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X-RAY DIFFRACTION STUDIES OF HYDRIDE FORMATION ⇌ DECOMPOSITION IN DISPERSED PALLADIUM PARTICLES

Jerzy PIELASZEK

Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

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Dispersed palladium particles disintegrate when subjected to multiple hydride formation-decomposition cycling. The effect is much more pronounced for palladium supported on gamma alumina.

The behaviour of dispersed Pd particles during hydrogen treatment is of especial interest in studies of catalysts. In some hydrogenation reactions on Pd catalysts an excess of hydrogen can cause the transformation of the metal into its hydride thereby influencing the catalytic performance [1]. For the case of the Pd supported on Al_2O_3 it was found that in the hydrogenation of acetylene the selectivity depends on the degree of transformation into hydride [1,2]. It is also possible that hydride decomposition can induce desintegration of the metal particles, and indeed, the particle size effect has long been discussed as one of the factors influencing certain catalytic reactions (e.g. ref. [3]).

The effect of desintegration of single crystals and polycrystalline material with large particles (more then few μm) is known for nickel which had undergone multiple hydride formation-decomposition cycles [4]. This phenomenon is explained by the formation and interaction dislocations during hydride formation and decomposition [5]. For the case of nickel it was found that the desintegration goes down to particle size diameters of about 200 Å [4], which coincides well with the so-called dislocation-cell structure size observed as a result of dislocation interaction during the plastic deformation of metals [6]. Nickel-hydrogen and palladium-hydrogen systems are structurally analogous; both metals have f.c.c. structures, and in each case the hydride phase has the same type of Bravais lattice where hydrogen occupies the octahedral sites. Only the lattice parameter differs: it is about 3.5 percent higher than the host lattice in the case of palladium hydride [7] as compared to about 6 percent in the case of nickel hydride [8]. Decomposition of hydride in Pd single crystals is also known to cause crack formation [9]. Taking into account the structural similarities between nickel-hydrogen and palladium-hydrogen systems one should expect that the decomposition of palladium hydride in palladium particles of few hundred Angstrom units can induce

Table 1

Sample	Treatment	Particle size D (Å)	$\langle\epsilon\rangle_{50}^{1/2}$
#1 Pd black	fresh	280	0.0108
	after 1-st decomposition of hydride	230	0.0107
# 2 Pd black	fresh, annealed	310	0.0026
	after 1-st decomposition of hydride	310	0.0096
	after 2-nd decomposition of hydride	290	0.0098
	after 10-th decomposition of hydride	270	0.0098
#3 Pd black	fresh	94	0.0107
	after 1-st decomposition of hydride	92	0.0118
	after 2-nd decomposition of hydride	90	0.0119
3 wt percent Pd/γ-Al_2O_3	fresh	160	0.0067
	after 1-st decomposition of hydride	80	0.0135
	after 2-nd decomposition of hydride	75	0.01

change in their size, and that there should also be a limiting value for the particle size thus obtained.

In the present work different samples of palladium were studied (table 1). Pd black #1 and #2 were each obtained from Ventron Co. and they differed only in preliminary treatment. Sample #3 was obtained by precipitation from tetrachloropalladous acid with hydrazine, and was dried in air at 400 K. The Pd/γ-Al_2O_3 sample was the one already studied in this laboratory [10]. These samples were deposited on a thin wafer of a porous glass and subsequently placed in the holder of an X-ray diffraction camera which permitted X-ray diffractometric examination under controlled atmosphere. All measurements were done at room temperature. Hydride transformations were effected by alternately flowing hydrogen (to form the hydride) and flushing it with helium (to decompose the hydride). The Fourier method [11] was used to calculate mean particle size

diameter D and strains $\langle \epsilon \rangle_{50}^{1/2}$. For the Pd supported on gamma alumina the recently developed approach [12] for separation of a diffraction peak originating only from metal was used. Palladium filings were used as a standard and for calculations the (111) and (222) reflexes were used.

The results show (table 1) that, independently of the number of hydride transformations and particle size, the strains, as represented by the $\langle \epsilon \rangle_{50}^{1/2}$, are practically identical. Significant decrease of strains are noticed only in the fresh, annealed sample. For the Pd blacks with starting particle sizes of 310 and 290 Å the cycling causes slight lowering of their value. This is not, however, the case for Pd black with starting particle size of 94 Å, where the cycling has no effect. In contrast the Pd supported on gamma alumina exhibits a pronounced particle size decrease after multiple hydride formation-decomposition cycles, in spite of the fact that the starting particle size is much lower than the ultimate one obtained for Pd blacks with large starting particle sizes.

The particle size diameter can also be calculated from measurements of the integral breadths of the diffraction reflexes. Apart from the different meaning of the particle size from this method and the Fourier method (see e.g. [13]) the former one can be used only when the sample is strain-free or when comparisons are made between samples with similar strains. In our case if the particle size of sample #3 really does not change during the cycling the integral half widths of starting and cycled palladium diffraction reflections and corresponding hydride diffraction reflections should differ only as much as the difference of their lattice parameters implies it does. This was indeed found only for sample #3.

It can, therefore, be concluded that the strains induced by hydride formation do not depend on the Pd particle size. The desintegration of particles depends not only on the starting particle size of the metal but also on the form of the sample, i.e. whether the metal is supported or not. The more pronounced effect observed in the case of supported Pd can be explained by interaction of metal with its support (as observed in Pd on silica gel catalytic system [14]) which inhibits free relaxation of stresses in metal particles during hydride decomposition and results in their cracking.

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