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Author
Somorjai, G.A.

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G. A. Somorjai

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On the Mechanism of Sulfur Poisoning of Platinum Catalysts

G. A. Somorjai

Inorganic Materials Research Division, Lawrence Berkeley Laboratory,
and Department of Chemistry; University of California
Berkeley, California 94720

The inhibition of a large variety of surface reactions that are catalyzed by supported platinum particles, by a very small amount of sulfur has been well documented.[1] Estimates based on experimental data indicate that each sulfur atom may render 10^3-10^4 platinum atoms ineffective for the ring opening of cyclopentanes,[1] dimethylation[2] or for other catalytic surface reactions. In chemical reactions that take place in the solid state, a large chemical change that is associated with the presence of small amounts of impurities frequently indicate the onset of phase transformations that are accompanied by marked changes of atomic structure.

It has been reported[3-5] that surfaces of various solids undergo faceting, i.e., changes of surface structure, in the presence of impurities at the surface. During faceting new crystal planes form at the surface, these planes having crystallographic orientations that are different from those that were present in the absence of the surface impurities. Silver surfaces have developed crystal planes with (100) orientation in the presence of sulfur.[3] The (111) crystal face of nickel develops (100) orientation in the presence of H_2S, C_2H_4, or benzene.[4] The (110) crystal face of chromium develops crystal planes of (100) orientation in the

presence of sulfur on the surface [6] The rearrangement of surface structure is, in general, by a rapid surface diffusion process, although selective vaporization of atoms from certain crystal faces of the solid that facilitate the structural rearrangement cannot be ruled out as a path for surface recrystallization, in some cases. It has been found that sulfur or other impurities (halogens) can increase the surface diffusion rates of silver atoms by 1-2 orders of magnitude.[7] On removal of the impurities the surface is expected to establish its original surface structure again, although in most experiments the removal of the impurities from the faceted surface has not been attempted or could not be carried out.

Foreign atoms that adsorb on the crystal surface change its surface free energy. A lowering of surface free energy would be expected, in general, in the presence of adsorbed impurities with respect to the surface free energy of the clean surface.[8] If the adsorbed impurity changes the surface free energy of the various crystal planes by different amounts, it can induce the rearrangement of the surface structure to form crystal planes that have lower surface free energy in the presence of the adsorbed impurity than the crystal planes that bound the clean solid.

In general, surfaces that exhibit the highest atomic densities have the lowest free energies. These surfaces are the (111), (100) and (110) orientations of face-centered cubic crystals and the (110), (100) and (111) faces of body-centered cubic solids (listed in order of decreasing surface atom density). The ratio of surface free energies of these higher density surfaces has been found to be typically .9-.95 when it

was measured for typical face-centered cubic (copper[9]) or body-centered cubic (molybdenum[10]) solids. It is expected that these surfaces are present predominantly on small catalyst particles whether they were grown using precipitation rates that were fast (far from equilibrium) or slow (near equilibrium). It has been shown[11] that under growth conditions far from equilibrium the (100) crystal face of lead developed preferentially from the melt, while at slow growth rates the somewhat denser (111) surface orientation is dominant. Other face-centered cubic solids are likely to have this same growth-rate dependence of the surface orientation. It is very likely that one or the other surface orientation will be the dominant surface structure of the polydispersed particles of face-centered cubic metals that are supported on silica or on alumina. Although one crystal face has the lower surface free energy (the (111) with highest atomic density) particles may be bounded by other low index crystal planes even though these have slightly greater surface free energies. There are several minima in the surface free energy curves as a function of crystal orientation[12] which, while they do not represent the lowest free energy configuration, can give rise to surface structures of remarkable thermal stability. Surfaces that are characterized by ordered steps of monatomic height that are separated by atomic terraces of (100) or (111) orientation is one type of surface structure of platinum and other solids with a local surface free energy minimum, that has been found remarkably stable.[13] The stability of these surface structures is due to the difficult reaction paths by which restructuring to the surface structure of lower surface free energy may occur. The activation energy to rearrange

whole crystal planes is, in general, so large that the surface structure with a free energy minimum is well stabilized with respect to transformation to the surface structure with the lowest free energy by high activation energy barriers.

Schmidt[5] and Luss have reported that platinum wires used in the catalytic oxidation of ammonia have recrystallized in the presence of H_2S gas in the feed. Electron microscopy studies have shown that the wire surface that was composed of predominantly (111) crystal planes has restructured in the presence of H_2S to (100) crystal planes. It appears that adsorption of sulfur lowers the surface free energy of the (100) crystal face of platinum more than that of the (111) face and the surface free energy difference provides the driving force for surface diffusion controlled recrystallization. The experimental information that is available on the interaction of silver[3] and nickel[4] surfaces with sulfur, in addition to the results obtained by Schmidt and Luss using platinum surface, indicates that the (100) crystal face of face-centered cubic solids is stabilized in the presence of sulfur with respect to the (111) face. Hence sulfur catalyzes the recrystallization of (111) surfaces to that of (100) crystal faces. Such an effect is expected if the strength of the chemical bonds of the impurity with atoms in the various crystal planes or the surface concentration or impurities on the different crystal faces are different.

If this model of sulfur poisoning of platinum surfaces is correct, it indicates that the chemical surface reactions that are inhibited by sulfur are sensitive to changes of the surface structure of platinum, i.e., are structure sensitive. Boudart[14] has suggested that isomerization

or hydrogenolysis reactions belong to the class of structure sensitive reactions, while hydrogenation is likely to be structure insensitive. It is well known[2] that hydrogenolysis of end methyl groups is very sensitive to sulfur poisoning. Thus sensitivity to sulfur poisoning might be used to indicate that the particular catalytic reaction is sensitive to the surface structure of the catalyst. It should be noted that the f.c.c. (111) face is characterized by six-fold while the (100) face by four-fold rotational symmetry. Ring opening of methyl-cyclopentane would be expected to be surface structure sensitive on this basis. On the other hand, isomerization[15] and dehydrocyclization,[16] both known to be structure sensitive, would be likely to be poisoned by the presence of sulfur.

If selected impurities cause recrystallization of the catalyst surface, how may such poisoning effect be counteracted? It is proposed that the addition of other impurities that lower the surface free energy of the (111) planes of face-centered cubic solids more than that of the (100) planes and have similar binding energies to that of sulfur, could either prevent or reverse recrystallization of the platinum surfaces. In the absence of detailed experimental studies on the effects of various impurities on the surface structure, it is difficult to suggest such impurities. If sulfur acts as an electron acceptor at the platinum surface, similar to oxygen, it is likely that electron donors are good candidates for stabilizing the (111) crystal faces of platinum. However, if sulfur is an electron donor, electron acceptors may be used to stabilize the platinum (111) crystal face.

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LAWRENCE BERKELEY LABORATORY
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