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# The oxidation kinetics of spherically shaped palladium powder

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The oxidation kinetics of spherically shaped palladium (Pd) powders was investigated over the temperature range between 350 and 800 °C. Two types of Pd powders differing from each other in particle sizes were used in this study, 0.30 and 0.85 $\mu$m in diameter. The fraction of total oxide formed was measured *in situ* by means of a thermobalance method. In this system, the volume of product palladium oxide (PdO) increases significantly vs. the volume of reactant Pd, and consequently the experimental data were explained well by Valensi-Carter equation. Apparent activation energies of oxidation for the two types of Pd powders were both estimated to be 140 kJ/mol.

## 1. Introduction

It is known that elements of the platinum (Pt) group are stable at ordinary temperature and they tend to adsorb gas molecules when they are in the form of fine powder, such as Pt black, because of large surface area. Palladium (Pd), which belongs to the Pt group and is relatively cheap, has been used in practice as a catalyst for the treatment of exhaust gases, such as nitric oxide [8] from motor cars, and so on. Generally, to maintain high catalytic activity, it is necessary to prevent any chemical reactions of the catalyst. In the case of the Pd catalyst, the oxidation of Pd itself at high temperature is considered to have a detrimental effect on the catalytic activity. To prevent the oxidation, determination of the kinetics of Pd oxidation is needed.

While there have been some studies on Pd oxidation [1–3] or decomposition of the oxide (or PdO) [4], few studies have been reported on the kinetics aspect of the oxidation. Ota and Takahashi studied the oxidation kinetics of bulk Pd such as Pd wire and plate [5]. However, they did not do a quantitative analysis. Several models have already been established for kinetic analysis of the reaction in a powder system; therefore, it is reasonable to analyze the kinetics of Pd oxidation using Pd powder rather than a bulk sample. Using Pd powder, Sugiyama reported that the oxidation rate of Pd depended on both the grain size and particle size of the powder [6]. In his paper, it was made clear that the oxidation rate of Pd powder with large grain or particle size tended to be slower than that with small grain or particle size. However, a kinetic analysis was not yet attempted.

In this study, two types of fine Pd powder were used, whose grain sizes were the same but the particle sizes were different. It was hoped that we could investigate the effect of particle size on the kinetics of Pd powder oxidation, separating the effect of grain size. Considering the fact that oxygen diffusion in the oxide layer is generally the rate-determining step in the oxidation of the metal and that the volume of the product (PdO) is large compared to the volume of the reactant (Pd), the Valensi-Carter equation [7] was adopted for the analysis. From the results of the analysis, the activation energy for the Pd powder oxidation was determined.

## 2. Experimental

Two types of Pd powder provided by Sumitomo Metal Mining Co., Ltd. were used in the experiments. The sizes and shapes of the powders, before and after the oxidation reactions, were observed by scanning electron microscopy (SEM, JEOL, JSM-T20). X-ray diffraction (XRD, Philips PW1840, using Cu$K_\alpha$ radiation) was performed to identify the product and to estimate the grain size of Pd. The grain size ($D$) was calculated from the Sherer formula:

$$D = 0.9\lambda/\beta\cos\theta \tag{1}$$

where $\lambda$ is the wavelength of the X-ray, $\theta$ is the diffraction angle, and $\beta$ is the corrected half-width of the diffraction peak given by:

$$\beta^2 = \beta_m^2 - \beta_s^2 \tag{2}$$

where $\beta_m$ is the measured half-width of Pd powder and $\beta_s$ is the measured half-width of a standard Si sample (single crystal powder of 200 mesh). Because the diffraction angles of Pd are close to those of Si, the half-widths of Pd and Si at the angles nearest to each

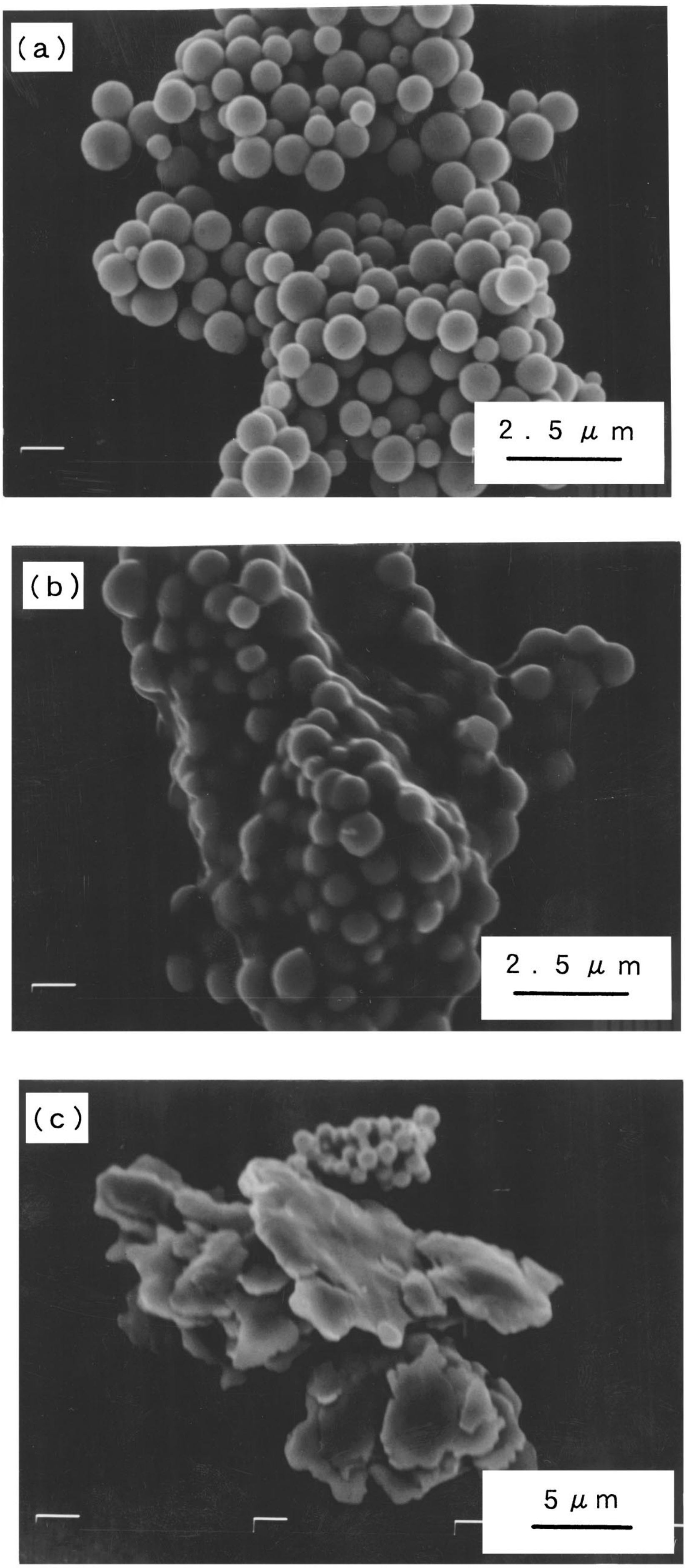

*Figure 1* Scanning electron micrographs of the Pd powder sample during heat treatment. The sample was large particle size Pd powder oxidized at 400 °C: (a) the as-received Pd powder sample, (b) 30-min heated sample, and (c) 50-min heated sample.

other were assigned as $\beta_m$ and $\beta_s$. The value of $\beta$ calculated in this way was further averaged for three Pd diffraction angles and was used to determine the grain size.

The oxidation of the sample was carried out in a closed chamber (ca. 1300 cm$^3$) at a constant temperature in the range of 350–800 °C in an oxygen atmosphere at a low constant pressure, $6.7 \times 10^3$ Pa. To keep the oxygen pressure constant during the oxidation, the amount of Pd powder was limited to about 10 mg. The Pd powder was placed in a crucible made of silica glass and was placed in a Pt crucible attached to one side of a microbalance (Shimadzu Corp., Electric Microbalance, RMB-50V) with a counterbalance made of a Pt wire attached to the other side. Silica glass was used to hold Pd because it does not react with Pd even at high temperature. In this instrument, only the part around the sample was heated and the counterbalance was not heated. However, by performing blank experiments at all the temperatures, we confirmed that there was very little effect (less than 1%) of thermal convection. The mass changes in the samples with time caused by the Pd oxidation were measured *in situ* under above-mentioned conditions.

## 3. Results and discussion

The grain size of the two Pd powders was determined to be about 0.011 $\mu$m using Equation 1 and the results of XRD. Average particle size (diameter) of the small Pd powder was 0.30 $\mu$m and that of the large Pd powder was 0.85 $\mu$m, determined by measuring about 100 particles for each powder with SEM. The shape of those powders was almost spherical before the heat treatment (Fig. 1a). After heating in oxygen, the particles seemed to be covered with something, combined with each other (Fig. 1b), and finally changed to masses in which there were no spherical particles left (Fig. 1c).

From the results of XRD, the Pd oxidation reaction under our experimental condition was expressed by

$$\mathrm{Pd} + 1/2\mathrm{O}_2 \rightarrow \mathrm{PdO}. \qquad (3)$$

The X-ray diffraction peaks of Pd decreased and those of PdO increased during the heat treatment. Applying Equation 3, the reaction ratio was calculated from the weight change of the sample during the heat treatment. Some of the results of the reaction ratio, $x$, versus reaction time were plotted for (i) the small particle powder (Fig. 2) and for (ii) the large particle powder (Fig. 3). In the figures, the reaction time was set at zero when the thermocouple near the sample arrived at the desired temperature. On the whole, the reaction occurred very quickly in the early stage and became gradually slow in the intermediate stage of the reaction. The higher the reaction temperature was, the faster oxidation rate was. At higher temperatures (750 and 800 °C), the value of $x$ increased before the desired temperature was reached and then started to decrease instantly when the temperature was reached. The decrease in weight resulted from the high temperature decomposition reaction of the PdO product [4].

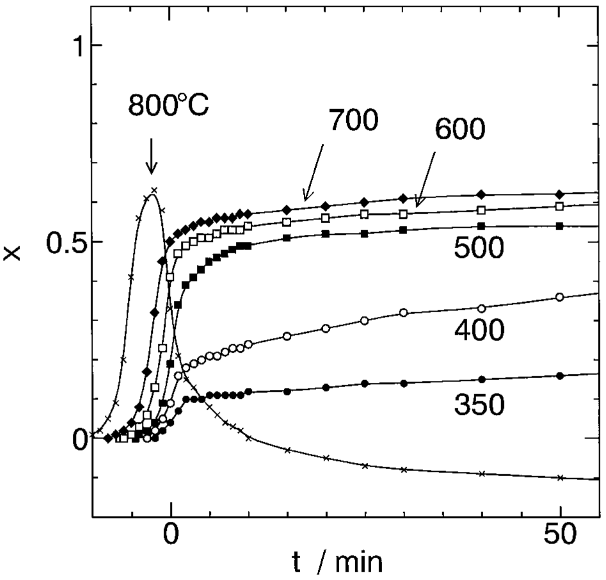

*Figure 2* Reaction ratio $x$ vs. reaction time $t$ for small particle size Pd powder.

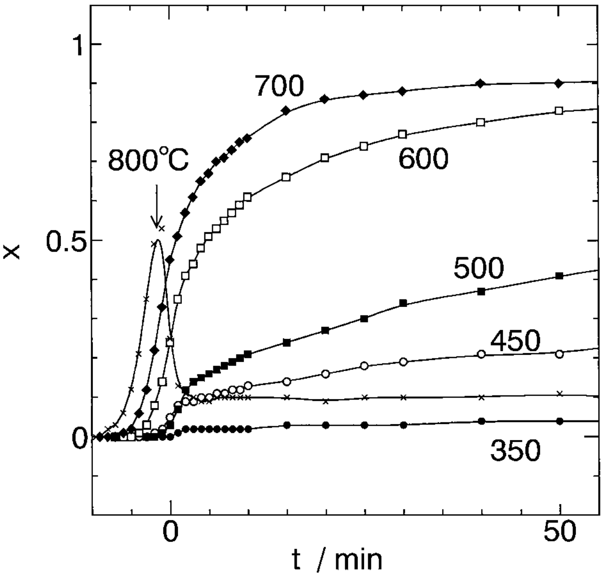

*Figure 3* Reaction ratio $x$ vs. reaction time $t$ for large particle size Pd powder.

To discuss the kinetics of these results, we adopted Valensi-Carter's model [7]. This is a useful equation for kinetic analysis of reactions of a powder system in which the reactant diffusion process is the rate-determining step and the volume of product is large (or small) compared to the volume of reactant. The Valensi-Carter equation is given by:

$$[\{1+(z-1)x\}^{2/3}+(z-1)(1-x)^{2/3}-z]/(1-z) = Kt \qquad (4)$$

where $K$ is a kinetic constant, $t$ is reaction time, and $z$ is the volume of product formed per unit volume of reactant consumed. For the reaction (3), $z$ is 1.681. $K$ is proportional to the reciprocal of the square of the initial radius of a particle, $r$.

$$K \propto 1/r^2 \qquad (5)$$

Equation 4 is valid if the sample retains the spherical shape. In this system, on observing the sample under

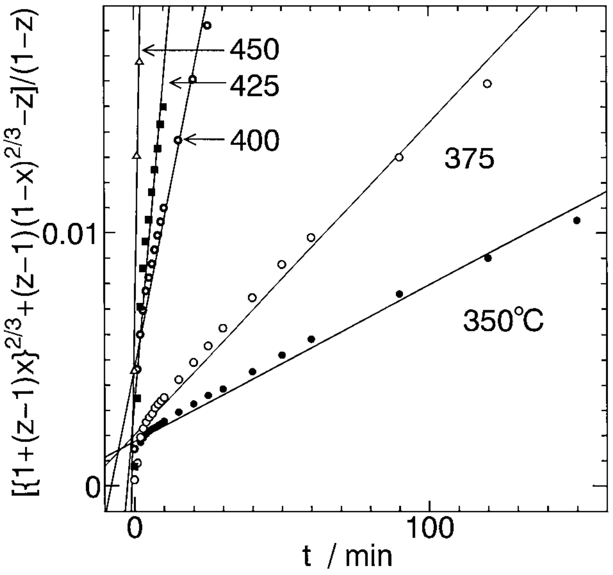

*Figure 4* $[\{1+(z-1)x\}^{2/3}+(z-1)(1-x)^{2/3}-z]/(1-z)$ vs. $t$ for small particle size Pd powder.

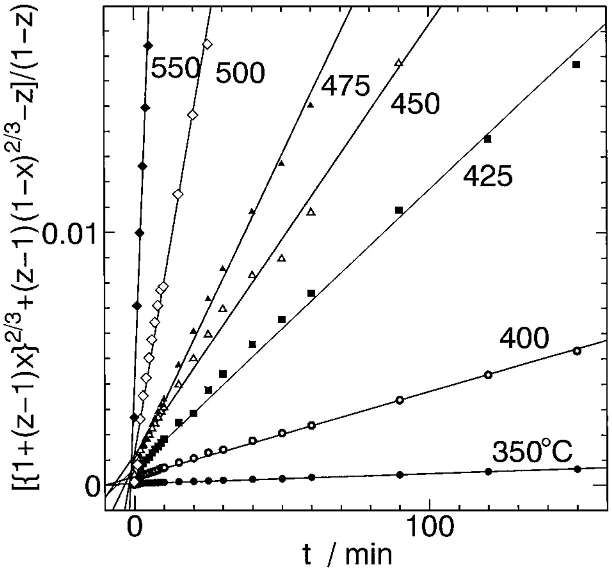

*Figure 5* $[\{1+(z-1)x\}^{2/3}+(z-1)(1-x)^{2/3}-z]/(1-z)$ vs. $t$ for large particle size Pd powder.

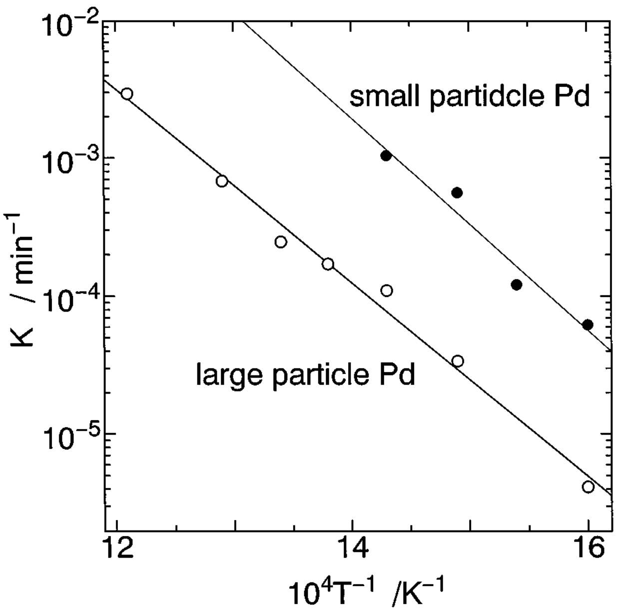

*Figure 6* Arrhenius plots of $K$ for the oxidation of the two types of Pd powders.

SEM, it was found that the sample did not maintain the spherical shape at a large value of $x$. Consequently, the experimental results for $x$ smaller than 0.3 were plotted according to Equation 4 in Fig. 4 ($2r = 0.30$ $\mu$m) and Fig. 5 ($2r = 0.85$ $\mu$m). As shown in these figures, every plot showed good straight lines. From the slopes of these lines, $K$ values were obtained at each temperature for each powder. Fig. 6 shows Arrhenius plots of $K$ for each powder. The data followed straight lines and the apparent activation energies of Pd oxidation for both sizes of powders were $1.40 \times 10^2$ kJ/mol. The Valensi-Carter equation is valid for the reaction controlled by a diffusion process. This implies that the activation energy is related to the diffusion coefficient of either Pd or O in PdO. Because any diffusion coefficient in metal oxides which have a crystal structure similar to that of PdO, such as PtO, PbO and SnO, has not been determined yet, it is impossible to discuss the validity of the current results in detail. However, this value of activation energy estimated for the diffusion of Pd or O in PdO is intermediate between those of the energies in common metal oxides (ca. 50–280 kJ/mol), so it is considered to be qualitatively reasonable.

The value of $K$ for the large Pd particle powder was smaller than that for the small Pd particle powder (Fig. 6). The ratio of $K$ for the large Pd to $K$ for the small Pd is 0.07 on the average (350–425 °C). This is slightly smaller than the value expected from Equation 5, 0.12, using the particle diameters. This discrepancy is explained as follows. When the reaction ratio increases to some extent, it is difficult to keep the particle spherical. The small particles were oxidized rapidly; therefore, the effect of the deformation of spheres may be severer for small particles than for large particles. That is, for small particles, local oxidation may occur rapidly, and as a result, the experimental value of $K$ may be larger than the value calculated assuming that the samples remain completely spherical.

## 4. Conclusion

The oxidation kinetics of spherically shaped Pd powders which were different from each other in size, 0.30 and 0.85 $\mu$m, were investigated at 350–800 °C. The kinetics could be analyzed using Valensi-Carter's model, and from the kinetic constant $K$ obtained for each powder, the activation energies were determined to be 140 kJ/mol for both powders. The ratio of $K$ for large Pd to $K$ for small Pd was close to the ratio estimated from the diameters of the powders.

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