Electronically Induced Geometrical Catalytic Effects

Recent work has shown that small additions of chemical modifiers can cause major structural rearrangements on Ag, Cu (1–3), and Pt (4) surfaces. The first purpose of this letter is to explain how these electronically driven geometrical changes arise. Second, we suggest that in catalysis, the role of electron donor/acceptors may often be an indirect one, namely to cause such geometrical changes. We also point out that particle size effects may often be due to the reverse case of a geometrically driven electronic effect.

Recent experimental (5–8) and theoretical investigations (6, 9) have established an understanding of what goes on at noble metal surfaces, which can be extended to explain the modifier effects on Ag, Cu, and Pt mentioned above. We start with a consideration of the tension between the pairwise d-electron forces and the more metallic sp bonding in the bulk metal. This is fairly well understood (10, 11). In the middle of the transition metal series, the d electrons provide the primary cohesion, and indeed would like to establish a shorter interatomic spacing than is observed in the metals. They cannot do so in the *bulk* metals because the sp electrons exert a balancing, outward pressure. (A bond shortening is observed in some *molecules* especially when the sp electrons are partially removed by electronegativity effects (11).) In the noble metals the situation is reversed, with the sp bonding favoring a smaller atomic volume but prevented from contracting the structure by the repulsion of the full d shells. There is a trend across the periodic table as the antibonding d orbitals becoming progressively filled, with

the change over between the two cases occurring perhaps at Ir in the $5d$ series.

Both the d bonds and the sp bonds are far away from their own individual equilibria, which can result in substantial changes when they react differently at a surface. While the d bonds stay relatively unchanged as pairwise interatomic forces, the sp electrons are mobile, tending to respond to attractive and repulsive pseudopotential forces: in a sense their pressure is short-circuited at a surface. In the middle of the transition series the sp electrons can escape outward, allowing the d electrons to draw the atoms closer together, see, for example, the lattice contractions normal to the surface in Ta(001) (12) and Fe(111) (13). In the noble metals the situation is a little more complicated. The d electrons contribute an expansive stress both tangential and normal to the surface, while the effect of the sp electron redistribution (rehybridization) is somewhat dependent upon the surface geometry. An example is shown in Fig. 1 for a noble metal surface with a corner. This is discussed in more detail elsewhere (9), but the basic ideas are quite straight forward. The pressures or stresses on the atomic cores are defined by the electrostatic forces of the surrounding electron cloud through the Hellman–Feynmann theorem (see, for instance, Ref. (14)). Whereas in a long, flat region of surface these can lead to a compressive stress, around a step they give the opposite effect of a large expansion. The point is that we have an inherent instability which can lead to *either* an expansion *or* a contraction, *heavily* dependent upon the local geometry. This comes out from the experimental data. While large, flat surfaces
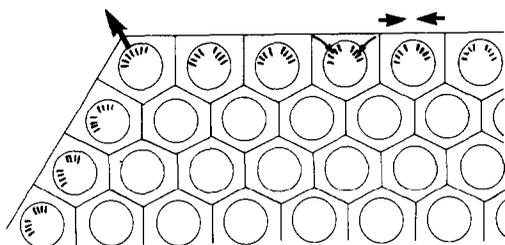
FIG. 1. Diagram of an area of noble metal surface with a corner. The *sp* electrons redistribute into the attractive shaded areas as indicated to the right. Using the Hellman–Feynmann theorem, on the flat regions there is probably an attractive stress (marked as → ←) but the geometry of the corner leads to a large expansion as arrowed. For further details, see Ref. (9).

of Au(111) contract (15, 16), short rafts expand (6–8). In particular, (110) surfaces (which can be thought of as very short rafts) show a large (20 ± 5%) expansions (5). Surface phonon results which clearly indicate substantial weaking of the surface bonding on both Ag and Au (111) surfaces (17–20) show precisely the same result. The system of opposing forces from the *sp* and *d* electrons is inherently unstable at a free surface, but precisely how this instability is relieved is not as well defined as the fact that a change is required for its relief. The crucial point for our purposes here is that these instabilities can lead to major structural changes, in some cases far larger than any simple surface relaxation. For example, one consequence of the surface stresses is to favor close-packed surfaces on the noble metals, leading to a hexagonal (111-like) overgrowth (21). Following Binnig et al. (22) we see the 2 × 1 reconstruction of the (110) Au surface as essentially a microfacetting transition to (111)-type surfaces, also driven by the same mechanism.

The key point of both the experimental and theoretical analysis is that a structural change is arising from an inherently electronic effect. This immediately points to a possible structural role for electronic modifiers, either simple electron donors or acceptors. One can think of an electron donor as pumping an electron into the *sp* band

in Au and hence increasing the instability, the opposite being true for a simple acceptor species. (Strictly, changing the local density of states at the Fermi level, e.g., Ref. (23).) We would expect the most sensitive region to be near the end of the transition series where the *d* band is nearly full and there is a very high density of states. An electron donor can easily fill the *d* band changing its essential nature from attractive to repulsive. This is precisely where many of the catalytically important metals are.

We turn now to the implications for catalysis. We have seen that there exists an instability, which can lead to large geometrical changes, is electronically driven, and sensitive to electron donor/acceptor additives, particularly so around the end of the transition metal series. Clearly such geometrical changes induced by additives can result in major catalytic effects. The evidence for this is quite compelling. The selectivity of the epoxidation of ethylene over silver is enhanced by alkali additives (24–26), which implies that the alkali modifiers inhibit the further oxidation of the ethylene oxide to carbon dioxide and water. It has recently been demonstrated that alkali additives induce the 2 × 1 reconstruction of the Ag (110) surface (1–3). Following Binnig et al. (22), the (110) fcc reconstructions are essentially microfacetting transitions to (111) type surfaces. We would suspect that alkalis will also induce a hexagonal overgrowth ((111)-type layer) on Ag (100), as occurs for clean Au, Pt, and Ir (100) (21). This implies that the close-packed (111) surfaces are good for ethylene epoxidation, but the rougher, more open unreconstructed (100) and (110) surfaces tend to give the undesirable further oxidation.[1] A second, similar example is the oxidation of CO on the Pt (100) surface. It has recently been demonstrated by Norton et al. (4) that the reaction oscillates depending upon the

[1] We are oversimplfying. The active catalyst has both chlorine and oxygen on the surface, so some of the effect may be to offset undesirable electron withdrawal.

exact surface structure at any one time, predominantly a hexagonal surface ((111)-type overlayer) with CO adsorbed and a 3 × 1 surface when oxygen is adsorbed. Since CO is an electron donor while O is an electron acceptor, this is exactly the type of behavior that we would expect.

As a final point, there are other well-known effects which are essentially the same as those we are dealing with here, or rather the converse. The most obvious of these is the case of epitaxy of small particles upon a substrate when the pseudomorphic growth (27) results in a different crystal structure for the particles from the normal bulk structure (28). In such a case the geometrical epitaxial effect can result in a large change in electronic structure which in turn could induce an electronic catalytic effect.

In conclusion, we believe that there are excellent grounds for large catalytic effects due to a substrate geometry change which are driven by the electronic effect of a chemical modifier, either promoter or poison. The reverse case of an electronic effect induced by a geometrical change may also be important in catalysis.

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