LETTER TO THE EDITORS

Interstitial Carbon in Palladium

In a recent paper published in this journal, Zaidi (1) proposed that palladium hydride represents the site responsible for selective synthesis of vinyl acetate on 10% Pd/C. The author postulated formation of β -PdH by abstraction of hydrogen from dissociatively adsorbed ethylene. This hypothesis was based on the observed expansion of the palladium lattice, as measured by X-ray diffraction of catalyst samples removed from the reactor. The values of lattice parameters given by Zaidi (1) are a =0.38872 nm for Pd, and a = 0.3986 nm for the phase detected after exposure of the catalyst to ethylene-rich vinyl acetate synthesis gas. This phase is identified by the author as β -PdH. A candid assumption is thus made that palladium hydride is stable under the reaction conditions (415 < T <435 K; $P_{O_2} = 9.47 \text{ kN/m}^2$, $P_{C_2H_4} = 25.99 \text{ kN/m}^2$ m^2 , plus CH₃COOH and N₂).

It is well established, however, that β -PdH decomposes at 433 K if the hydrogen pressure is lower than ca. 100 kN/m^2 (2). Our results show disappearance of the hydride phase below 373 K at subatmospheric pressures of H₂ (Fig. 1). In addition, presence of even trace amounts of oxygen accelerates hydride decomposition (3). Consequently, the phase characterized by a =0.3986 nm, found by Zaidi (1) in palladium catalysts used in vinyl acetate synthesis, cannot be identified as β -PdH. Investigation of the interaction of ethylene with palladium, and extensive characterization of the new phase formed, allows us to conclude that the lattice expansion is due to interstitial solid solution of carbon in palladium.

To eliminate possible effect of the support, our experiments were conducted using palladium black (Johnson Matthey, Cat. No. 12066). The uptake of hydrogen associated with palladium hydride formation was measured using a modified temperatureprogrammed reduction (TPR) apparatus. Structural changes occurring in an atmosphere of C_2H_4 and H_2 at various temperatures were followed *in situ* in a theta-theta diffractometer equipped with a heated stage and a gas-flow chamber, described earlier (4).

Figure 2 shows the X-ray diffraction spectra of palladium black contacted with ethylene, air, and hydrogen at indicated temperatures. Exposure to ethylene at room temperature does not alter the structure of Pd (curve A), but further heating in a flow of ethylene (20 min at each temperature step) causes shifts of both the (111) and (200) peaks of Pd to lower values of the scattering angle. The shift first becomes apparent at 373 K and seems to be completed (a = 0.3999 nm) at 473 K, as shown on curve B. That structural change can be reversed by heating the sample in air. Again, transformation is completed after 20 min at 473 K, with restoration of the lattice param-



FIG. 1. X-Ray diffraction pattern of Pd black in flow of 4% H₂/He: dotted line, at 298 K; solid line, at 373 K. C* indicates the internal standard (diamond).



FIG. 2. Changes in the X-ray diffraction pattern of palladium black following 20-min exposures, in sequence, to (A) ethylene at 298 K; (B) ethylene at 473 K; (C) air at 473 K; (D) hydrogen at 298 K; (E) nitrogen at 298 K. C* indicates the internal standard (diamond).

eter of bulk palladium, and a small amount of PdO formed (see curve C). After cooling down to 298 K and exposure to 4% H₂ in He, the PdO peak disappears and β -PdH (a = 0.4025 nm) is formed (see curve D). The hydride phase is unstable at room temperature in the absence of hydrogen, and in N₂ flow reverts to palladium (curve E). The sample of Pd black treated in C₂H₄ at 473 K, and not heated in air before exposure to H₂ at 298 K, does not form hydride. In addition, it should be noted that the structure shown on curve B is stable up to ca. 800 K in an inert atmosphere.



FIG. 3. Uptake of hydrogen on cooling the sample of palladium in flow of 5% H₂/N₂: (A) 10 mg of Pd black; (B) 50 mg of Pd black previously treated in ethylene for 1 hr at 453 K. The time scale runs from right to left.

Formation of β -palladium hydride was also measured by a modified TPR technique. Figure 3 shows the uptake of H₂ associated with formation of hydride, observed when Pd black is cooled in a flow of 5% H₂ in N₂. Curve A shows hydrogen uptake by 10 mg of Pd. The hydrogen uptake starts below 330 K and reaches the maximum rate around 300 K. Integration yields the H/Pd ratio of 0.66. The same experiment was repeated with 50 mg of Pd black pretreated in flowing ethylene at 473 K for 2 hr. This time no hydrogen uptake is observed (curve B), in agreement with the Xray diffraction results.

The phase created by exposure of Pd black and Pd foils to ethylene was characterized. Depth profiling by ion bombardment with ISS and XPS analyses shows a constant C/Pd ratio in the bulk of the metal. Preliminary neutron scattering data suggest that the carbon atom is located in the octahedral holes of the Pd lattice. The composition of the PdC_x phase was found by various approaches to be in the range of 0.10 < x < 0.15. Details of this work will be reported shortly.

In summary, exposure of Pd to flowing ethylene above 373 K leads to formation of a new phase, characterized by lattice expansion and suppression of hydride formation on subsequent exposure to H₂. This phase is identified as interstitial solution of carbon in palladium, and not β -PdH as postulated by Zaidi (1).

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