Electronic Structure of a "Poisoned" Transition-Metal Surface

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The authors report self-consistent linearized-augmented-plane-wave calculations of the electronic structure perburbations induced by a catalytic "poison," S, on a Rh(001) surface, focusing particularly on their distance dependence. The S-induced charge density vanishes beyond the immediately adjacent Rh atoms. However, the Fermi-level density of states, which is not screened, and which governs the ability of the surface to respond to the presence of other species, is substantially reduced by the S even at nonadjacent sites.

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Studies of adsorption and kinetics on transition-metal surfaces show that the addition of less than 0.1 monolayer of a "poison" species such as S, can cause drastic reductions in reactant sticking probabilities, coverages, and reactivities.[1] While in some cases additive effects may be the result of blocking a small number of "defect sites" essential for surface chemistry, in the methanation of CO the evidence suggests that poisons act at low coverage by perturbing surface electronic structure over distances larger than that to their nearest neighbors. We report here results of self-consistent surface linearized-augmented-plane-wave (SLAPW) calculations[2] for relatively low coverages ($\frac{1}{4}$ and $\frac{1}{3}$ monolayer) of S on thin Rh(001) films. We identify features of the electronic structure of S-covered surfaces that might bear on their decreased chemical activity, and we distinguish effects of S atoms that can manifest themselves at low coverages from those that cannot.

It is commonly held[1,3,4] that poisoning by an electronegative atom such as S is the result of its removing charge from the surface that would otherwise facilitate a rate-limiting reaction step. For example, in CO dissociation, the C-O bond is supposedly weakened by the transfer of a *d* electron from the surface into the antibonding $2\pi^*$ orbital. One finds that coadsorption of low coverages of K, an electropositive atom, causes a lowering of the C-O stretch vibration frequency,[4] presumably because of increased $2\pi^*$ occupancy. Thus for an electronegative additive like S, one anticipates less charge transfer into the $2\pi^*$ orbital, a stronger CO bond, less CO dissociation, and the inhibition of reactions that depend on its occurrence.

However, this "charge-transfer mechanism" does not explain how S atoms can inhibit chemistry beyond a screening length. Since our results show (see Fig. 1) that the charge associated with a S atom is screened to zero at distances larger than that to the neighboring metal atoms, charge transfer cannot be the source of the poisoning effect of S at low coverages. Indeed, generally, any "long-range" effect of electronegative surface additives must stem from an

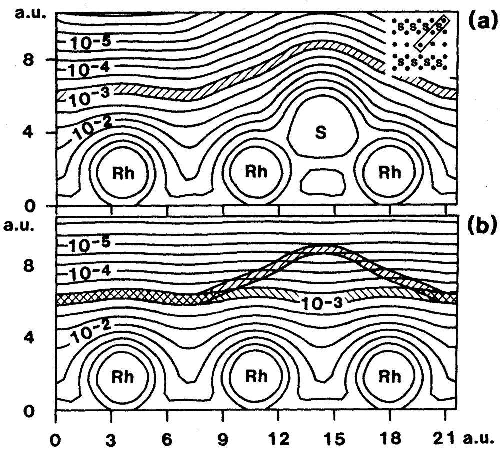

FIG. 1. Valence charge densities (in atomic units) for two-layer Rh(001) films (a) with and (b) without a S(3× 1) adlayer. The density changes by the factor 2.154 (= $10^{1/3}$) from one contour to the next. To facilitate comparison, we have hatched in the region between contours of charge density ~ 10^{-3} a.u., about 4 a.u. above the Rh nuclei, and we have transcribed the hatched region from the S/Rh plot onto that for clean Rh. Note that the effect of the S atom is negligible near the next-neighbor Rh. The geometry of the plot is indicated in the inset.

electronic perturbation that is *not screened*. In the present work, we have focused on the local density of states (LDOS) at the Fermi level. This quantity, which is essentially an energy-resolved charge density, has obvious significance for chemistry. It governs the degree to which energy must be supplied to remove electrons from occupied states and transfer them into unoccupied ones. The lower the Fermi-energy LDOS, the less well the surface can respond to the presence of reactants. At the same time, a large E_f LDOS indicates that considerable energy can be gained by a reaction which moves the states that lie at E_f to lower energies. In addition to its bearing on chemical activity, the E_f LDOS is a quantity which is unscreened. Screening is the consequence of the electron gas' tendency to seek total local charge neutrality. The charge corresponding to any narrow energy window is not screened. Thus the E_f LDOS is a quantity whose perburbation by S atoms can be expected to extend considerably farther than a screening length.

The SLAPW method[2] that we use self-consistently evaluates the electronic structure of a thin film with two-dimensional lattice periodicity. Obviously, to study a laterally "long-ranged" perturbation of the surface, we must choose an overlayer geometry with a large enough surface unit cell that there exist sites with no S neighbor. For good convergence, the LAPW basis must typically contain ~40 augmented plane waves per atom in the unit cell. We can handle up to about 400 plane waves. Thus to study a surface unit cell with long lateral periodicity, we must confine our attention to rather thin films.

Since we are particularly interested in CO as a reactant, and CO adsorbs atop metal atoms,[5] we first perform calculations for the smallest supercell, for S/Rh(001), which has an atop site with no S neighbors, a S(3×1) overlayer, whose geometry is indicated in the inset of Fig. 1. In this case, we can accommodate a S layer on either side of the film, giving us an additional symmetry, which speeds computations. To be precise about the locations of the S atoms on the two surfaces, if on the upper surface, the S atoms were located at $(n, 3m)$, then on the lower surface, they were at $(n-\frac{1}{2}, 3m-\frac{1}{2})$. There are accordingly three inequivalent types of Rh atom on either surface: those with no S neighbor; those with a S neighbor and a S atom directly below, on the other side of the film; and those with a S neighbor and no S atom directly below. In all our calculations, we have chosen the S-Rh bond length to equal 2.30 Å, the low-energy electron-diffraction value for S-$c(2\times2)$/Rh(001).[6]

As an initial check on the charge-transfer picture, we compare calculated work functions, φ, for the clean and S(3×1)-covered, two-layer Rh(001) films. Charge transfer to the S atoms would imply an increased φ for the covered film, as is the case for S/Ni(001). The electronegativities of S and Ni are, respectively, 2.5 and 1.8,[7] and measured φ increases for $p(2\times2)$ and $c(2\times2)$ overlayers are 0.24 and 0.38 eV.[8] For S/Rh, since Rh has an electronegativity of 2.2, the charge transfer to an S overlayer and, correspondingly, the work-function increase should be smaller. What we find, however, is that φ actually *decreases* from 5.6 to 5.4 eV with the addition of the S(3×1) adlayers. This result invites several possible conclusions, and has led us to perform calculations for several additional overlayer geometries, to check our results. The first question posed by the φ decrease is whether it is an artifact of an overlayer supercell wherein the S atoms lie too close to one another. In the 3×1 cell, the inter-S distance equals the nearest-neighbor Rh spacing, 2.69 Å. Although this is larger than the *atomic* diameter of S, it is smaller than the *ionic* diameter. It seems possible, therefore, that the S atoms do not take up charge from the surface because the overlap of S ionic charges makes it energetically unfavorable to do so. We have tested this possibility by redoing our calculation for a $c(2\times2)$ overlayer on the Rh two-layer film (S-S distance = 3.90 Å). The result is again that $\varphi = 5.4$ eV. The next question is whether the φ decrease is a quantum size effect,[9] i.e., a result of comparing two very thin films of different thickness. To test this hypothesis, we have calculated φ for a $c(2\times2)$ overlayer on a three-layer Rh(001) film. Again the result is 5.4 eV.

Finally we have checked whether the φ decrease is an effect of choosing a coverage as high as $\frac{1}{3}$ monolayer. Computer-storage limitations prevent us from looking at very low coverages, but by eliminating the S adlayer on one of the film surfaces, we can study a coverage as low as $\frac{1}{4}$ monolayer. The particular geometry we use is again not a physically realized one [i.e., it is not the $p(2\times2)$], but rather is one which has atop as well as hollow sites with no S neighbors (specifically, it is the $\sqrt{2}\times\sqrt{2}$-$R45°$ hollow-site geometry).[10] In this case we find $\varphi = 5.5$ eV on the S-covered side of the film, and 5.6 eV on the uncovered side. These results show convincingly that the interaction of S with Rh does not involve substantial charge transfer. Rather, it is essentially covalent, and the unexpected sign of the predicted change in φ is a rehybridization effect.[11]

One final point must be noted before leaving the subject of work functions: The value of φ that we obtain for the clean Rh surface is rather high compared to experimental values of 4.6 eV,[12] and 5.1 eV.[13] That our theoretical value of 5.6 eV is not an artifact of our use of a two-layer Rh film is shown by our earlier calculation[14] for seven-layer Rh(001). In that case we found $\varphi = 5.5$ eV. At this point the source of the discrepancy between theory and experiment is not clear. But for various metal surfaces the SLAPW method gives work functions to within 0.2 eV.[2,15]

Even though no net charge transfer from Rh to S atoms is indicated by our calculated work functions, it still might be thought that S-induced charge redistribution is responsible for poisoning by S atoms. Figure 1, which shows contours of constant charge density for a two-layer Rh film with and without a S(3× 1) overlayer, indicates otherwise. The effect of the S atoms on the charge density is totally screened out beyond the Rh nearest neighbors. If the S atoms act via the charge density, their effect can only be "steric," not long-ranged. We have obtained similar results for other overlayers: the $\frac{1}{4}$-monolayer S adlayer mentioned above, and a coadsorption case, S,C(3× 1)/Rh, in which each row of S atoms is accompanied by a row of C atoms in neighboring hollow sites.

Matters are quite different when we plot contours of constant Fermi-energy LDOS. We calculate this quantity approximately as the charge density associated with all states that lie within ±0.2 eV of E_f (divided by 0.4 eV). Figure 2 shows the results for the S(3× 1)-covered versus clean Rh films. Here the S effect is large and extends well beyond the nearest-neighbor Rh atoms. At a distance of about 4 a.u. above the second-neighbor Rh atoms, the E_f LDOS is reduced to about $\frac{1}{2}$ its clean-Rh value by the presence of the S atoms. This decrease reflects the formation of S-Rh bonding and antibonding states, and its long range is possible because a LDOS is not a screened quantity. For the $\frac{1}{4}$-monolayer geometry mentioned above, we find a similar, though smaller effect.

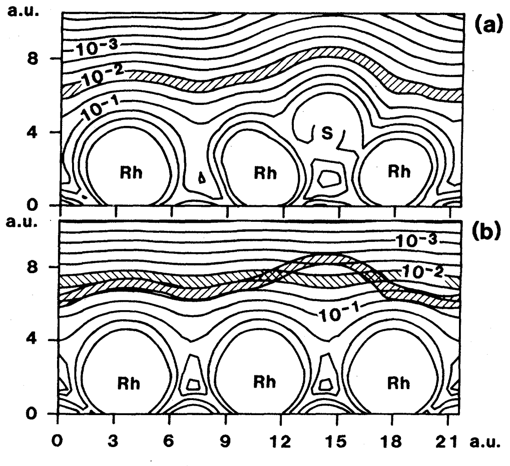

FIG. 2. Fermi-level LDOS, in $(\mathrm{eV}\times a_B{}^3)^{-1}$, for two-layer Rh(001) films (a) with and (b) without a S(3 × 1) adlayer. As in Fig. 1, we have hatched in regions of equal LDOS in the two plots, and have transcribed the hatched region from the upper to the lower plot for comparison. Notice that at a given height above the Rh with no S neighbor, the LDOS is reduced by a factor of 2.

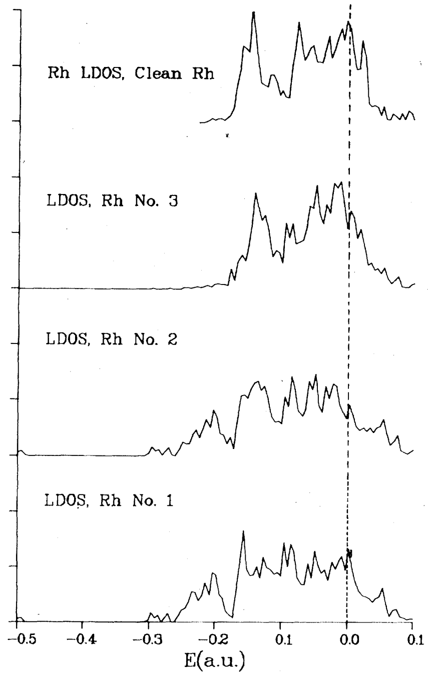

FIG. 3. Muffin-tin LDOS for clean two-layer Rh(001) and for the three inequivalent Rh sites of the S-covered film. Rh No. 3 is that with no S neighbor. No. 2 has same-side S neighbors, but no S directly below it on the other side of the film, while No. 1 has both. Notice that in the vicinity of E_f, the LDOS is reduced for all three Rh sites of the covered film, relative to the clean case.

Finally in Fig. 3 we show muffin-tin DOS for the three inequivalent Rh sites of the $S(3\times 1)$-overlayer geometry, and for a Rh of the clean two-layer film. Again we see a reduction of the E_f LDOS, not only in the muffin tins of the Rh atoms with an S neighbor, but also in that for the Rh with no S neighbor. Thus we might expect the effect of S atoms to be visible in Auger spectra, which are sensitive to LDOS near nuclei. Recently, Houston and Goodman[16] have measured such spectra for 0.5 monolayer of C/Ni(111) with and without 0.25 monolayer of coadsorbed S. The analysis shows that with S present, the C LDOS at E_f is reduced, while it is increased at somewhat greater binding energies. This result is in qualitative agreement with what is seen in Fig. 3, and with what we find in a calculation for coadsorbed S and C (to be published).

We have identified the E_f LDOS as a quantity that plausibly inhibits the ability of the surface to respond to the presence of reactants, and that is affected by relatively low coverages of S. In future work, we will show how changes in E_f LDOS vary with poison species. We hope to obtain a predictive correlation with parameters such as activation energies that characterize surface reactivity, and thereby make results such as those of Fig. 2 quantitatively useful. We also plan to study other aspects of surface electronic structure that might be responsible for poisoning at low coverages. A recent manuscript suggests, e.g., that when poison atoms cause a large change in work function, the change in electrostatic potential fairly far outside the surface is the important quantity.[17]

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