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AN EXAFS STUDY OF THE INFLUENCE OF THE METAL PARTICLE SIZE, NATURE OF SUPPORT, AND ADSORPTION OF H_2 AND CO ON THE STRUCTURE OF PALLADIUM CATALYSTS

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Regardless of the nature of the support (SiO_2, C) and the size of the Pd metal particles (19–108 Å), the Pd-Pd interatomic distances are close to those for the bulk metal. Adsorption of CO does not change the structure of the Pd particles, while H_2 adsorption at 25 °C leads to an increase of 5–7% in the Pd-Pd distance, evidently as a result of the formation of bulk palladium hydride.

The catalytic activity of palladium, supported on SiO_2, Al_2O_3, and C, in the gas-phase hydrogenation of vinylacetylene is constant over a wide range of metal particle size (30–180 Å). On decreasing the particle size from 30 Å to 10 Å, however, the specific catalytic activity falls by almost an order of magnitude [1]. In order to clarify the reasons for the lower activity of highly dispersed supported palladium particles, in the present paper we present results on their structural properties as studied by the EXAFS method.

The samples were prepared by interaction of $C_3H_5PdC_5H_5$ with the surface hydroxyl groups of SiO_2 (300 m^2/g) and carboxyl groups of a wide pore carbon support (600 m^2/g) with graphitic structure, according to the method described in ref. [1]. Different Pd particle sizes were obtained by pretreating the samples in an atmosphere of O_2 and H_2 at temperatures in the range 100–600 °C. Pd K-edge adsorption spectra were collected on the spectrometer on the VEPP-3 storage ring at the Institute of Nuclear Physics, Siberian Branch of the USSR Academy of Sciences. The spectra were analysed in the interval 3.8–15.0 $Å^{-1}$ according to the method described in ref. [2]. A cubic spline function was used to subtract off the smooth part of the absorption coefficient, spectra, and Fourier analysis of the EXAFS spectra was carried out. The first interatomic distances R_1 were determined by comparison with the reference sample, namely bulk Pd metal

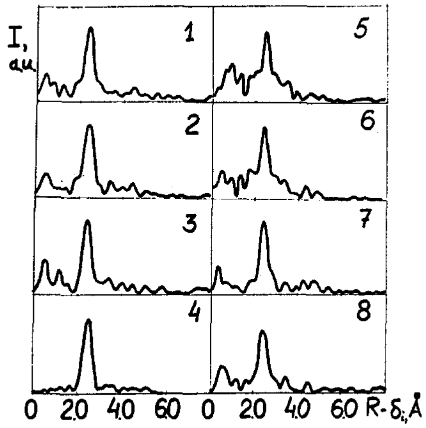

Fig. 1. Atomic radial distribution curves for supported palladium. The number of the curves corresponds to the sample numbers in table 1.

($d = 3.89$ Å, $R_1 = 2.74$ Å). The amplitude of the maxima, corresponding to subsequent coordination spheres is comparable to the noise level, and therefore they were not considered further in this work. The accuracy in the determination of the peak positions is ±0.04 Å. The Pd-Pd phase shift correction, experimentally determined from the spectrum of bulk Pd, is 0.23 Å.

For all the atomic radial distribution curves, obtained by Fourier transform of the fine structure, coordination maxima are present at $(r - \delta) \approx 2.5$ Å (fig. 1). Taking account of the phase shift correction, the position of this maximum at 2.70 ± 0.04 Å is close to the radius of the first coordination sphere in the Pd lattice. On changing the metal particle size in Pd/SiO_2, by reducing in H_2 and evacuating at 300 ° C, it is seen that for particles in the range 19–38 Å, the Pd-Pd interatomic distance hardly changes (fig. 1, curves 1–3), and remains close to that

Table 1
The dependence of the radius of the first coordination sphere of Pd (Å) on the metal particle size, the nature of the support, and the pretreatment conditions.

Sample number	Catalyst composition (wt%)	$\bar{d}_S$ (Å)	Vacuum (300 ° C)	H_2 (250 ° C)	CO (250 ° C)
1	2.2% Pd/SiO_2	19	2.70	2.87	2.72
2	2.2% Pd/SiO_2	27	2.66	2.80	2.72
3	1.6% Pd/SiO_2	38	2.68	2.80	2.70
4	Pd foil	∞	2.74	–	–
5	1.9% Pd/C	19	2.74	–	–
6	3.3% Pd/C	23	2.70	–	–
7	1.9% Pd/C	26 [a]	2.68	2.89	2.72
8	1.9% Pd/C	108 [a]	2.70	2.84	2.72

[a] Average Pd particle size determined by electron microscopy; all remaining $\bar{d}_S$ are determined by H_2 titration [1].

for bulk Pd (fig. 1, curve 4). Similar results are obtained for Pd/C; on changing the metal particle size in the range 19–108 Å, the Pd-Pd distance shows little variation and also remains close to that for the bulk (fig. 1, curves 5–8). The most highly dispersed samples 5 and 6 are characterised by a lower signal/noise ratio and are evidently not fully reduced.

Treating samples 1–3 and 7, 8 in H_2 at 250 °C, with subsequent cooling in a H_2 atmosphere to 25 °C ($p_{H_2} = 370$ Torr), is accompanied by an increase in the atomic distance to 2.84 ± 0.04 Å (table 1). This increase takes place, evidently, as a result of the solution of hydrogen in the bulk of the metal particles, forming a palladium hydride phase. In accordance with [3], the final conditions of H_2 adsorption (25 °C, $p = 370$ Torr) are thermodynamically favourable for the formation of bulk palladium hydride. On the other hand, treatment of these samples in CO at 250 °C with subsequent cooling under CO to 25 °C ($p_{CO} = 370$ Torr) hardly changes the Pd-Pd distance, as compared to the values for samples simply evacuated at 300 °C (table 1). From this result, we conclude that even at 250 °C, dissociation of CO on palladium, accompanied by dissolving of carbon atoms in the bulk of the metal particles, does not take place.

In ref. [4], a shortening of the Pd-Pd interatomic distances was observed for very small metallic clusters. Thus, it is surprising that in our present study the interatomic distances remain unchanged and close to that for bulk palladium, even when the palladium particle size is decreased down to 19 Å. A possible reason for such a discrepancy may be the presence of a small number of particles with large sizes. In this case, the large particles would give rise to the basic intensity of the EXAFS spectrum. Small-angle X-ray scattering experiments suggest the presence of some large particles. However, the methods of chemisorption, X-ray diffraction and TEM show no evidence of this. Further investigation of this enigma is underway.

When $\bar{d}_S$ is decreased from 30 Å to 10 Å, a positive shift of 0.7 eV is observed for the Pd $3d_{5/2}$ level, as compared with bulk Pd [1]. The data obtained here, together with the correlation found in ref. [1] between the turnover number and the binding energy E_b of the Pd core level, lead us to the tentative conclusion that the decrease in the turnover number for highly dispersed palladium is most likely caused by the stronger chemisorption of acetylene molecules on small electron-deficient Pd clusters, and not by any structural peculiarities.

For a definitive discrimination between these two possibilities, we are at present carrying out EXAFS studies of catalysts containing Pd particles that are less than 20 Å.

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