ESR- AND SUSCEPTIBILITY MEASUREMENTS ON PALLADIUM PARTICLES SUPPORTED ON Y-ZEOLITES

By

F. SCHMIDT, K. NAUMANN and W. GUNSSER
Institut für Physikalische Chemie, Hamburg

Pd(II)-ion exchanged zeolites have been dehydrated with flowing oxygen at 900 K. The dehydrated zeolites have been reduced with flowing hydrogen at 77 K and at 300 K and have been outgassed at 300 K and at 700 K respectively. Particle size and the size distribution of the Pd particles have been determined by electron microscopy and X-ray diffractometry. The results indicate that not all the palladium particles are atomically dispersed. A new resonant absorption at $g = 2.16$ has been observed for the reduced samples. The temperature dependence of this line has been shown to give a maximum at significant temperatures depending on the particle size. Analogous results have been obtained by static magnetic measurements.

Introduction

Zeolites containing palladium belong to the most investigated metal loaded molecular sieves. The dispersion of the metal depends on the cation content, treatment before reduction and the condition of reduction. In recent years a number of papers dealt with the state of the metal in equally pretreated and equally reduced PdY-zeolites of the same composition. As was shown by GALLEZOT ET AL. [1] by crystal structure analysis, reduced palladium remains atomically dispersed inside the sodalite cage up to about 500 K. Between 500 K and 600 K the Pd(0) atoms migrate towards the outer surface of the zeolite, where they agglomerate into 2 nm diameter particles. NACCACHE ET AL. [2] demonstrated by ESR and IR spectrometry that the electron density of the Pd(0) is low because of its strong interaction with Lewis acid sites of the zeolite network due to the pretreatment conditions: actually 8% palladium was shown to be in the Pd(1) state. The electron deficient character of the isolated metal atoms was also evidenced by pyridine adsorption as reported by PRIMET ET AL. [3].

In the present study we are mainly interested in the magnetic properties of small metallic palladium clusters. Most of these particles are likely formed within the zeolite cavities; their diameters will be limited by the supercage size. In order to achieve this, we employed the same pretreatment conditions reported by the authors mentioned above; however, the conditions for the reduction have been modified.

Experimental Section

The starting material was the LINDE Na-Y-form (SK 40), the Mn(II)- and Fe(III)-impurities of which were less than 5 ppm. The desired exchange level was readily obtained by stirring a suspension of the zeolite at room temperature for 24 h in a tetramminepalladium ion solution containing a suitable amount of palladium. The zeolite was filtered and then washed with ammonia solution to eliminate Cl^- ions. The sample was analysed by neutron activation analysis. The palladium content was 12 wt% on a dry weight basis.

First, the sample, being in a shallow bed geometry, was slowly heated at a rate of 5 K/min in flowing oxygen followed by an overnight calcination in oxygen at 900 K. Then the zeolite was evacuated at the same temperature at a pressure of $1.3 \cdot 10^{-3}$ Pa for 15 h.

Secondly, the dehydrated zeolite was reduced by hydrogen, dried over activated molecular sieves at 77 K. Hydrogen gas at a pressure of $1.33 \cdot 10^4$ Pa was introduced through a breakseal into the vessel at 77 K and at 300 K respectively during 15 h.

Thirdly, the sample, reduced at 77 K was evacuated at 300 K for 12 h at a pressure of $1.3 \cdot 10^{-3}$ Pa. This sample will be referred to as PdY77/300/72. The zeolite reduced at 300 K followed by evacuation at 700 K for 36 h or 48 h at $1.3 \cdot 10^{-3}$ Pa will be referred to as PdY300/700/36 and PdY300/700/48 respectively. After reduction all samples were handled under argon atmosphere.

Magnetic susceptibility data were obtained using a Foner vibrating sample magnetometer at temperatures between 4 K and 300 K and fields up to 1.6 T. The ESR spectra were taken on a Bruker X-band spectrometer at temperatures between 4 K and 300 K. Electron micrographs and electron diffraction patterns were obtained of ultramicrotom cut samples after embedding the samples in Spurr without exposure to air. Final magnification up to 300 000 times was carried out on a Philips EM 301.

Results and Discussion

Before reduction the Pd(II)-ions are mainly located on SI' sites (GALLEZOT ET AL. [1]). Furthermore, about 1% of the palladium is found in the Pd(III)-form as was shown by NACCACHE [4]. Our pretreated samples show a reddish-brown colour and an ESR signal assigned to Pd(III) in agreement with the samples of [1] and [2].

All the reduced and evacuated samples were characterized by X-ray diffractometry line broadening analysis and electron microscopy. The results are summarized in Table I.

Table I

Particle sizes of the reduced and evacuated samples

Sample	X-ray Mean diameter nm	Electron Microscopy Diameters nm
PdY77/300/72	7.6	.6—1.8 many 5—8 few
PdY300/700/36	20	.6—2.4 less 4—22 more
PdY300/700/48	35	.6—2.5 few 4—36 many

The sample PdY77/300/72 contains larger crystallites on the outer surface of the zeolite. This result, which is in contrast to the 100% dispersion found by other authors, should be due to the low reaction temperature or/and to the additional evacuation procedure. GALLEZOT ET AL. [1] found that, after room temperature reduction, 40% of the Pd atoms are distributed inside the sodalite units. Only after reduction at 500 K and 600 K larger Pd crsytallites were found on the outer surface. This result shows that a high energy of activation is needed for the Pd to migrate into the large cages and then out of the pores. Since we find particles in the supercage as well as on the external surface when applying the same pretreatment conditions without rising the temperature above 300 K, some Pd atoms should be removed from the sodalite unit during reduction at 77 K. From the supercage the atoms can migrate to the external surface during evacuation. With our conditions most of the Pd particles were found to be in the large cage. This was our goal.

Upon reduction of the first few Pd ions, water molecules are converted to structural hydroxyl groups, [3]. These groups behave in a similar way to those of decationated zeolites. However, $O_{(3)}H$ groups appear to have a more pronounced acid character than those of H-Y zeolites. The Pd atoms in reduced Y-zeolites are situated close to the acid centers formed by the pretreatment. These withdraw electrons from palladium and as a result, some Pd(0) atoms are oxidized to Pd(I). This was demonstrated by ESR [3].

Recently, however, atomically dispersed Pd(0) was shown to give XPS positive chemical shift [5]. But these shifts were assigned to smaller electron relaxation energies and not to reducing properties of the zeolite surface. In addition, Pd(0) aggregates supported on zeolites, were shown by ESR not to give rise to significant electron transfer [5]. On the other hand, Pt microcrystals on zeolite supports form charge transfer complexes with Lewis acid sites.

Similar results were obtained for iron [6]. For the 250 atom cluster inside Y-type zeolites and even for the 13 atom cluster inside mordenite, prepared by sodium vapour reduction, we found nearly the same electronic configuration as in bulk iron. In A-type zeolites, however, which were reduced by sodium vapour, Lewis acid sites are present after dehydration, caused by a hydrolysis mechanism during ion exchange, producing on the metal cluster, an inner and an outer shell of different electron density, as was evidenced by NGR spectroscopy.

The X-ray patterns of our larger f.c.c. palladium particles show a slight lattice contraction. This should make quite sure, that the Pd on the outer surface does not contain any hydrogen, because this would cause a lattice expansion. A lattice contraction in microcrystals has been frequently observed. It should be a function of $1/$(particle size). As an example, a_0-values of 10 nm gold particles on a substrate (KARIOS [7]) decrease by 0.3%, or 0.1% (20 nm microcrystals) and 0.07% (35 nm), respectively. This effect sometimes is called internal pressure. In Pd and Pt particles on zeolites no such observations are reported (GALLEZOT [8]). From the measured lattice contraction we should expect different magnetic properties of the palladium particles.

The results of the ESR spectra of the reduced samples are summarized in Table II. All samples show signals due to Pd(I), $g_{//}(1)$, $g_{//}(2)$. Only in the reduced samples we observed an additional intensive resonance absorption at $g = 2.16$. The ESR absorption of Pd(I) $g_{\perp}(1)$, $g_{\perp}(2)$ overlaps with the Pd(0) signal. The temperature dependence of the peak to peak height of the differentiated absorption curve for the

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Table II.

g-values of the reduced and evacuated Pd-zeolites

Sample	Pd(I), $g_{//}$	Pd(I), $g_{//}$	Pd (0) and Pd(I), $g_{\perp}$
PdY77/300/72	2.52	2.31	2.16
PdY300/700/36	2.53	2.31	2.16
PdY300/700/48	2.53	2.31	2.16

PdY77/300/72 is shown in Fig. 1 and for PdY300/700/36 and PdY300/700/48 in Fig. 2. Fig. 1 exhibits a maximum at 12 K $\pm$ 3 K whereas the maxima in Fig. 2 are to be found at 72 K $\pm$ 10 K and 110 K $\pm$ 10 K, respectively. For bulk palladium, the susceptibility has a broad maximum at 100 K $\pm$ 10 K.
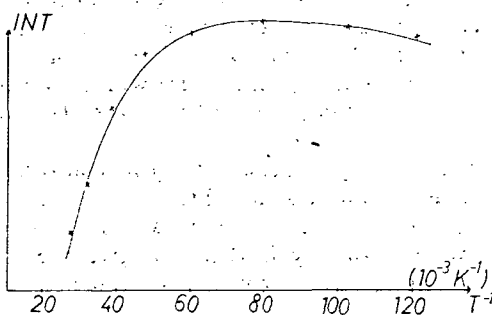

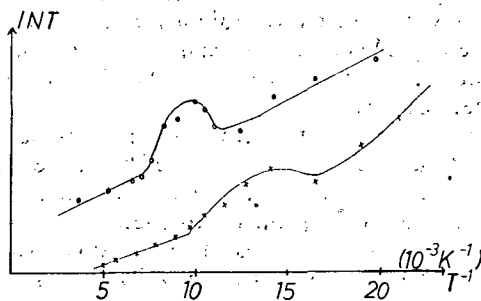*Fig. 1.* Temperature dependence of the ESR-absorption at g=2.16 of the PdY77/300/72 sample

Fig. 2. Temperature dependence of the ESR-absorption at g=2.16 of the PdY300/700/36 (x) and PdY300/700/48 (○) samples.

Similar results were obtained from the susceptibility measurements. In Fig. 3 we illustrate, as an example, the relative susceptibility as a function of temperature of the PdY77/300/72 and PdY300/700/36 samples. The respective maxima lie at 82 K and 44 K. The slight difference with respect to the ESR results can be explained by
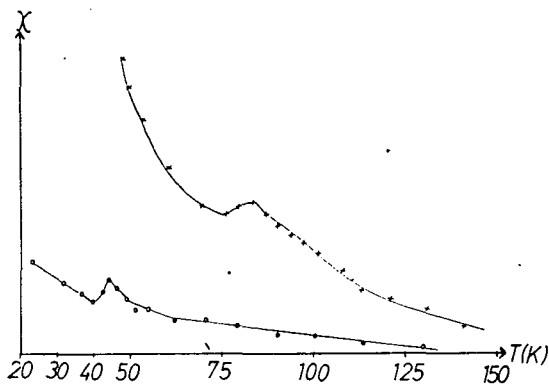
Fig. 3. Temperature dependence of the susceptibility
(arbitrary units) of the PdY77/300/72 (-O-) and
PdY300/700/36 (x) samples

the partial overlap of the Pd(0) and Pd(I) $g_\perp$ signals in the ESR spectrum and the restriction caused by the fact that we only employed the peak to peak height of the differentiated absorption curve as a relative measure of the susceptibility.

Another important result is the ratio of ESR signals due to Pd(0) and Pd(I) (*cf.* Table III). The amount of Pd(I) decreases as the temperature and the evacuation time increases. This behaviour is in contrast to the expected increase of Pd(I) caused by an increase in acidity at elevated temperatures. A possible explanation is a disproportionation of Pd(I) to Pd(0) and Pd(II) at higher temperatures.

Table III

Pd(0)/Pd(I) *ratio of the reduced
and evacuated samples*

Sample	Temperature	
	50 K	35 K
PdY77/300/72	2.6	2.2
PdY300/700/36	4.2	3.5
PdY300/700/48	4.9	4.3

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