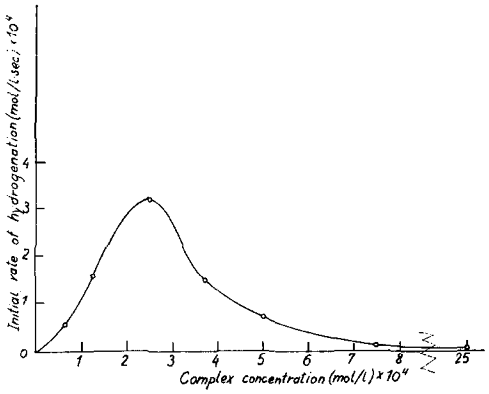

FIG. 1. Initial rate of reaction for hydrogenation of cyclohexene versus complex concentration at fixed temperature (50°C) and hydrogen pressure (30 atm).

10^{-4} mol/liter dissociation [according to the equation $RhH(CO)(PPh_3)_2 \rightleftharpoons RhH(CO)(PPh_3) + PPh_3$] becomes important and that $RhH(CO)(PPh_3)$ should be a more active but less selective catalyst than $RhH(CO)(PPh_3)_2$. An increase of the total concentration of the Rh-complex will decrease the relative concentration of $RhH(CO)(PPh_3)$, but the absolute concentration of $RhH(CO)(PPh_3)$ can never decrease by increasing the total concentration of the Rh-complex.

Supposing that $RhH(CO)(PPh_3)$ is the only active catalyst by the hydrogenation of cyclohexene, one should expect the rate to be increased and eventually level off by increasing the total Rh-complex concentration. However, a maximum at an Rh-complex concentration of 2.5×10^{-4} mol/liter and the complete deactivation of the catalytic system at concentrations above 10^{-3} mol/liter cannot be explained by the dissociation.

It is difficult to find a reasonable explanation for this extraordinary behavior, but perhaps it may be due to some sort of interaction of complex molecules.

At a fixed complex concentration of 2.5×10^{-4} mol/liter and a temperature of 50°C the dependence of the rate of hydrogenation on hydrogen pressure was investigated in the range 0–70 atm. The rate of the reaction rose with the pressure, but the increase was not linear and diminished at higher pressures. The reaction order with respect to hydrogen was found by regression analysis to be 0.73 ± 0.09.

REFERENCES

1. O'CONNOR, C., AND WILKINSON, G., *J. Chem. Soc. A*, 2665 (1968).
2. EVANS, D., YAGUPSKY, G., AND WILKINSON, G., *J. Chem. Soc. A*, 2660 (1968).
3. YAGUPSKY, M., BROWN, C. K., YAGUPSKY, G., AND WILKINSON, G., *J. Chem. Soc. A*, 937 (1970).

JES HJORTKJÆR
ZDZISLAW KULICKI

Institutet for Kemiirdustri
DtH
Bygning 227
DK-2800 Lyngby, Denmark
Received January 14, 1972

On the Mechanism of Sulfur Poisoning of Platinum Catalysts

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 6 to 10 platinum atoms ineffective for the ring opening of cyclopentanes (*1*), demethylation (*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 indicates 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. Platinum 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 (*5*). 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 facilitates 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 (*6*). 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 the surface's 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 (*7*). *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 (*8*)) or body-centered cubic (molybdenum (*9*)) 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 (*10*) 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 (*11*) which, while they do not represent the lowest free-energy configuration, can give rise to surface structures of remarkable thermal stability. A surface that is 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 to be remarkably stable (*12*). 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 (*3*) 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 (*6*) and nickel (*1*) surfaces with sulfur, in addition to the results obtained by Schmidt and Luss using the 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 that are characterized by sixfold rotational symmetry to (100) crystal faces with fourfold rotational symmetry. 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 of 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 (*13*) 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. The ring opening of methylcyclopentane would be expected to be surface structure-sensitive on this basis. On the other hand, isomerization (*14*) and dehydrocyclization (*15*), 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 a 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 that have binding energies similar 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 in a manner 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.

It is also possible that sulfur may drastically alter the path of catalytic reactions by direct chemical interactions with the adsorbed molecules instead of by inducing surface recrystallization. However, in this circumstance a larger steady-state surface concentration of sulfur (nearly a monolayer) would be required to cause a noticeable change in the distribution of reaction products.

It is likely that other impurities (oxygen, carbon, nitrogen, hydrogen) that strongly chemisorb on metal surfaces may also induce rearrangements of surface structure that have long-lasting effects on the reactivity of metal catalysts.

ACKNOWLEDGMENTS

I am indebted to Dr. S. Csicsery and Professor F. S. Stone for helpful discussions. This work was supported by the U. S. Atomic Energy Commission.

REFERENCES

1. SMITH, R. L., NARO, P. A., AND SILVESTRY, A. J., *J. Catal.* **20**, (1971).
2. CSICSERY, S. M., AND HOUSTON, R., (private communication).
3. SCHMIDT, L. D., AND LUSS, D., *J. Catal.* **22**, 269 (1971).
4. MCCAROLL, J. J., EDMONDS, T., AND PITKETHLY, R. C. *Nature (London)* **223**, 1260 (1969).
5. KAPLAN, R., (private communication).
6. DELAMARE, F., AND RHEAD, G. E., *Surface Sci.* **28**, 267 (1971).
7. HONDROS, E. D., AND MCLEAN, M., "Structure et Proprietes des Surfaces des Solides 1969." Ed. du Centre Natl. de la Recherches Scientifique, 1970.
8. ROBERTSON, W. M., AND SHEWMON, P. G., *Trans. AIME* **224**, 804 (1962).
9. WINTERBOTTOM, W. L., *in* "Surfaces and Interfaces" (J. J. Burke *et al.*, Eds.). Syracuse Univ. Press, Syracuse, 1967.
10. GOODMAN, R. M., AND SOMORJAI, G. A., *J. Chem. Phys.* **52**, 6325 (1970).
11. HERRING, C., *in* "Structure and Properties of Solid Surfaces" (R. Gomer and C. S. Smith, Eds.). Univ. of Chicago Press, Chicago, 1953.
12. LANG, B., JOYNER, R. W., AND SOMORJAI, G. A., *Surface Sci.* **30**, 440 (1972).
13. BOUDART, M., *Advan. Catal.* **20**, 153 (1969).
14. BOUDART, M., ALDAG, A. W., PTAK, L. D., AND BENSON, J. E., *J. Catal.* **11**, 35 (1968).
15. SOMORJAI, G. A., *Catal. Rev.* (in press).

G. A. SOMORJAI

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

Received February 22, 1972

Interparticle Hydrogen Migration on Pd–Al_2O_3 Catalysts for Benzene Hydrogenation?

A variety of catalytic systems are reported to be influenced by hydrogen migration or hydrogen spillover (*1–6*). Boudart, Vannice and Benson have reported the ease with which WO_3 is reduced when physically contacted with platinum black after water had been preadsorbed on the mixture (*3*). It is believed that water provides an interface between the mechanically mixed platinum black and WO_3 particles. Dissociated hydrogen then migrates from platinum particles to WO_3 particles and hence room temperature reduction of WO_3 occurs. Such migration phenomena are potentially important both in understanding surface catalytic behavior and in the preparation and practical use of catalysts.

A recent study by Sancier (*6*), using a pulsed reactor system for the hydrogenation of benzene on a Pd–Al_2O_3 catalyst, shows an increase in specific activity when the catalyst bed is diluted with inert Al_2O_3. These results were interpreted as being caused by interparticle hydrogen migration or spillover. This interpretation has been questioned by Vannice and Neikam (*7*), who collected data on a comparable catalyst under steady state conditions. Steady state runs showed no evidence that spillover occurs. Hence, dilution of the Pd–Al_2O_3 catalyst bed with inert Al_2O_3 only enhances productivity in the pulsed reactor system. In his rebuttal, Sancier (*8*) stated that ". . . the conditions employed in the pulsed reactor are particularly suitable for the detection of surface migration phenomenon because the catalyst, the support, and the diluent have ample time to become populated with chemisorbed hydrogen preceding the arrival of the benzene pulse." The catalytic surface which contacts a benzene pulse could very well differ from the