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The Magnetic Susceptibility of Dispersed Palladium

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The magnetic susceptibility of palladium black of controlled purity with the average, roentgenographically determined, crystallite size of 50–450 Å and surface area of 44.0–5.8 m^2/g, was investigated at temperatures of 85–290°K. With increasing dispersion of palladium a decrease of paramagnetism, as compared with the massive metal, was found. The results are tentatively associated with occurrence of atomlike electronic states in the highly dispersed metal.

INTRODUCTION

In previous investigations of the structure of palladium catalysts with different oxide carriers (*1*) it was established that at sufficiently high dispersion of supported palladium a decrease of its paramagnetic susceptibility occurs as compared with the massive metal. It should be noted, however, that other authors have described an increase of paramagnetism of highly dispersed metals such as palladium and platinum, both supported and nonsupported (*2*, *3*, *4*).

In this paper the results of magnetic susceptibility measurements are presented for different palladium black samples, for which the crystallite size was roentgenographically determined, and the surface area estimated by the BET method. The analytical control of palladium content and its gaseous contaminations and also the spectral analysis completed the data. In such a material there exists no influence of the carrier substance on the magnetic properties of palladium.

EXPERIMENTAL

The palladium black was precipitated from water solution of palladous chloride with hydrazine or formic acid. The precipitate was washed many times with threefold distilled water and dried in a desiccator over phosphorus pentoxide. The dried powder was transferred into a suitable glass tube, which was sealed to the vacuum apparatus. After evacuation at room temperature and then at 100° at a pressure of 10^{-6} mm Hg, the sample was treated with hydrogen at about 30 mm Hg in order to reduce the partially oxidized surface, and then evacuated again. The treatment with hydrogen and the following evacuation were repeated four times. After the last run the tube with the sample was sealed under high vacuum and preserved for magnetic and other investigations.

The amount of gas desorbed by some samples during their successive sintering at 1000° within 6–10 hr was determined volumetrically, using an adequate, small quartz vessel connected with the measuring burette of the BET apparatus described earlier (*1*). The desorbed gas was identified by the mass-spectrometric method as pure hydrogen. The control of palladium content in the samples was carried out gravimetrically with dimethylglyoxime.

Palladium metal (Heraeus) and reagents of highest purity were used for preparation. The spectral analysis of the final Pd black showed only trace amounts of the following impurities: Rh ($<10^{-2}\%$); Pt, Fe, Si ($<10^{-3}\%$); Mn, Mg, Al, Cu, Ag ($\sim 10^{-4}\%$).

The magnetic susceptibility was measured with the Gouy method in the temperature range 85–290°K at the field strength 3190–13870 Oe, and in some cases compared with

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the Faraday method at room temperature and H = 5790–18 680 Oe. The apparatus described earlier (*1*) was used. The susceptibility of all samples investigated was field-strength-independent within ±1%. The results obtained with the Gouy and Faraday methods agreed within 2%.

The diffractograms were obtained in the range of $2\theta = 30–90°$ with the Hilger diffractometer using CuK_α radiation. The average crystallite size of palladium was determined from the half-maximum breadth of the diffraction line corresponding to the reflecting plane set (100). The Jones corrections for the doublet α_1 and α_2 and for the apparatus line breadth were applied (*5*). The latter was determined by means of quartz powder of the particle size 8–16 μ.

The surface area was determined with the BET apparatus, using nitrogen gas at liquid nitrogen temperature.

RESULTS

Several palladium black samples were obtained with an average crystallite edge D of about 50–450 Å. A highly dispersed palladium black with D below about 100 Å was prepared by reduction of $PdCl_2$ solution with hydrazine at temperatures of −10° to 0°. All samples consisted, after reduction and degassing, of practically 100% Pd and showed on the diffractograms only broadened lines of palladium. The other results are summarized in the Table 1 and Figs. 1–3. The data for a palladium sample sintered at 1000° in vacuum and for a sample of palladium sponge (Johnson & Matthey) previously investigated (*1*) are also given.

The contribution of surface atoms was calculated from the X-ray data, assuming the cubic form of the crystals, and using the following equations:

$$N_{\text{surface}} = 12(D/a)^2 + 2$$

and

$$N_{\text{total}} = 4(D/a)^3 + 6(D/a)^2 + 3(D/a) + 1$$

where the lattice constant of palladium is given by $a = 3.88$ Å. It is much higher than calculated from the surface area according to the relation

$$\frac{N_{\text{suface}}}{N_{\text{total}}} = \frac{S \times M}{S_{\text{at.Pd}} \times N}$$

where S is the surface area of the sample in Å²; $M = 106.7$; $S_{\text{at.Pd}} = 7.53$ Å², surface occupied by a Pd atom on the crystallographic plane (100); and $N = 6.023 \times 10^{23}$. The discrepancies should be ascribed to the microcrystalline structure of the samples, for which the surface is only partially available for nitrogen adsorption.

TABLE 1
PROPERTIES OF PALLADIUM BLACK

Pd sample	Average crystal edge D (Å)	Surface area S (m²/g)	Surface atom contribution calculated from: X-ray data (%)	Surface atom contribution calculated from: surface area (%)	Magnetic mass susceptibility ($\chi \times 10^6$): 85°K	Magnetic mass susceptibility ($\chi \times 10^6$): 290°K	H_2 desorbed at 1000°: (mole/g × 10⁴)	H_2 desorbed at 1000°: n (at. %)
1[a]	≫1000	—	≪1	—	7.70	5.26	—	—
2[b]	520	—	2.2	—	7.64	5.17	—	—
3	450	5.8	2.6	1.4	7.40	5.20	—	—
4	380	5.1	3.1	1.2	7.40	5.05	—	—
5	260	7.2	4.4	1.7	6.80	4.95	—	—
6	160	19.9	7.0	4.7	6.86	4.77	0.91	1.95
7	117	22.0	9.5	5.2	—	4.40	—	—
8	113	28.4	9.8	6.7	5.86	4.30	—	—
9	103	31.0	10.7	7.3	6.02	4.10	1.16	2.48
10	97	31.6	11.3	7.3	5.60	4.09	1.32	2.83
11	88	32.6	12.4	7.7	5.78	4.02	—	—
12	61	37.5	17.4	8.8	5.00	3.57	1.99	4.25
13	50	44.0	20.8	10.4	4.44	3.33	2.24	4.78

[a] Palladium powder obtained by sintering of Pd black at 1000° in vacuum.

[b] Palladium sponge (Johnson & Matthey).

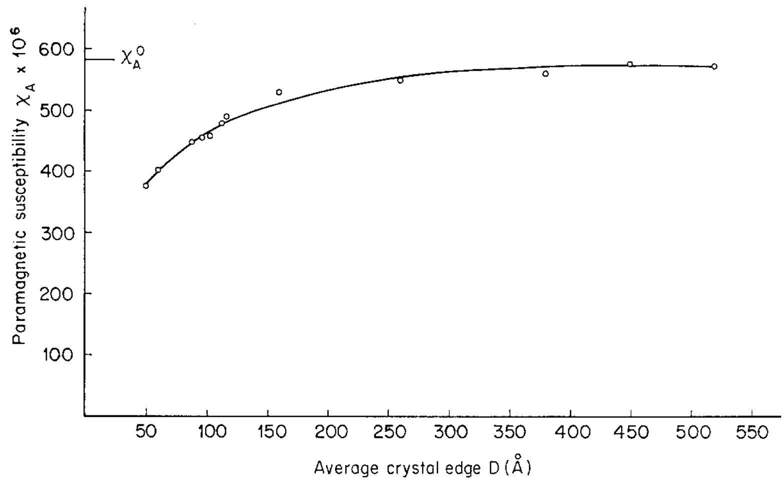

FIG. 1. The paramagnetic susceptibility of palladium black at 290°K

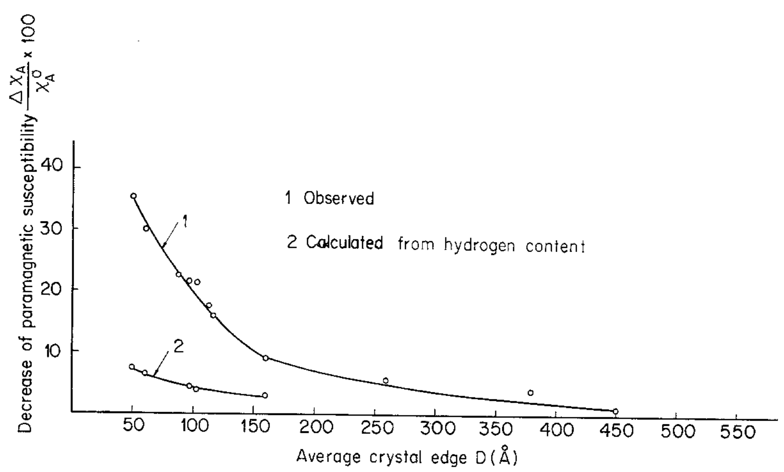

FIG. 2. The percentage decrease of the paramagnetic susceptibility of palladium black at 290°K.

The susceptibilities of samples with the average crystal edge above about 380 Å ($\chi = 7.40$–7.70×10^{-6} at 85°K and 5.05–5.26 $\times 10^{-6}$ at 290°K) are rather close to that of massive palladium (7.55×10^{-6} and 5.27×10^{-6}), reported by Hoare and Matthews (*6*).

With increasing dispersion of palladium its paramagnetism gradually diminishes. Samples of crystal edge decreasing from 160 to 50 Å showed paramagnetic susceptibility per g atom χ_A (after taking into account the diamagnetic correction -20×10^{-6}) from 458×10^{-6} to 376×10^{-6} at 290°K (Fig. 1), which was by 9% to 35% lower in comparison with the value of $\chi_A{}^0 = 581 \times 10^{-6}$ determined for the sintered palladium (Fig. 2).

The gas desorbed from these samples at 1000° consisted only of pure hydrogen, as was determined mass-spectrometrically. The amount of hydrogen desorbed was 1.95–4.78 at. %, which corresponds only to about 40% of the monatomic layer, following from surface area, and to about 20% of the monatomic layer, resulting from X-ray data. Sintered samples, after desorption experiments, showed the precisely normal lattice constant 3.88 Å and susceptibilities which were close to that of massive metal (sample

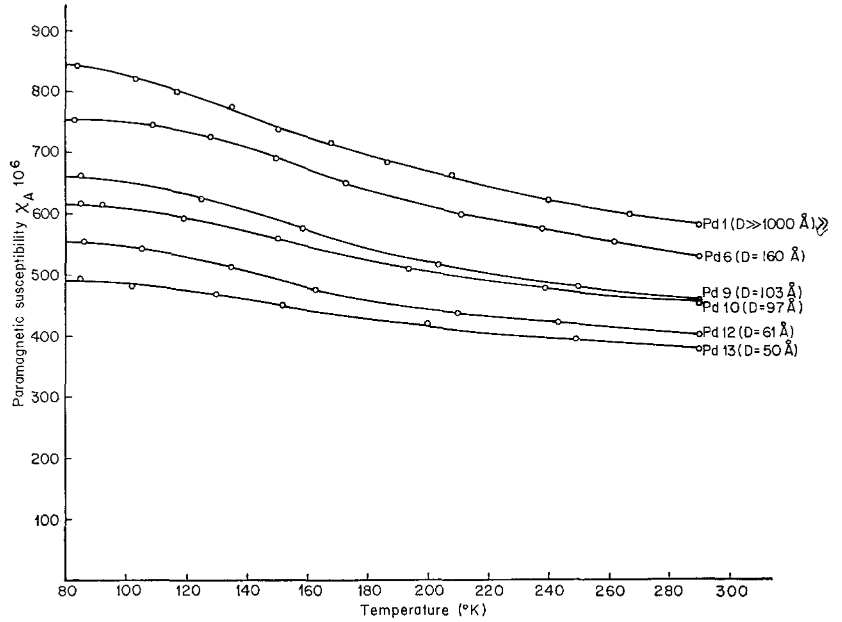

FIG. 3. The temperature dependence of the paramagnetic susceptibility of some palladium black samples.

No. 1), pointing to the practically complete removal of gaseous contaminations from the metal.

The decrease of the paramagnetic susceptibility of samples with $D < 160$ Å, resulting from hydrogen content, $\Delta\chi_A/\chi_A{}^0 \times 100$ calc. $= (n/65) \times 100$ (n is hydrogen concentration in atom percent), should not exceed 3.0–7.4%. These values were calculated by assuming 0.65 electron holes per Pd atom in the pure metal, in which one electron hole is destroyed by one atom of occluded or adsorbed hydrogen, accompanied by the linear decrease of palladium paramagnetic susceptibility, known in the literature for the massive metal (*7*). It is evident (Fig. 2), that the change of paramagnetic susceptibility, resulting from hydrogen content and calculated according to the above assumptions, would be only about 20% of the observed decrease.

DISCUSSION

The investigations presented show that the magnetic properties of highly dispersed palladium black with an average crystal edge of about 50 to 160 Å do not correspond to the properties of the massive metal. With decreasing crystallite size or increasing surface area of palladium the gradual diminution of its paramagnetic susceptibility occurs.

It has already been suggested (*1*), that the influence of high dispersion on the magnetic properties of palladium may result from different electron distribution within the isolated atoms in comparison with the metal. The atoms have the closed electronic shell $4d^{10}$ and are diamagnetic. For the metal the configuration $4d^{9.4}5s^{0.6}$ is assumed and its strong paramagnetism is attributed to about 0.6 electron holes per P*d* atom in the *d* band.

The experimental results might be explained if one assumes that with increasing dispersion of palladium its electronic structure approaches gradually the structure of isolated atoms. The occurrence of atomlike electronic states in highly dispersed palladium might be associated with different factors such as: (1) the presence of extremely small particles, in which the overlapping of energy bands does not approach the same extent as in the massive metal; (2) the large number of different defects and irregularities of crystal lattice, affecting the change of interatomic distances and also the electron distribution within the atoms, as should be expected from considerations of Goodenough (*8*); (3) the large fraction of surface atoms with different electronic characteristics as compared with the atoms in the three-dimensional lattice. It should also be noted, that the contribution of hydrogen remaining in the samples after evacuation was considered on the basis of magnetic properties of the system: massive metal–hydrogen. This assumption cannot be accepted without ambiguity. The diminution of palladium paramagnetism under the influence of hydrogen may be associated not only with the electronic interaction between hydrogen and palladium but also with the change of electron distribution within Pd atoms, resulting from the spreading of these atoms, since the lattice constant of β-phase Pd–H equals 4.02 Å. This effect may be more significant if the nuclei of β phase were formed in the surface layer of highly dispersed palladium rather than in the massive metal.

Finally it must be noted that the results presented do not confirm the effect of increased paramagnetism of dispersed palladium described by Reyerson and coworkers (*3*). According to these authors the sample of palladium reduced with hydrogen *in situ* and degassed, with an average crystallite size of 134 Å and a surface area of 32.7 m^2/g, presents a mass susceptibility of 12.0×10^{-6} at room temperature, which is 2.34 times higher than that of the massive metal. The authors have interpreted their results, extending the discussion of Hulburt (*9*) based on the Tamm surface states theory. According to the calculations following from this discussion, one could expect a deep minimum of the paramagnetic susceptibility of palladium at an average crystal edge about 180 Å and its sharp maximum at a crystal edge of about 95 Å. The results presented show that the susceptibility of highly dispersed palladium decreases continuously with decreasing particle size and therefore the calculations of the authors cited could not be confirmed in the whole crystallite size region investigated.

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