The Magnetic Susceptibility of Small Palladium Particles

S. LADAS, R. A. DALLA BETTA, AND M. BOUDART[1]

Stauffer Laboratories of Chemistry and Chemical Engineering, Stanford, Califorina 94305

The magnetic susceptibility, κ, of small Pd particles supported on silica gel and alumina has been studied at 150 and 298 K as a function of metal dispersion, D, over a range of 0.1 to 0.8. As ferromagnetic impurities prevented the correct measurement of κ, a new method was developed which is based on the known observation that exposure of the samples to 30 kPa of H_2 for 1800 s at both 150 and 298 K masks the major fraction of the paramagnetic susceptibility of Pd. Values of this quantity, denoted as κ_{sp} decrease linearly with increasing D at both 150 and 298 K and can be extrapolated to a temperature independent value at complete dispersion ($D = 1$). This value is considered to be a surface susceptibility as it is found to be equal, for all samples, to $\Delta\kappa_{sp}/D$ where $\Delta\kappa_{sp}$ is the difference of κ_{sp} for samples without and with a monolayer of chemisorbed hydrogen.

INTRODUCTION

Supported metal catalysts frequently possess a high degree of metal dispersion, D, defined as the fraction of metal atoms exposed. As D increases a point is reached at which most of the metal atoms in a small particle exist at the surface. It is expected that some of the properties of such extremely small metal particles, e.g., their magnetic susceptibility, κ, may be significantly different from those of the bulk metal.

In fact, measurements of κ/ρ of finely dispersed Ni, Pd, and Pt have been reported by several groups of workers. Carter and Sinfelt (1) studied the susceptibility of silica-supported nickel in the paramagnetic region and found it to decrease markedly with increasing D. The decrease resulted from a decline in both the paramagnetic Curie temperature and magneton number. The authors attributed this effect at least

in part to differences in the electronic structure of surface atoms and atoms in the bulk, but they did not elaborate. Recently, Marzke et al. (2) measured the κ/ρ of small Pt crystallites 2.2 nm in size from 1.5 to 200 K. They found that the κ/ρ of the microcrystals was nearly as temperature-independent between 85 and 200 K as that of massive Pt, but with a value 2.5 times smaller than that of the massive metal. From 85 to 1.5 K, κ/ρ increased according to a Curie Law behavior and finally exceeded that of massive Pt. The authors explained their results in terms of the "quantum size effect" theory first proposed by Kubo (3) and further developed by Denton et al. (4).

Palladium is a well-suited metal for κ measurement because it exhibits the strongest paramagnetism among the nonferromagnetic transition metals. At 298 K massive Pd has a dimensionless susceptibility equal to 7.9×10^{-4}. This value is the sum of a small diamagnetic contribution

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estimated to be -3×10^{-5} and the Pauli spin susceptibility κ_{sp} equal to 8.2×10^{-4}. The latter arises predominantly from the d-band structure of the metal and is temperature-dependent (5). The dimensionless susceptibility is the product of the usually reported κ/ρ and the density ρ. The SI system and rationalized units are used throughout this paper to report the magnitude of magnetic and other quantities.

Values of κ/ρ measured as a function of the degree of dispersion for both supported and unsupported Pd can be found in the literature (6–9), but the data contradict each other as shown in Table 1. In the earliest work for silica-supported Pd, the value of D was not determined, but pre-presumably decreasing metal loading for samples prepared by impregnation under identical conditions led to higher dispersion. Table 1 reveals that two groups of investigators have found κ of supported or unsupported Pd to increase anomalously with increasing dispersion, whereas two other groups have found κ to decrease gradually below its value for massive Pd. This discrepancy motivated us to investigate further the magnetic susceptibility of highly dispersed palladium.

At first, a measurement on a Pd/SiO_2 sample with $D = 0.76$ resulted in a value of κ of Pd four times higher than that of massive Pd in agreement to the results of Reyerson and Solbakken (6). The magnetic susceptibility of the supported metal was obtained from the total susceptibility of the sample corrected for the diamagnetism of the support by means of a blank experiment. A closer look into the variation of κ with magnetic field and determination of the ferromagnetic impurities in the sample suggested that the high values of κ might be an artifact due to the Pd-catalyzed reduction of the impurities to the metallic state.

The catalytic effect of supported Pd on the reduction of minute amounts of iron native in commercial silica gel was first substantiated by Sancier and Inami (10). These authors observed by means of ESR that hydrogen treatment of silica gel at 970 K cannot reduce iron impurities to the metallic state, but the presence of supported Pd makes this reduction possible at

TABLE 1

Susceptibility κ of small Palladium Particles

Investigator and reference	Sample	Reduction treatment	Out-gassing	Suscepti-bility measured as function of:	Tempera-ture of experiment (K)	Behavior of ratio κ/κ_{bulk}
Reyerson and Solbakken (6)	Pd/SiO₂ by impregnation	473 K, flowing H₂	10⁻⁴ Pa 473 K	Pd loading, 16.0 to 0.4 wt%	298	Oscillating between 1 and 4
Trzebiatowski and Kubicka (7)	Pd/SiO₂ by impregnation	— Flowing H₂	10⁻⁴ Pa —	Pd loading, 7.0 to 1.5 wt%	298	Monotonic decrease 1 to 0.65
Zuehlke (9)	Pd powder	343 K, in H₂	10⁻⁴ Pa 343 K	Particle size, 55 to 10 nm	293	Oscillating between 0.6 and 2.2
Kubicka (8)	Pd powder	373 K, in 40 kPa of H₂	10⁻⁴ Pa 373 K	Particle size, 55 to 5 nm	85 to 190	Monotonic decrease 1 to 0.65 at 290 K

even lower temperature. The same effect was observed by Garten and Ollis (11) by means of Mössbauer spectroscopy of iron deposited on Al_2O_3 in the presence of supported Pd. In addition, these authors found evidence of Fe–Pd bimetallic clusters. This has been further confirmed in a recent paper by Garten (12).

In the present study, we first demonstrated the spurious effect of ferromagnetic impurities on the measured κ of supported Pd. Then we developed a new method to obtain what will be defined later as the spin susceptibility κ_{sp} of Pd even in the presence of small amounts of metallic ferromagnetic impurities. This method was used to measure κ_{sp} of silica- and alumina-supported Pd with a metal dispersion between 0.11 and 0.80.

EXPERIMENTAL

Apparatus and procedure. The magnetic measurements were made using the Faraday method. The powdered sample was suspended from a Cahn electrobalance, sensitive to 1 μg, in a quartz bucket located midway between the pole faces of a model V4007 Varian electromagnet. The bucket weighed about 100 mg and the sample about 500 mg. The electrobalance was attached to a vacuum manifold so that the sample could be outgassed at 10^{-4} Pa and treated *in situ* in both static and flowing purified gases at temperatures from 85 to 770 K. The electrobalance measures the force F exerted on the sample by the magnetic field of strength H. The dimensionless magnetic susceptibility κ is determined from

$$\kappa = \frac{F\rho}{\mu_0 m H (dH \ dz)} \tag{1}$$

where m is the mass of sample, ρ is the density, dH/dz is the field gradient, z is the vertical distance from a horizontal reference line between the pole faces and $\mu_0 = 4\pi \times 10^{-7}$ J m^{-1} A^{-2}. Since the density of the samples was not known exactly, κ/ρ

was actually measured. Specially designed pole caps obtained from Varian Associates gave a constant value of $H(dH/dz)$ over the sample region. The apparatus was calibrated using ferrous ammonium sulfate hexahydrate as standard susceptibility material. Magnetic field strength at the sample position up to 3.0×10^5 A m^{-1} was attainable in the apparatus. Prior to measurements the samples were evacuated overnight at 400 K and reduced in flowing hydrogen (2 cm^3 s^{-1}) for about 10^4 s at the highest pretreatment reduction temperature. Then, they were outgassed at the reduction temperature and 10^{-4} Pa to remove absorbed and adsorbed hydrogen and finally cooled to the temperature of measurement. Hydrogen was purified by passage through a Deoxo converter and a molecular sieve trap cooled by liquid nitrogen. The value of κ/ρ of each sample was measured at five different values of H at the sample position from 3.0×10^5 to 1.5×10^5 A m^{-1}. To correct for the diamagnetism of the bucket, blank measurements were made with the empty bucket over the whole range of temperature and field strength and in the various gaseous atmospheres employed for the samples.

Samples. Three different kinds of silica gel were used to make the Pd samples studied in this work. They are designated as supports A, B, and C. Support A was Cabosil HS-5 obtained from Cabot Corporation. Support B was silica gel (grade 950) obtained from Davison Chemical Co. Support C was obtained from B by a special cleaning treatment designed to lower the iron impurity content. In this treatment B was boiled in 5 N HCl, then washed with an aqueous solution of NH_4SCN and finally rinsed thoroughly with distilled water until no Cl$^-$ or SCN$^-$ could be detected in the wash. By this procedure iron content was lowered from 10 ppm in B to about 5 ppm in C, with respect to total amount of sample, i.e., metal plus support.

TABLE 2

Purity of Samples

Sample No.	Support[a]	Precursor preparation method[b]	Precursor pretreat- ment method[b]	Palladium loading (wt%)	Impurity content (ppm with respect to Pd only)		
					Fe	Co	Ni
1	A	IE	DR	3.1	61	1220	3050
2	A	IMP₁	DR	2.1	1350	1800	4500
3	C	IE	DR	3.0	380	190	506
4	C	IMP₁	DR	2.4	950	237	632
5	C	IMP₂	CR	2.0	500	300	800
6	C	IMP₂	DR	2.9	340	430	1160
7	B	IE	OR	2.4	5500	237	632
8	Al₂O₃	—	—	4.2	1350	—	—
9[c]	—	—	—	—	40	120	320

[a] A, SiO₂, Cab-O-Sil HS-5; B, SiO₂, Davison (grade 950); C, acid-washed B.
[b] IE, ion exchange; IMP₁, impregnation by aq. Pd(NH₃)₄Cl₂; IMP₂, impregnation by aq. PdCl₂; DR, direct reduction; CR, calcination–reduction; OR, oxidation–reduction.
[c] Pd powder.

Nine different samples were studied in this investigation, and they are listed in Table 2. Samples 1 through 7 were silica-supported Pd samples prepared in our own laboratory. The precursors of samples 1, 3, and 7 were prepared by cation exchange. The method has been described (13). The precursors of samples 2, 4, 5, and 6 were prepared by impregnation of silica with aqueous solutions of $Pd(NH_3)_4Cl_2$ or $PdCl_2$. After preparation the precursors were dried in vacuo at 400 K and then pretreated to reduce the Pd. Two main pretreatment variations were employed: either direct reduction in flowing hydrogen at 573 K or calcination in air at 800 K followed by hydrogen reduction at 720 K. Sample 7 was first oxidized in oxygen at 650 K and then reduced in flowing hydrogen at 573 K. Further details on the preparation and pretreatment of the samples can be found elsewhere (14). Sample 8 was alumina-supported Pd obtained from Engelhard Industries Inc. (Lot No. 19638). This sample was directly used for the experiments after reduction in flowing hydrogen at 653 K and outgassing for 10^4 s at 10^{-4} Pa and 653 K. Sample 9 was commercial Pd powder from Engelhard Industries Inc. (Lot No. 19722). The powder was directly used for the experiments after reduction in flowing hydrogen at 673 K and outgassing for 10^4 s at 10^{-4} Pa and 673 K.

The Pd content of the samples was determined by analysis and varied between 2 and 4.2% w/w. The impurity content was also determined by analysis and is given in Table 2 normalized with respect to Pd content only. The dispersion of Pd in samples 1 through 8 was determined by the hydrogen backsorption method developed by Benson et al. (15). For the adsorption measurements, hydrogen was purified by passage through a Pd thimble (space velocity, 1.0 s^{-1}). Oxygen was purified by passage through a Dry-ice–acetone-cooled molecular sieve trap (space velocity, 1.0 s^{-1}). The specific surface area of the Pd powder was determined after susceptibility measurement by the BET method using N_2 as the adsorbate. It was found to be less than 2 m^2 g^{-1} corresponding to a dispersion less than 0.01. The diamagnetic susceptibility of the silica blanks was found to be constant for each sample to within less than 1% independent of H, T, and gaseous
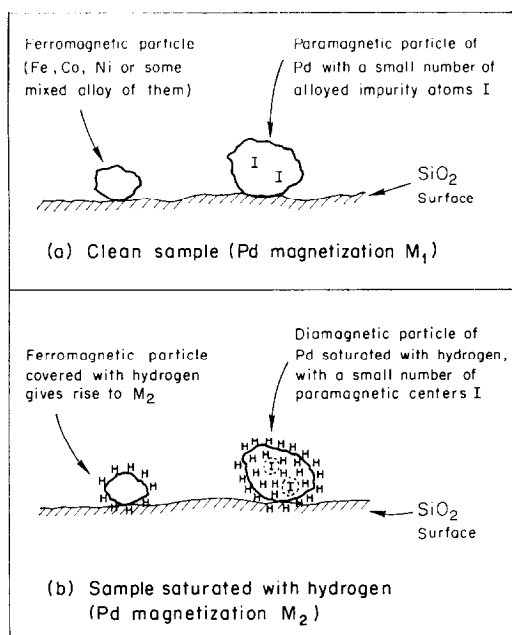
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FIG. 3. Schematic representation of Pd supported on SiO_2.

remained unchanged on prolonging exposure to hydrogen up to a few hours or increasing the hydrogen pressure to 101.3 kPa. The main characteristic of M_2 is that it flattens out at the highest H values. Curve M_{1-2}, obtained by subtracting M_2 from M_1, was for all samples a straight line through the origin. We claim that the slope of this curve gives the spin susceptibility, κ_{sp}, of our Pd particles possibly enhanced by a negligible amount due to impurities of Fe, Co, or Ni *alloyed* into these particles.

To explain this claim, let us consider a schematic representation of the samples (Fig. 3). The flattening of M_2 is characteristic of the presence of some ferromagnetic substance in the sample. This corresponds to the ferromagnetic particle of Fig. 3. The small residual slope of M_2, approximately $0 \pm 3 \times 10^{-5}$, suggests that within experimental uncertainty saturation of the samples with hydrogen completely masked the paramagnetism of the small Pd particles. This is a well-known fact for massive Pd *(16)* and arises from the interaction of

dissolved hydrogen with the d-holes of the metal. As a result of this interaction, the major fraction of the paramagnetic susceptibility of Pd vanishes. This fraction will be called the spin susceptibility of Pd, κ_{sp}. The diamagnetism of Pd arises from the interaction of the field with inner core electrons and is not affected by hydrogen sorption. The diamagnetic susceptibility of both Pd and hydrogen is of the order of magnitude of our experimental uncertainty. The interesting observation here is that hydrogen affects the spin susceptibility of Pd particles with as many as 80% of the atoms at the surface in the same way as it does that of massive Pd. In the case of the small Pd particles the effect is brought about by hydrogen both adsorbed on the surface and dissolved in the bulk.

The fact that M_{1-2} is a straight line through the origin shown that saturation of the sample with hydrogen nulls the spin susceptibility of Pd particles, but does not affect substantially the magnetization of the ferromagnetic particles. The question now is whether M_{1-2} represents only the spin magnetization of Pd or there is some additional paramagnetic contribution to it. It is possible that some, if not all, of our small Pd particles contain a few alloyed impurity atoms like Fe, Co, or Ni. These are designated as I in Fig. 3. From bulk studies it is known that alloys of Pd with about 1 at% or less of Fe, Co, or Ni behave paramagnetically above 50 K *(17)*. The alloys exhibit an enhanced paramagnetic susceptibility compared to pure Pd. It has been found *(18)* that a giant paramagnetic moment of about 11 Bohr magnetons (m_B) at 100 K was associated with each Fe atom in a 1-at% Fe–Pd alloy. This giant moment decreased with increasing temperature and became about 6 m_B at 298 K. In contrast, the atomic paramagnetic moment of pure metallic iron above the Curie point is 3.5–4 m_B. Dilute alloys of Fe in Pd absorb hydrogen at amounts comparable to those absorbed by pure Pd. The spin suscepti-

bility of these alloys has been found to decrease linearly with increasing hydrogen content down to a residual value depending on the Fe content (19). The paramagnetic moment of Fe in the hydrogen saturated alloy is 3.5–4 m_B. The disappearance of the giant moment could manifest itself in our case by making M_{1-2} somewhat larger than the true spin magnetization of Pd particles. Such enhancement could also arise from alloyed Co or Ni and can be estimated from data in reference (17) if the amount of alloyed impurity is known. This enhancement is indeed negligible as discussed below.

An extension of the method just described was also used to measure the contribution of surface Pd atoms to the spin susceptibility of the particles at 298 K. This was done as follows. Following exposure to 30 kPa of hydrogen at 298 K the samples were outgassed at 10^{-4} Pa for about 1800 s. Then another M vs H curve was obtained in the same way as M_1 and M_2. Subtraction of this new curve from M_1 resulted in all cases in a straight line through the origin

designated as M_3 in Figs. 1 and 2. Benson et al. (15) have found that absorbed hydrogen in the β-phase Pd hydride could be removed readily by outgassing supported Pd samples for 1200 to 1800 s at 298 K and 10^{-4} Pa. Hydrogen adsorbed on the surface was not significantly removed under these conditions. Therefore M_3 represents the loss of paramagnetism of our supported Pd particles due to hydrogen adsorption on their surface. The slope, $\Delta\kappa_{sp}$, of M_3 is then the contribution of the surface Pd atoms to the total spin susceptibility of the supported particles.

RESULTS

The results of this investigation are summarized in Table 3. The dispersion of the supported samples varied between 0.11 and 0.80. This corresponds to an average particle size between 9 and 1.2 nm. The palladium powder sample had a very low dispersion and was used to check the κ value of massive Pd given in the literature (5). The values of κ_{sp} of Pd at 150 and 298 K

TABLE 3

Summary of Results

Temperature (K)	Sample No.	Sample description[a]	D[b]	d (nm)	$\kappa_{sp} \times 10^{4c}$	$\Delta\kappa_{sp} \times 10^{4c}$
298	1	3.1% Pd/A	0.81	1.2	6.0	4.4
	2	2.1% Pd/A	0.11	9	8.1	0.6
	3	3.0% Pd/C	0.76	1.2	6.2	4.2
	4	2.4% Pd/C	0.11	9	8.1	0.6
	5	2.0% Pd/C	0.80	1.2	6.0	4.4
	6	2.9% Pd/C	0.49	2	6.6	2.6
	7	2.4% Pd/B	0.75	1.2	6.0	—
	8	4.2% Pd/Al₂O₃	0.21	4.5	7.6	1.1
	9	Pd powder	<0.01	>100	8.2[d]	—
150	3	3.0% Pd/C	0.76	1.2	6.5	—
	4	2.4% Pd/C	0.11	9	9.9	—

[a] A, SiO₂, Cab-O-Sil; B, SiO₂, Davison (grade 950); C, acid-washed B.

[b] Experimental uncertainty ±0.05.

[c] Experimental uncertainty ±3 × 10^{-5}.

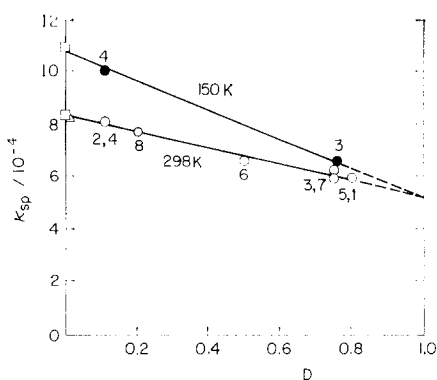[d] Experimental uncertainty ±6 × 10^{-6}.

FIG. 4. Spin susceptibility κ_{spin} of Pd vs dispersion D (numbers refer to samples in Table 2). $\bigcirc$, 150 K, supported samples; $\bullet$, 298 K, supported samples; $\square$, reference (5), bulk Pd; $\triangle$, this work, Pd powder, sample 9.

listed in Table 3 were obtained from the slope of straight line M_{1-2}. It is worth noting that samples with the same dispersion have very reproducible values of κ_{sp} although the method of preparation and precursor pretreatment of each sample was quite different. This reproducibility also suggests that there is no appreciable enhancement of the true κ_{sp} of Pd due to alloyed impurities. From the data of Gerstenberg (17) the expected enhancement is estimated to be less than 3% if the atomic concentration of alloyed impurity is less than the following: 600 ppm at 298 or 300 ppm at 159 K for Fe or Co, and 4000 ppm at 298 or 1000 ppm at 150 K for Ni. By inspection of the series of highly dispersed samples 1, 3, 5, and 7 one can see that κ_{sp} remains constant although the total amount of impurities varies significantly from sample to sample. This indicates that most of the impurities are not alloyed into Pd, probably because only the part of the impurities which is on the surface of the support has a good chance of being reduced and alloyed. An upper limit of the possible alloyed amount is the minimum concentration of each impurity in the series of samples 1, 3, 5, and 7. From Table 2 this can be found to be: 60 ppm of Fe, 190 ppm

of Co, and 500 ppm of Ni. These numbers are also good for the rest of the samples which have less chance of undergoing impurity reduction due to the low dispersion of Pd. From the above it can be concluded that within less than 3%, κ_{sp} in Table 3 is the true spin susceptibility of Pd in our samples. This susceptibility is plotted in Fig. 4 vs dispersion at 150 and 298 K. The experimental points for all samples fall on two straight lines, one at each temperature. These lines pass through the literature values of κ_{sp} for massive Pd when they are extrapolated to zero dispersion. The value of κ_{sp} of the massive metal at 298 K obtained directly from measurement on sample 9 also agrees with the literature value for bulk metal. Since the latter was obtained by Hoare and Matthews (5) after subtracting a calculated diamagnetic contribution to the total measured κ, the agreement supports our definition of κ_{sp} as the major fraction of the paramagnetic susceptibility of Pd. Note also (Fig. 4) that the strong increase of κ_{sp} with decreasing temperature observed in the massive metal becomes less pronounced as dispersion increases. Actually, there is almost no change in κ_{sp} between 150 and 298 K for the 80% dispersed Pd samples. The contribution of surface Pd atoms to the total κ_{sp} of the supported particles, designated as $\Delta\kappa_{sp}$ is plotted vs dispersion in Fig. 5. The experimental points fall nicely on a straight line through the origin.
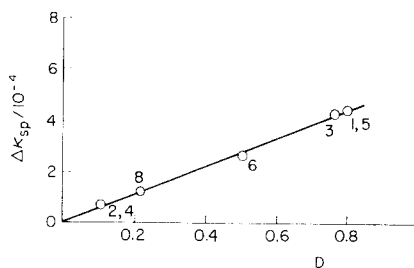

FIG. 5. Difference in spin susceptibility, $\Delta\kappa_{spin}$, without and with a monolayer of chemisorbed hydrogen vs dispersion D, at 298 K.

DISCUSSION

Experimental Method

An important observation of this work is that small amounts of iron impurity can be reduced into the metallic state under the relatively mild conditions employed for the preparation of our supported Pd samples. Iron impurities are almost ubiquitous in most commercial supports. Thus their possible catalytic effect as a result of a reduction in the presence of supported noble metals must be taken into account. This is the first conclusion of the present investigation. The reduction of iron and possibly other ferromagnetic impurities was shown to result in anomalously high values of the measured magnetic susceptibility of silica- or alumina-supported palladium. A new method to extract the spin susceptibility of Pd from the impurity affected measurements has been discussed in detail in this paper. The usefulness and limits of applicability of the method arise directly from that discussion. As long as ferromagnetic metals are present in sufficiently small amounts to assure linearity of M_{1-2}, one can obtain the κ_{sp} of Pd and its dilute paramagnetic alloys with these metals at high dispersion on any support as well as in the form of metal powder.

Spin Susceptibility: Surface and Bulk

The main feature of the results is the observed variation of the spin susceptibility of small Pd particles with dispersion. As the latter increases from about zero to 0.80, κ_{sp} decreases linearly below its value for the massive metal at both 150 and 298 K. Although the decrease is rather mild as compared to that reported for supported Ni and Pt ($1, 2$), it demonstrates that the paramagnetic behavior of highly dispersed Pd is less than that of bulk Pd as intuitively expected since individual atoms of palladium are diamagnetic. The results of this work are in qualitative agreement

to those of Trzebiatowski and Kubicka (7). A quantitative comparison cannot be made because the investigators did not measure the dispersion of Pd in their samples. The same trend of κ_{sp} with D was also observed by Kubicka (8) for Pd powders. It is worth noting that Kubicka's is the only work where the effect of iron impurities on the results can be excluded on the basis of the reported concentration of iron in the samples (10 ppm). The smallest particle size of unsupported Pd studied by Kubicka (8) was 5 nm corresponding to a dispersion of about 0.2. The κ_{sp} value for that size was 5.3×10^{-4} at 290 K compared to 7.6×10^{-4} at 298 K found in this work. The difference can be attributed tentatively to incomplete reduction of Kubicka's samples because the reduction conditions used in her work were not severe enough.

Our results disagree completely with those of Reyerson and Solbakken (6) and Zuehlke (9). We consider the anomalously high Pd susceptibility reported by these authors an artifact due to minute amounts of ferromagnetic impurities reduced in the presence of Pd and not taken into account by the authors.

The observed decrease of κ_{sp} with increasing dispersion reflects a change of electronic properties of Pd particles. This change could be partly due to an influence of the support on the electronic structure of the finely dispersed metal. The fact that the measured κ_{sp} and $\Delta\kappa_{sp}$ of alumina supported Pd (sample 8) fall on the same straight lines with those of the silica supported samples indicate that the support does not affect significantly the susceptibility of the particles. The support effect is also made unlikely by a recent study of the catalytic hydrogenation of cyclohexene in the liquid phase on Pd/SiO_2 samples similar to those used in this work. It was found that the rate of reaction did not change with dispersion of Pd in the same range of dispersion (20). This eliminates not only structural effects due to change in

size of the metal particles but also effects due to interaction with the support.

Two alternative interpretations of the observed decline of κ_{sp} as particle size decreases have been alluded to in the Introduction. One of them invokes a "quantum size effect" theory (3, 4), according to which κ_{sp} decreases below some particle size because the spacing between electronic level increases as particle size decreases. The size for this effect is of the order of a few nanometers and varies from metal to metal and also with temperature. The second interpretation views the decrease of κ_{sp} as a simple "surface effect" according to which the surface atoms have a lower value of κ_{sp} than those in the bulk.

In our work, the linear decrease of κ_{sp} and the linear increase of $\Delta\kappa_{sp}$ with increasing dispersion suggest a surface effect. Quantitatively, the slope of the line $\Delta\kappa_{sp}$ vs dispersion should be the average κ_{sp} value for the surface atoms. This value is $(5.5 \pm 0.3) \times 10^{-4}$, from Fig. 5. But in Fig. 4 one can see that both straight lines, extrapolated to complete dispersion $(D = 1)$, pass through a κ_{sp} value of about 5.4×10^{-4}. This remarkable agreement indicates that the observed gradual decrease of κ_{sp} with increasing dispersion is due to the surface atoms exhibiting a lower κ_{sp} than the bulk. This "surface susceptibility" has a value of about 5.5×10^{-4} at 298 K and seems to remain the same at 150 K.

No theoretical explanation of the "surface susceptibility" will be attempted here. It is an interesting experimental observation which will hopefully prove useful and challenging to theoreticians working on the electronic properties of metal surfaces or small metallic clusters of catalytic interest.

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