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# NOTES

## The Effect of Palladium Hydride Phase Transformations on the Reconstruction and Catalytic Activity of Palladium Films

The bulk and surface structures of a palladium catalyst can undergo considerable change in the course of catalyst preparation and in its subsequent use in a reactor under the influence of reactants and of process parameters (*1*). In order to understand phenomena involving supported palladium we decided to carry out investigations on palladium films and single crystals.

Palladium films were evaporated from a 0.1-mm-diameter 99.9% Pd wire wrapped around a tungsten heater. The palladium layer was deposited on glass or on an amorphous carbon layer (on glass) in a vacuum better than $10^{-3}$ Pa at room temperature. The carbon layer was evaporated by an arc discharge between two carbon electrodes of spectroscopic purity. The palladium films were 19 or 48 nm thick. The dimensions of their crystallites were 14 and 18.5 nm, respectively, as estimated by X-ray line broadening. The films were not annealed, except for being kept several hours at room temperature.

Palladium single crystals of spectroscopic purity were purchased from Johnson–Matthey with orientation (100), (111), or (110). They were cleaned by standard procedures. Auger electron spectroscopy was used to examine their cleanliness. Hydrogen was of spectroscopic purity (VEB Technische Gas-Werke, Berlin); acetylene was 99% pure (Merck).

For X-ray diffraction measurements the Pd film samples were placed in a holder of a catalytic reactor designed as an attachment for a Rigaku-Denki X-ray diffractometer (*1, 2*). Hydrogen, argon, or a mixture containing hydrogen, acetylene, and argon was passed through a thermostated heat exchanger and then over the film sample surface, finally leaving the reactor. X-Ray diffraction patterns have been recorded simultaneously with chromatographic analysis of the composition of the gas product mixture leaving the reactor. The profiles of the palladium and $\beta$-palladium hydride (111) reflections were recorded continuously by oscillating the goniometer between 37° and 41° ($2\theta$). Ni-Filtered Cu radiation was used.

After reduction of a residual surface oxide layer in hydrogen at atmospheric pressure and 400 K, the palladium film was cooled in a stream of argon to 300 K. After recording the palladium (111) line, a flow of hydrogen was switched on. Palladium was transformed into its $\beta$-hydride phase, which, as is well known, has a lattice parameter about 4% larger than palladium itself (*3*). The corresponding shift of the X-ray diffraction peak was observed. Argon was again introduced into the reactor, bringing about the decomposition of the hydride and the return of the palladium X-ray reflection to its initial position. The procedure was repeated several times.

For LEED and AES measurements the cleaned Pd low-index faces of the single crystals were exposed to hydrogen or to acetylene at room temperature at pressures up to $10^{-3}$ Pa. The respective LEED patterns, AES, and mass spectra were studied. A Vacuum Generators all-metal UHV chamber equipped with facilities for LEED, AES, and QMS was used in this work.

The results obtained with the films were as follows. The repeated process of formation–decomposition–formation etc. of the palladium hydride led gradually to a considerable increase in intensity of the (111) reflection of Pd (and of Pd hydride). The height of the Pd peaks finally became

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constant after about seven successive cycles of hydrogen treatment of the films. (Fig. 1). The shape of the curves representing the X-ray diffraction (111) peak area as a function of the number of hydrogen cycles was identical and the observed width of the X-ray pattern "line" at half peak height remained unchanged. The phenomenon did not depend on which support was used for the palladium film. Reflections other than (111) vanished, this being checked independently. One can conclude that as a consequence of the phase transformations in the palladium–hydrogen system a rearrangement of palladium atoms in the crystallites was occurring even at room temperature. This reconstruction led to the appearance of a distinct (111) texture in the Pd film.

It is well known (*4*) that a similar rearrangement results from an appropriate heat treatment of a metal film at a sufficiently high temperature because the lowest energy plane is favored by annealing. The sintering process, however, results also in metal particle growth, which was not observed in this study.

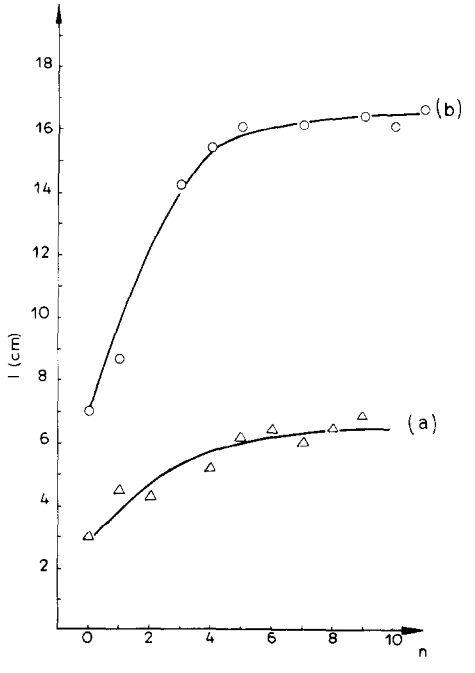

FIG. 1. Increase of the intensity, *I*, of the (111) reflection of Pd in the X-ray diffraction pattern after the Pd $\rightleftarrows$ $\beta$PdH transformation repeated *n* times. (a) Pd film on glass, 19 nm thick; (b) Pd film on glass, 48 nm thick.

The catalytic activity of palladium films before and after their reconstruction was examined under conditions of selective hydrogenation of acetylene to ethylene (*1*). A tenfold increase in the degree of total acetylene conversion was observed, indicating an increase in catalytic activity of the palladium sample with the (111) texture (*5*).

In the light of these results, we carried out experiments on single crystals to compare the behavior of different crystal planes of palladium during their exposure to acetylene and hydrogen or their mixtures.

Adsorbed hydrogen at a pressure up to $10^{-3}$ Pa did not change the initial LEED pattern from any sample. In contrast, the adsorption of acetylene at room temperature caused significant changes depending on the particular palladium crystal face: the (100) face developed a distinct $c(2 \times 2)$ structure, the (111) face did not change, and the (110) face showed a very feeble $c(2 \times 2)$ structure. Heating the sample covered with acetylene adspecies to almost 500 K led, for the (100) face, to the formation of a $c(4 \times 2)$ and, for Pd(110), to $(4 \times 1)$ R30° structures characteristic of carbon, or rather carbonaceous residues, confirmed by AES. Similar heating of the (111) sample produces no change in the LEED pattern, nor any increase in the carbon AES peak.

The implications of the results and the conclusions which may be drawn are as follows. The repeated hydrogen treatment of randomly oriented, polycrystalline palladium thin layers, within the range of conditions characteristic of formation and decomposition of the $\beta$-palladium hydride phase, leads to a low-temperature rearrangement of palladium crystallites and to the formation of the (111) texture without any visible growth of the metal particles.

The phenomenon of palladium crystallite reconstruction in the course of interaction with hydrogen at low temperature has been observed previously. Brownlie *et al.* (*6*) as well as Pope *et al.* (*7*) observed a "sintering" of palladium crystallites on a charcoal support or a thin carbon layer, during the reduction process in hydrogen even at ambient temperature. Sermon (*8*) reported "a remarkable increase in the extent and ordering of macroscopic aggregations" of Pd blacks resulting from hydrogen treatment at ambient temperature; the phenomenon was explained by a temperature increase produced by hydrogen sorption on the Pd black surface. The authors did not emphasize any connection of this effect with the phase transformation in the Pd–H system.

Lattice rearrangement in metal crystallites which led to an energetically more favorable crystal structure had been observed earlier for the Ni–Cu alloy system (*9*). Two alloys, representative of the equilibrated phases of the Ni–Cu system at room temperature, precipitated from a "frozen" single phase alloy as a consequence of $\beta$-hydride phase formation and decomposition.

Both these examples of lattice rearrangement in metal crystals have much in common, being due to large changes of lattice parameter accompanying the phase transformation from metal to metal hydride. The shift of the metal atoms enables states of lower free energy to be achieved, even at room temperature.

Our results show that the rearranged polycrystalline palladium layer displays a surface structure of enhanced catalytic activity with respect to hydrogen and acetylene mixtures. Supposing that the crystallites expose their (111) faces also toward the gas phase, the understanding of that catalytic behavior is to be based on the LEED observations of different Pd single-crystal faces exposed to acetylene or acetylene–hydrogen mixtures. Of the orientations studied, only on the (111) Pd crystal plane does acetylene not form a strongly bound adspecies, which would decompose and leave carbon on the palladium surface. Similar specific behavior of the (111) nickel face with respect to ethylene was observed by Dalmai-Imelik and Massardier (*10*). This experimental evidence obtained for large, well-oriented crystals may shed light on the high catalytic activity of (111) textured palladium films in acetylene hydrogenation and the reported increase in activity of commercial Pd catalysts after special treatment with hydrogen (*11*).

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