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# XPS analysis of the oxidation of palladium model catalysts

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## Abstract

The oxidation of 5 and 8 nm palladium particles supported on $SiO_2$/Si(1 0 0) has been studied with XPS. During oxidation the thickness of the oxide layer increases linearly with time. The lattice rearrangement needed for the formation of a new oxide layer at the metal–oxide interface is probably the rate-determining step. There were no significant differences between the oxidation of the 5 and 8 nm particles. The rate of the oxidation is strongly temperature-dependent. The activation energy for the oxidation is at least 100 kJ/mol. For comparison the oxidation and reduction of a 8 wt% Pd/$SiO_2$ catalysts was studied. The results indicated that oxidation and reduction of the Pd/$SiO_2$ catalyst proceeds in a similar way as on the Pd/$SiO_2$/Si(1 0 0) model catalysts. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* X-ray photoelectron spectroscopy; Palladium; Reduction; Oxidation; Particle size effects

## 1. Introduction

Research on heterogeneous catalysts is often hampered by ill defined systems and the poor accessibility of the active particles for surface science techniques. Traditionally, to overcome these problems, single crystals were used as a model for the surface of the active particles. Although the single crystal studies have provided valuable new insights into many fundamental issues of catalysis [1], they do not deal with two major aspects of supported catalysts: metal–support interactions and particle size effects. Therefore since a few years more realistic model catalysts are studied, i.e. metal particles deposited on a flat support. These model catalysts are chemically identical to 'real' supported catalysts (besides the lack of a high surface area) and they can be studied with almost all surface science techniques [2–7].

In a previous study [8] we demonstrated that the Pd/$SiO_2$/Si(1 0 0) system allows a very detailed analysis with XPS of the thermal reduction of palladium oxide particles. Equations were derived to calculate the size of the metallic core and the thickness of the oxide skin of a partly oxidised particle from non-angle resolved XPS spectra. By following the growth of the metal core inside the palladium oxide particles during reduction, information about the reduction kinetics and mechanism was obtained. The rate of the reduction is linearly proportional to the surface area; the rate-limiting step of the reduction is the formation of molecular oxygen on the surface. It appeared that the reduction rate of surface oxide is much lower than the reduction rate of 'bulk' or 'core' oxide. Very small palladium oxide particles ($d\approx3.5$ nm) are more difficult to reduce and show only 'surface oxide behaviour'. Larger palladium particles behave not different

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from bulk palladium and loose their oxide easily up to the last monolayer.

In this paper we present a similar analysis of the oxidation of palladium particles. We performed stepwise oxidations of two samples, one with 5 nm particles and another with 8 nm particles. Besides measurements on palladium model catalysts we also studied a 8 wt% palladium on silica catalyst. Due to the lower quality of the XPS spectra of the catalyst, a detailed analysis such as performed on the model catalysts was not possible. Therefore the results of the $Pd/SiO_2$ catalyst can only be compared qualitatively.

## 2. Experimental

The XPS data were obtained in a Vacuum Generators MT-500 system using a CLAM-2 hemispherical analyser for electron detection. Measurements were performed at room temperature and at normal emission angles using non-monochromatic Mg $K_\alpha$ (1253.6 eV) radiation. The analyser was operated at 20 eV (with the sample with the highest Pd loading) or 50 eV (other samples) pass energy and had a spotsize of approximately 4 mm in diameter. The base pressure in the analytical chamber was better than $10^{-8}$ Pa. The analytical chamber is connected to a preparation chamber (base pressure $10^{-4}$ Pa) which is equipped with a high pressure cell (for pressures up to 1 atm). Inside the preparation chamber the samples could be heated up to 873 K.

The palladium model catalysts were prepared by evaporating palladium at room temperature onto an oxidised Si(1 0 0) surface in high vacuum ($p<10^{-5}$ Pa), followed by calcination in air for 1 h at 773 K. After mounting the samples in the XPS system the samples were reduced by means of heating (773 K) in high vacuum for 1 h. During this last treatment the metallic particles sinter to a certain particle size dependent on the amount of palladium deposited. For this reason it was not possible to study very small particles (<5 nm). Two model catalysts were used, one with a Pd loading of $1.7\times10^{15}$ atm cm$^{-2}$ resulting in particles with a diameter of 5 nm and one with a Pd loading of $10\times10^{15}$ atm cm$^{-2}$ resulting in particles with a diameter of 8 nm. The particle sizes were determined with XPS. Both palladium metal and palladium oxide particles supported on silica are known to have a spherical shape [8]. The thickness of the oxide layer on the Si(1 0 0) is about 2.5 nm as calculated from the ratio between the $Si^0$ and $Si^{4+}$ 2 p peaks.

The 8 wt% $Pd/SiO_2$ catalyst was prepared by incipient wetness impregnation of 2 g silica (Aerosil 200, Degussa) with 10 ml of a 19.24 g/l solution of tetramine palladium(II) nitrate. Subsequent to drying, the catalyst was calcined in air at 723 K for 3 h. After mounting in the XPS system the catalyst was treated like the model catalysts. The average particle size of this catalyst was 11 nm as determined both with XRD as with XPS.

A series of experiments consisted of reducing the system for 60 min in vacuum at 773 K followed by a stepwise oxidation by means of heating in air at 623 K for 10 ($Pd/SiO_2$/Si(1 0 0)) or 15 ($Pd/SiO_2$) min. After each step XPS was performed. The heating time is the time between switching on and off the power of the heater. This means that the time to warm up is included and the time to cool down is excluded. The air flow was maintained during warming up and cooling down. The procedures for fitting and analysis of the XPS spectra are described in detail in [8].

## 3. Results and discussion

The particle and core radii during oxidation of the model catalyst with the lowest palladium loading, $1.7\times10^{15}$ atm cm$^{-2}$, are shown in Fig. 1. The other model catalyst, with a palladium loading of $10\times10^{15}$ atm cm$^{-2}$ and a particle size of 8 nm, behaves almost identical. In the figure it is clearly visible that the radius of the metallic core decreases linearly with time. The dashed line through the core radii is a linear fit. The dashed line through the outer (particle) radii represents the particle radii calculated from the linear fit through the core radii and using mass balance for the amount of palladium in a (partly oxidised) particle.

The rate of the oxidation is very temperature dependent. At 573 K even heating steps of 1 h result only in a slow decrease of the metallic core radius. At 673 K the oxidation is almost completed after one heating step of 10 min. Although the different temperatures cannot be compared quantitatively since the time to

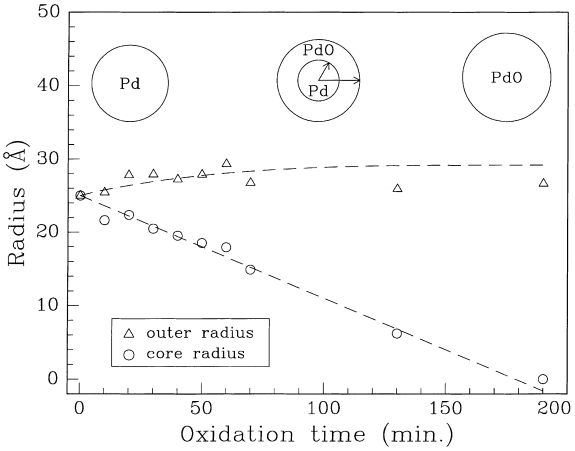

Fig. 1. The particle and core radii during oxidation of the model catalyst with a palladium loading of $1.7\times10^{15}$ atm cm$^{-2}$. The oxidation process is shown schematically in the top part of the figure.

warm up and to cool down differs, the activation energy for the oxidation can be estimated to be at least 100 kJ/mol.

The linear decrease of the core radius cannot be explained by a reversed reduction model from [8], i.e. the rate of oxidation is proportional to the particle surface area, since this model leads to an almost linear decrease of the core *volume* instead of a linear decrease of the core *radius*. Also the commonly used Cabrera–Mott and Fromhold–Cook oxidation models for the growth of a metal oxide layer, do not result in a linear increase of the oxide layer thickness [9], although one can argue that the equations and approximations used in these models should be adapted when they are used on spheres instead of flat surfaces.

An explanation for the linear decrease of the core radius is that the lattice rearrangement needed for the formation of a new oxide layer at the oxide–metal interface is the rate-determining step. The oxidation rate is in this case independent of the size of the interface or the thickness of the oxide layer. This is not unlikely since the crystal structure of palladium oxide is quite incompatible with the structure of the metal crystal [10]. A high activation energy is expected when a lattice reconstruction is the rate-determining step. A study of the interaction of oxygen with Pd(1 1 1) and Pd foil showed that at low pressures (≤1 Pa) only a surface oxide is formed, while PdO is thermodynamically favoured under the conditions used [11]. The structure of this surface oxide does not match with the Pd(1 1 1) surface at all. This supports the assumption that the formation of a new oxide layer inside a particle is kinetically obstructed.

## 4. Conclusions

Non-angle resolved XPS was used for a quantitative study of the oxidation of palladium particles supported on $SiO_2$/SiO(1 0 0). The radius of the metallic core inside the particles decreases proportionally to the oxidation time. The rate-limiting step in this process is the lattice reconstruction needed for the formation of a new oxide layer at the oxide–metal interface. The activation energy of the reconstruction is at least 100 kJ/mol. No significant differences were found between the oxidation of 5 and 8 nm particles. The 8 wt% Pd/$SiO_2$ catalyst studied as comparison, behaves similar to the $SiO_2$/Si(1 0 0)-supported palladium particles.

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