

Enhanced Reactivity of Ordered Monolayers of Gold on Pt(100) and Platinum on Au(100) Single-Crystal Surfaces

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Gold was deposited on Pt(100) and platinum was deposited on Au(100) single-crystal surfaces. Cyclohexene dehydrogenation rates were enhanced about fivefold relative to clean Pt(100) by just one monolayer of gold on Pt(100) and also by ordered platinum layers on inactive Au(100).

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Alloys formed from metals in group VIII and Ib in the periodic table are used increasingly as catalysts for hydrocarbon reactions.¹ Beneficial changes in the reaction rates selectivity and resistance to deactivation are produced by alloying the chemically active group-VIII metal with an inactive group-Ib metal.² These effects have been obtained with use of dispersed alloy particles for which it is difficult to control the composition and structure of the surface independently. The separation of these experimental variables, however, is essential for the better understanding of these systems. For this reason we undertook a study of the structure and chemical reactivity of well-defined surfaces of single crystals. In particular we investigated how the composition and structure of gold deposited on Pt(100) and platinum deposited on Au(100) single-crystal surfaces influence the rate of cyclohexene dehydrogenation to benzene.

Gold was deposited from the vapor phase onto a Pt(100) single-crystal surface that was kept at 300 K in amounts ranging from a fraction of a monolayer to several layers. The surface structures were determined from low-energy electron diffraction (LEED), while Auger-electron spectroscopy (AES) was used in conjunction with a piezoelectric quartz crystal thickness monitor (PQTM) to determine the surface coverages and mechanism of the film growth.³ In this way the surface coverages could be determined with an accuracy of about 10%.

The chemical reactivity of the surfaces was measured as a function of gold coverage using the dehydrogenation of cyclohexene to benzene at 373 K as test reaction. The UHV chamber in which the surfaces were prepared served as a low-pressure flow reactor. The reactions were carried out at hydrogen and cyclohexene partial pressures of 1×10^{-6} and 6×10^{-8} Torr, respectively. Reaction rates were monitored with a

mass spectrometer.

We found that the rate of benzene formation increases with gold coverage on Pt(100) up to one full monolayer. This maximum value of the reaction rate is four times higher than that for the clean Pt(100) surface, while a pure gold surface is inactive for this reaction under our conditions (Fig. 1). At gold coverages above one monolayer, the reaction rate decreases to a nonzero value because of the crystal edges which remain uncovered during the gold deposition.

Conversely, we deposited platinum on a Au(100) single-crystal surface. The rate of cyclohexene dehydrogenation to benzene was found to increase with platinum coverage and to reach a maximum value between one and two platinum layers. This value of the reaction rate is about six times higher than that of a clean Pt(100) single-crystal surface. The reaction rate retains that value at higher platinum coverages (Fig. 2).

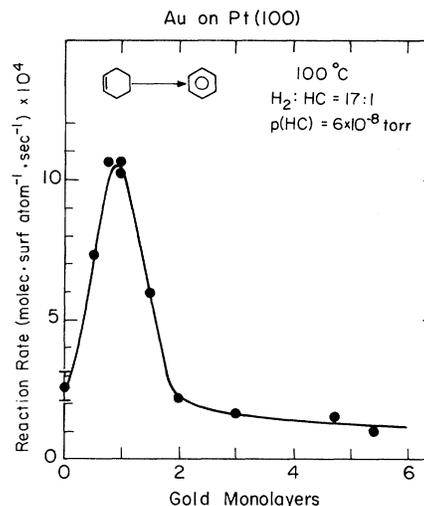


FIG. 1. Rate of cyclohexene dehydrogenation to benzene as a function of Au coverage on Pt(100).

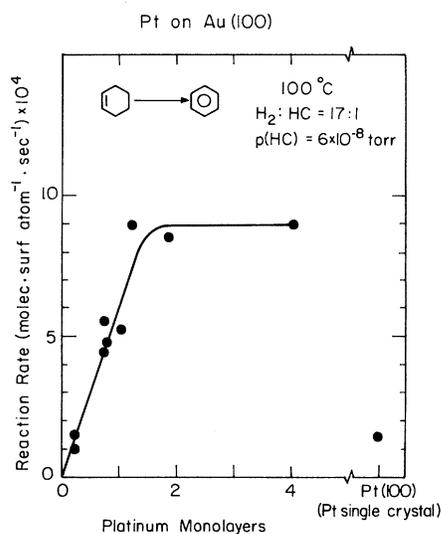


FIG. 2. Rate of cyclohexene dehydrogenation to benzene as a function of Pt coverage on Au(100).

The variation of the Auger signal intensities of gold and platinum as a function of adsorbate coverage (obtained by decomposition of the overlapping Auger lines³) contains information about the growth mechanism of the adlayer.⁴ The experimental data were fitted with the three basic growth models (Frank-van der Merwe, Stranski-Krastanov, and Volmer-Weber models). We found that the Frank-van der Merwe or layer-by-layer growth mechanism is preferred for the gold on Pt(100) system. The points of monolayer completion of the adlayer as obtained from the Auger analysis and the PQTM were in good agreement to within 10%.³ The Auger data of platinum on Au(100) indicate a Volmer-Weber, or crystallite-type, growth without a monolayer stage.

A LEED study was undertaken to investigate the structure of the deposited metal layers. Deposition of gold on Pt(100) gradually removes the reconstruction of the clean platinum surface^{5,6} and at a coverage of 0.5 monolayer a 1×1 pattern with sharp spots was observed. This structure does not change up to two monolayers of gold. Measurements of the spot-to-spot distances on the LEED photographs at various gold coverages showed that gold assumes the Pt(100) substrate lattice constant, up to a coverage of two layers. This implies a contraction of 4% with respect to the bulk gold lattice constant and allows the gold atoms to fit in exact registry on top of the Pt(100) substrate. During the dehydrogenation experiments the initially clean Pt(100) would also have

a 1×1 surface structure due to the interaction with the cyclohexene which removed the reconstruction. Deposition of platinum on Au(100) removes the reconstruction of the latter^{7,8} and at coverages from 0.5 layer to several layers a 1×1 pattern with sharp spots was observed. In this case platinum assumes the Au(100) substrate lattice constant, which implies a 4% expansion relative to bulk platinum.

It is not possible, at present, to provide a unique model to explain the observed enhancement of the dehydrogenation rate of cyclohexene when inactive gold is deposited on a Pt(100) single-crystal surface. More studies with systematic variations of the deposited metal and the substrate surface structure are needed. Deposited gold could certainly block those surface sites where the hydrocarbon molecule bonds with several neighboring Pt atoms, inhibiting the competing C-C-bond-breaking processes that lead to surface deactivation by carbon deposition.⁹ As a result the rate of C-H-bond breaking would increase. We have indeed observed, by AES, that on the Pt(100) surfaces covered by one or more layers of gold no carbon is deposited during the reaction. On the pure platinum surface the reaction deposits 0.5 monolayer of carbon under our experimental conditions.

It should be noted that the reaction rate reaches a maximum when the platinum is fully covered by monolayer of gold. Because of the 4% contraction of the gold atoms, this monolayer fits in exact registry on top of the platinum. Thus the gold monolayer has a square lattice in which relatively large hollows exist between the atoms, through which cyclohexene could bind to platinum atoms that are now in the *second* layer. Unique binding of this type may well be responsible for the observed high dehydrogenation activity. Also, the electron affinity of platinum is greater than that of gold (platinum has a higher work function). The resulting partial charge transfer between both metals could profoundly influence the bonding of hydrocarbons resulting in the observed enhancement of the reactivity. At a coverage of two monolayers, gold has completely covered the platinum atoms and, since gold itself is inactive, the reactivity decreases.

The platinum deposited on the Au(100) single-crystal surface seems to be present as crystallites with edge atoms that may well be more active than platinum atoms in a smooth plane. Also, an electronic interaction between platinum and gold might strongly affect the bonding of hy-

drocarbons, resulting in the observed enhancement of the reactivity. Another possibility is that the reactivity of platinum on Au(100) is altered as a consequence of its lattice expansion (by 4%) as compared to bulk platinum.

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¹For example, see J. H. Sinfelt, U. S. Patent No. 3 567 625 (1971).

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