorption energies among different facets showed that S adsorbs most strongly to the most open surface (110) and most weakly to the most close-packed surface (111). We found that the adsorption energy of S generally gets weaker with increasing coverage, and we related the coverage dependence to an adsorbate-induced surface electronic structure modification which broadens the surface *d*-band and which causes a consequent reduction in the average energy of the *d*-band centre due to conservation of *d*-band filling. The combination of site blocking and surface electronic structure modification leads to a reduction in the surface reactivity of the catalyst at higher coverages of S.

Keywords: density-functional theory calculations; adsorption; electronic structure modification; sulphur; copper

1. Introduction

Methanol is synthesised from a mixture of CO, CO_2 and H_2 over Cu/ZnO catalysts with CO_2 hydrogenation being the major path. The water-gas shift (WGS) reaction and its reverse (RWGS) reaction are an integral part of this synthesis [1]. WGS is primarily used to produce high purity hydrogen and RWGS is essential for upgrading CO_2 to CO for use in syngas as a first step in the utilisation of CO_2 [2]. The methanol synthesis reactions and the WGS reactions take place simultaneously. Because the WGS reaction is moderately exothermic, low temperatures favour a high equilibrium conversion of CO to CO_2, and Cu is the best pure metal for the low-temperature WGS reactions [2].

The interest in fundamental studies of S interaction with Cu originates from the fact that in many CO_2 feedstocks, there are sulphur (S) impurities. These S atoms can adsorb on Cu surfaces and block the active sites of the catalyst for the desired reaction and can result in catalyst deactivation [3]. Even the presence of a small amount of S in the feed streams can cause the deactivation of the catalyst due to the formation of a strong covalent bond between the adsorbate and the surface metal atoms [4–6]. Since S acts as a common poison for most of the metal catalysts and their alloys [3,7], the adsorption of S on surfaces has been widely studied both theoretically [3] and experimentally [8]. These investigations have received great attention since it is hoped that these studies will provide useful information to develop S-tolerant catalysts. The reactivity of the catalyst is also reported to be affected by a reduction in the density of *d*-states near the Fermi level of the surface atoms, due to the fact that S is more electronegative than the metal surfaces; thus, it withdraws charge from the surface [9]. Alfonso et al. [3] studied the adsorption energy of S on Pd and Pd alloy surfaces and determined that the adsorption energy of S is correlated with the *d*-band centre of the surface atoms on which it is adsorbed. By contrast, no correlation of H_2S and S adsorption energies with the *d*-band centre was reported on PdMPd (M = Au, Ag, Co, Cu, Ir, Ni, Pt, Rh) sandwich structures [10]. The presence of ligand effects combined with strain [11] for bimetallic surfaces results in a more complicated system that cannot be simply characterised by a single parameter model such as the *d*-band model.

Some experimental studies [22–24] report the formation of reconstructed Cu surface structures when the Cu surfaces are exposed to S poisoning. The analysis of these reconstructed structures is out of the scope of this study. Here, the aim is to explain the adsorption properties of S on Cu surfaces as a function of coverage and to analyse the interactions in terms of electronic structure modification of the catalyst surface.

Real catalysts are often composed of supported nanoparticles that expose a variety of crystal facets to the reactive environment, each of which may interact differently with the environment and lead to different

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stabilising effects on the poisoned surfaces, with subsequent changes in the particle morphologies. The low Miller index surfaces, (111), (100) and (110) tend to be the facets with the largest surface areas on catalyst particles [12]. In this work, we utilise the first-principles density-functional theory (DFT) calculations to investigate S adsorption on Cu(111), (100) and (110) facets for coverages between 0.25 and 1.00 ML on a range of different adsorption sites and the adsorbate-induced changes in the surface electronic structure. In this paper, we first discuss the computational parameters used in the DFT calculations and the details of the computational methods. We then present the results of these calculations showing the coverage-dependent adsorption energies and the densities of the states for several cases. We correlate the coverage of S on the surface and the adsorbate-induced modifications of the surface *d*-band utilising the Hammer–Nørskov adsorption model and rectangular *d*-band models.

2. Method and calculation details

Under WGS reaction conditions, there are substantial pressures of H_2, H_2O, CO_2 and CO with trace levels of H_2S that could result in adsorption of H, O, CO_2, CO or S on the Cu surfaces. In our previous work, we utilised a first-principles atomistic thermodynamics approach to evaluate the stability of different adsorbate structures on Cu surfaces in contact with a reactive environment through the surface free energy of the structures. We determined that under experimental reactive environment conditions, the surface energies of each facet change differently with the sulphur chemical potential [13]. In this current study, we focus on S adsorption on Cu(111), (100) and (110) facets considering the adsorbate-induced changes in the surface electronic structure of the catalyst.

2.1 Adsorption energies

In general, the adsorption energy of the adsorbate species is defined as

$$\Delta H_{\text{ads}} = E_{\text{slab}+i} - E_{\text{slab}} - \sum N_{i^*} E_i, \qquad (1)$$

where $E_{\text{slab}+i}$ is the energy of the Cu slab with possible adsorbates and E_{slab} is the energy of the clean slab. N_{i^*} is the number of possible adsorbates and E_i is the energy of the absorbate.

Considering the following equilibrium reaction of H_2S decomposition for S adsorption,

$$H_2S + {}^* \rightleftharpoons S^* + H_2$$

we express the S energy in terms of the energies of gas-phase H_2S and H_2. To make a comparison among S adsorption energies at different coverages, we focus on the adsorption energy per S atom, then Equation (1) becomes,

$$\Delta H_{\text{ads}} = \frac{E_{\text{slab+S}} - E_{\text{slab}} - N_{S^*}\left(E_{H_2S} - E_{H_2}\right)}{N_{S^*}}. \qquad (2)$$

2.2 Calculations and convergence

S adsorption energies were calculated using first-principles DFT utilising the DACAPO code [14]. Ionic cores were described by Vanderbilt ultrasoft pseudopotentials [15–17], and the one electron valence eigenstates were expanded in a plane wave basis set with a cut-off energy of 340 eV. The exchange correlation functional used was the generalised gradient approximation (GGA) due to Perdew–Wang (PW91) [18]. S adsorption energies were calculated at coverages of 0.25, 0.50, 0.75 and 1.00 ML in fcc, hcp/fourfold hollow, bridge and atop sites on the Cu(111), (100) and (110) surfaces for a total of 43 different structures.

The lattice constant of bulk Cu was calculated as 3.64 Å using the Murnaghan equation of state [19], which is in good agreement with the established experimental value of 3.61 Å.

The Cu(111) surface was modelled using a five-layer slab with S coverage on one side, while the Cu(100) and Cu(110) surfaces were modelled with six- and eight-layer slabs, respectively, preserving the thickness of each slab to be approximately 9 Å. A dipole correction scheme was tested and found to be unnecessary in these calculations. The vacuum region between the repeated slabs was 10 Å. Brillouin-zone integrations were performed using a $12 \times 12 \times 1$ Monkhorst-Pack grid for the 1×1 surface unit cell and $6 \times 6 \times 1$ for the 2×2 surface cell. For all calculations, the adsorbed atoms and the most upper two layers were relaxed until the forces were less than 0.05 eV/Å, whereas the other layers were frozen at the bulk Cu coordinates. These parameters were chosen to ensure that the calculated energies were well converged with an estimated numerical uncertainty in adsorption energies of less than 0.05 eV/S. Energies of the gas-phase H_2S and H_2 molecules were calculated in a $10 \times 10 \times 10$ Å^3 box with the same calculation parameters.

The interactions between adsorbates and transition metal surfaces involve the *d*-band [20,21]. The *d*-band density of states was determined by projection of the Kohn–Sham orbitals onto atom-centred spherical harmonic orbitals with the cut-off radius at infinity, as implemented in DACAPO. The *d*-band centre was calculated as the first moment of the projected *d*-band density of states on the surface atoms referred to the Fermi level, and the mean-squared *d*-band width was calculated as the second moment.

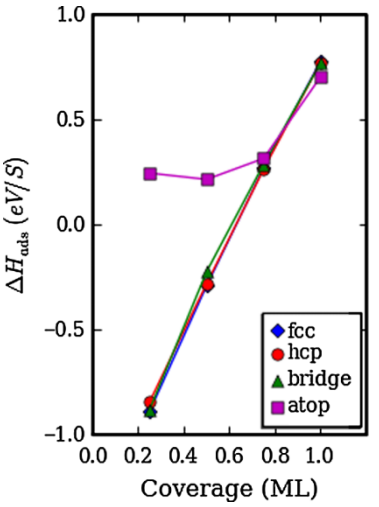

Figure 1. Sulphur adsorption energies on Cu(111) as a function of coverage for different adsorption sites.

3. Results and discussion

3.1 *Sulphur adsorption on Cu(111)*

For Cu(111), chemisorbed structures of S on threefold fcc and hcp hollow sites, on bridge and on atop sites were investigated at coverages of 0.25, 0.50, 0.75 and 1.00 ML. As a general trend, it is observed that S adsorption energy increases (gets weaker) as coverage increases, yielding weakening of the sulphur-metal bond at high coverages (Figure 1). The difference in S adsorption energies among fcc or hcp site is small; slightly more negative values were observed on fcc sites. Alfonso et al. [3] studied the adsorption of S on different metals like Pd (111), Cu(111) and Ag (111) at 0.25 ML coverage, and noted that fcc and hcp sites were the most favourable adsorption sites with the fcc site showing the strongest binding energy, with the hcp site being 0.06–0.08 eV less stable. They concluded that there is a preference for the fcc site over all other adsorption sites, which is consistent with our results. Our results are also consistent with other literature reports [7]. It is seen from Figure 1 that at coverages of up to 0.50 ML, adsorption on threefold hollow sites is energetically preferred over other sites. At coverage beyond 0.50 ML, we found that S adsorption on Cu(111) becomes thermodynamically unfavourable due to positive (endothermic) values of S adsorption energies. Structures with S adsorbed on the atop site are not thermodynamically favourable even at the lowest S coverage of 0.25 ML.

We now present the effect of the adsorption of S on the surface electronic structure of the metal catalyst. The metal *d*-states have a significant role in explaining the interactions of adsorbates with the surface metal atoms. The number of *d*-electrons per surface Cu atom was calculated for each coverage by integrating the projected surface *d*-band density of states (only for the surface Cu atoms) up to the Fermi level. In each case, we calculated the filling to be ~9.9 *d*-electrons/Cu atom, indicating that the *d*-band filling is practically conserved at all coverages. We also observed that the surface *d*-band generally broadens with increasing coverage. The fact that the *d*-band filling is apparently constant, yet the *d*-bands change shape means the *d*-band width and centre are not independent. If the band widens it has to move down in energy to conserve states and conversely if the band becomes narrower, it has to move up in energy in order to conserve the *d*-band filling. By assuming a simple rectangular form of the *d*-band, with the constraint that total number of states and the *d*-band filling are conserved, it can be shown [20] that the square root of the *d*-band width ($\sqrt{W}$, the square root of the second moment of the *d*-band) is linearly proportional to the first moment, the *d*-band centre (ε_d),

$$\sqrt{W} = \left(\frac{1}{0.5 - f_d}\varepsilon_d\right)\sqrt{\frac{1 - 3f_d + 3f_d^2}{3}}, \qquad (3)$$

where f_d is the fractional filling of the *d*-band. For $f_d = 0.99$, as observed in our calculations, Equation (3) predicts that $\sqrt{W}$ varies linearly with ε_d with a slope of -1.16. The actual correlation of the *d*-band widths and centres for all the coverages of S on all the Cu surfaces in this work is shown in Figure 2, where $\sqrt{W}$ is seen to vary linearly with a slope of -1.09. The linearity of the correlation and the sign of the slope are correct, and the actual magnitude of the slope differs only slightly from the predicted value. The actual surface *d*-bands are shown in Figure 3, where it can be seen they are not actually rectangular, even though their behaviour can be reasonably approximated by a rectangular band model.

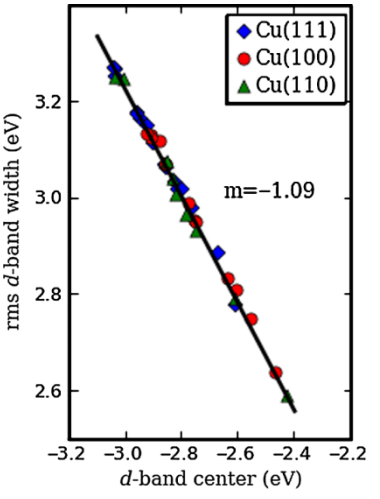

Figure 2. Correlation between the first and second moments of density of states for each coverage examined on the Cu(111), (110) and (100) surfaces.

For most of the highly coordinated adsorption sites, we observed an adsorbate-induced surface electronic structure modification that broadened the surface *d*-band, while maintaining the same number of filled *d*-states (Figure 3). The surface *d*-band broadening with increasing coverage corresponds to a decrease in the *d*-band centre and to weakening of the S adsorption energies. Considering the adsorption model of Hammer and Nørskov [21], we found out that there is almost a linear trend in adsorption energies versus the *d*-band centre for the fcc, hcp and bridge sites (Figure 4); the adsorption energy increases (gets weaker) as the *d*-band centre becomes more negative. When the surface *d*-band centre shifts to sufficiently negative values, then S adsorption becomes thermodynamically unfavourable. The lack of a *d*-band correlation for the atop results can be attributed to the fact that the surface *d*-band is not sufficiently modified by adsorption at the atop site, because there is much less overlap of the S orbitals with the Cu surface *d*-band than there is at the other adsorption sites.

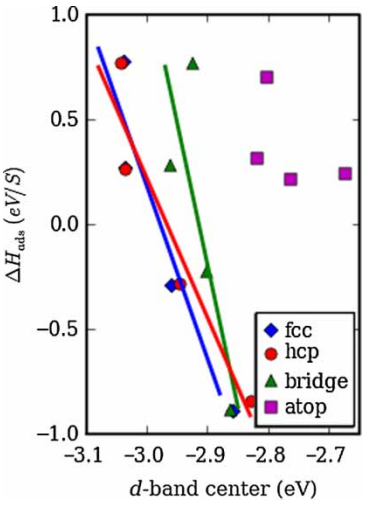

Figure 4. Trends in S adsorption energies on different adsorption sites with the *d*-band centre for Cu(111). Correlations are observed for fcc, hcp and bridge sites but not for the atop sites.

3.2 Sulphur adsorption on Cu(100) and on Cu(110)

The examined S-adsorbed structures on Cu(100) and (110) differ from those on the (111) facet; the most highly coordinated sites are fourfold hollow sites rather than threefold fcc and hcp sites. Similar to the (111) surface, increases (weakening) in S adsorption energies were observed with increases in coverage for the Cu(100) (Figure 5) and Cu(110) surfaces (Figure 7). S adsorption is thermodynamically favourable on fourfold sites up to 1.00 ML and on bridge sites only at 0.25 ML on the Cu(100) surface. For the Cu(110) surface, the bridge and atop sites were found to be unstable for the low coverages, since the adsorbed S would tend to relax to a neighbouring hollow site configuration during energy minimisation. Thus, for the bridge and atop adsorption sites only the adsorption energies for high coverages are reported. In general, the fourfold hollow site was found to be the most stable adsorption site for the whole coverage range considered in this study for both of the (110) and (100) Cu surfaces, and it was observed that S adsorption energies get weaker with coverage for all adsorption sites.

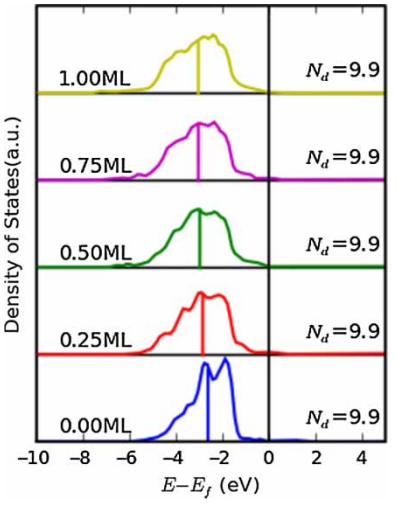

Figure 3. Calculated surface *d*-band DOS for S adsorbed at fcc on Cu(111) at different coverages. The number of *d*-electrons in the band, N_d, is shown for each coverage.

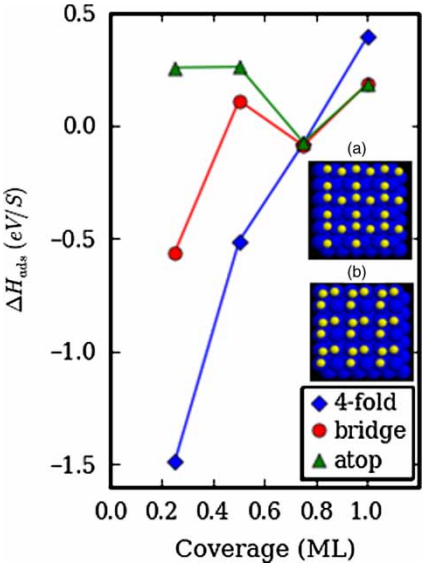

Figure 5. Sulphur adsorption energies on Cu(100) as a function of coverage for different adsorption sites. The insets show dimer and trimer formations at 0.75 ML for (a) bridge and (b) atop site.

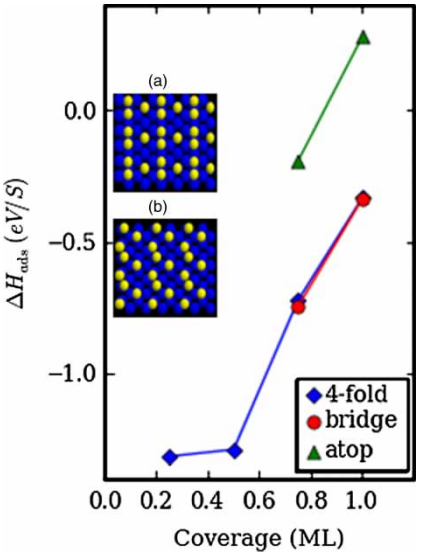

Figure 6. Sulphur adsorption energies on Cu(110) as a function of coverage for different adsorption sites. The insets show dimer and trimer formations at 0.75 ML for (a) bridge and (b) atop site.

At 0.75 ML, we observed dimer and trimer formations on the bridge and atop sites, which modify the adsorption trend by stabilising the adsorbates (Figures 5 and 6). The observed coverage dependence can also be partially explained by adsorbate-induced changes to the surface electronic structure in the same way as the (111) surface. A notable deviation from the trend is observed, where we have dimer and trimer formations of adsorbed S atoms from the bridge and atop sites at 0.75 ML.

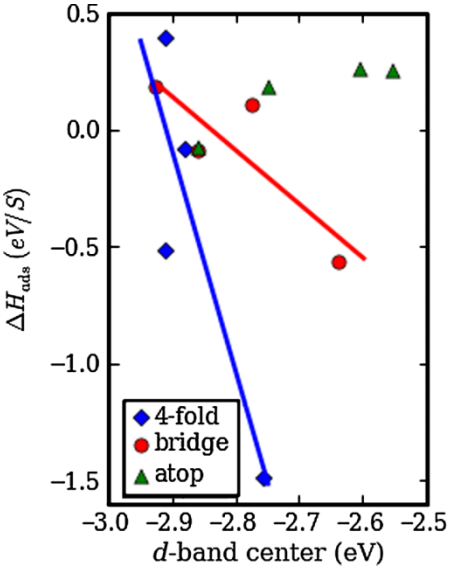

Figure 7. Trends in S adsorption energies on different adsorption sites with the *d*-band centre for Cu(100). Correlations are observed for fourfold and bridge sites but not for the atop sites.

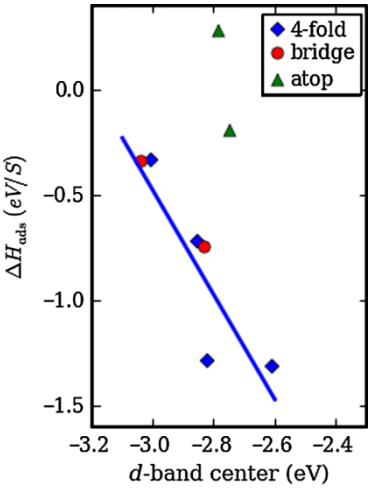

Figure 8. Trends in S adsorption energies on different adsorption sites with the *d*-band centre for Cu(110). Correlation is observed for the fourfold sites, but not for the lower coordinated sites.

There is almost a linear trend in adsorption energies versus *d*-band centre on the Cu(100) surface for the hollow and bridge sites with the exception of the configuration obtained for bridge sites at 0.75 ML in which there was the dimer formation (Figure 7). It is not surprising that the correlations break down for the dimer and trimer geometries; *d*-band centre correlations are only anticipated for geometrically similar structures. The formation of dimer and trimer structures indicates there are other bonding factors not considered in the simple *d*-band correlation. Similar to the results for (111) facet, there is no correlation between adsorption energies of S on atop site with the *d*-band centre for (100) surface.

We also observed a general broadening of the *d*-band width with increasing coverage in highly coordinated sites leading to a shift in the *d*-band centre to more negative values and corresponding weakening of the adsorption energies on the (110) surface. The correlations between the adsorption energy on the (110) surface and the surface *d*-band centre are shown in Figure 8. The constant adsorption energy of S at low coverages of 0.25 and 0.50 ML at fourfold hollow site cannot be explained with the change in electronic structure. Although we observed a slight broadening of the *d*-band of first layer Cu atoms and a shift in *d*-band centre, there is no weakening of the S and Cu bond as S coverage increases from 0.25 to 0.5 ML. This may be due to the distance between the sites on this surface, which limits the interactions between them.

4. Conclusions

In this study, we performed DFT calculations to investigate the interactions between S and Cu. The preferred adsorption sites, adsorption structures and

energies were determined, and we found out that S forms a strong bond with Cu surface and adsorbs preferentially on the most highly coordinated sites for the three surfaces of Cu examined in this work. This shows that Cu is susceptible to S poisoning, which is in good agreement with an experimental study of Campbell and Koel [8], who reported that Cu-based catalysts poison very easily even at ppm levels of H_2S. The strength of adsorption energy was obtained in the order of (110) > (100) > (111). It was also determined that the adsorption energy of S generally gets weaker with increasing coverage. This coverage dependence was related to an adsorbate-induced surface electronic structure modification that broadens the surface *d*-band, leading to a shift in the *d*-band centre to more negative values and a corresponding weakening of the adsorbate bonds. Thus, the catalyst poisoning by sulphur is not simply site blocking but also an intrinsic deactivation of the metal surface.

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