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Loss of Palladium from Model Platinum–Palladium Supported Catalysts during Annealing

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The phenomena taking place during the annealing of bimetallic-supported catalysts may differ in several respects from those involving monometallic-supported systems. One such phenomenon can be the preferential loss from the catalyst of one of its active components. Reported here are the results of experiments on the thermal stability of model, supported platinum–palladium catalysts in which preferential loss of palladium was indeed observed. These experiments sought to determine the factors responsible for the loss. The variables investigated included the atmosphere surrounding the catalyst, the substrate material, and the effects of time and temperature.

The study was performed on model, flat substrate catalysts of a type developed for previous studies of crystallite growth and sintering (*1–4*). The substrates used in the experiments consisted of thin (~10 nm) continuous films of either Al_2O_3 or CeO_2 deposited onto polished SiO_2 microscope slides. Thin (~2 nm) films of platinum–50 atom% palladium were deposited onto the substrates. Both the substrate and the metal films were deposited by radio-frequency sputtering in argon from high-purity targets (*1–4*). The metal sputtering target was an alloy of platinum–50 atom% palladium. Measurements of as-deposited film compositions could not be made directly, but it can be presumed that the film compositions were identical to the target compositions, because platinum and palladium form a continuous solid solution (*5*), and they have nearly identical sputtering rates (*6*). In general, even if the sputtering rates of the two components in an alloy are different, it can be shown from the work of Shimizu *et al.* (*7*), that the composition of the sputtered deposit will be identical with the bulk composition of the target, once the target has achieved a steady-state surface composition.

All samples were pretreated by heat treating for 1 hr in sealed silica capsules under an air atmosphere (20 kPa oxygen partial pressure) at 900°C. This pretreatment caused a break-up of the metal film into discrete crystallites on the substrate. The average crystallite radius in all samples after this pretreatment was approximately 30 nm.

The pretreated samples were subsequently subjected to additional heat treatments either in air or in vacuum. In particular:

(1) Alloy crystallites supported on Al_2O_3 were encapsulated in silica glass in air (20 kPa oxygen partial pressure at temperature) and heat treated from 2 to 32 hr at 800, 900, 1000, and 1100°C.

(2) Alloy crystallites supported on Al_2O_3 were encapsulated under vacuum (10^{-3} Torr) and heat treated for 16 hr at 800, 900, 1000, and 1100°C.

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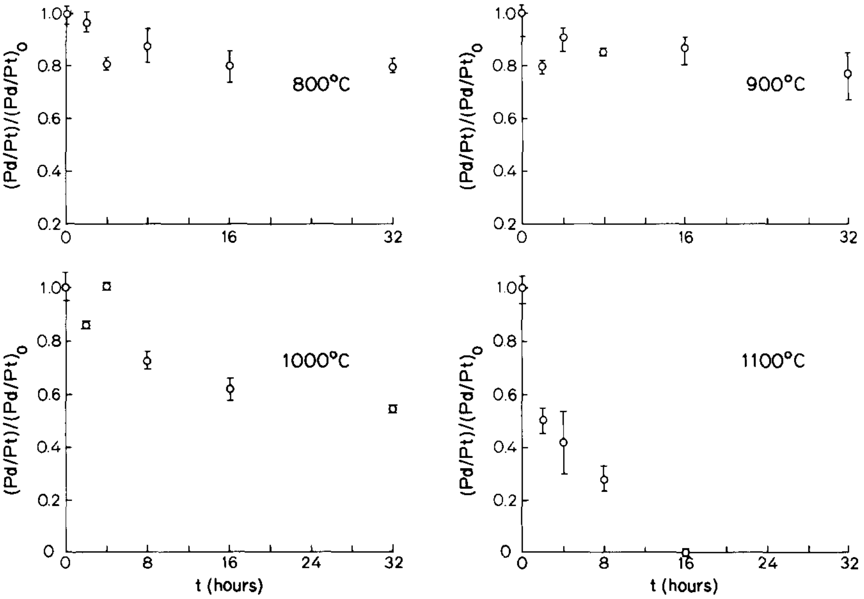

FIG. 1. Results of experiments using Pt–Pd crystallites on Al_2O_3 substrates in air environment.

(3) Alloy particles supported on CeO_2 were encapsulated in air (20 kPa oxygen partial pressure at temperature) and heat treated for 16 hr at 900, 1000, 1100°C.

Measurements of average particle compositions in each sample were made by X-ray energy spectroscopy (XES) in a scanning electron microscope (SEM) equipped with a solid state X-ray detector and a multichannel analyzer. The electron beam was rastered over 300 to 400 crystallites in a sample, which resulted in an averaging of crystallite compositions. Composition measurements were based on the L-palladium peak (2.84 keV) and the M-platinum peak (2.05 keV). Three measurements were made for each sample. With the XES technique, a reproducibility of ±6% is expected for composition measurements in well-polished, bulk alloy samples (*8*). Considering the irregular geometry and thin film nature of the samples used, a reproducibility of ±10% is estimated in the experimental results.

The results of experiments on Al_2O_3–substrate samples, heat treated in air at 800 to 1100°C, are shown in Fig. 1. The figure gives the variation of the ratio of X-ray peak intensities (L-Pd/M-Pt) normalized by the ratio of peak intensities from the pretreated samples, as a function of time. Each plotted point represents the mean of the three measurements. The error bars represent the spread in the three measurements.

While the results at 800 and 900°C showed a possible decrease in the relative concentration of palladium, this decrease was too close to the limits of experimental error for definite conclusions to be drawn.

At 1000°C, however, a steady, systematic decrease in the relative concentration of palladium was observed. The mean normalized ratio, 0.55, plotted at 32 hr may be translated to a composition of 35 a/o palladium. Accordingly, under the assumption that no platinum was lost from the samples,[2] we estimate a loss of Pd of approximately 15 atom%.

At 1100°C, there was an even sharper decrease in the relative concentration of pal-

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[2] This assumption is consistent with previous work on the growth of supported platinum crystallites in which no Pt loss was apparent when samples were heat treated in silica capsules (*1–3*).

ladium. By 16 hr, within the detection limits of the technique, there was no palladium left in the sample.

In contrast to the results of heat treatment in air, samples heat treated in vacuum for 16 hr showed no change in palladium concentration from 800°C all the way up to 1100°C. The results of the vacuum experiments are plotted in Fig. 2, where the Pd/Pt ratios are normalized by the lowest temperature (800°C) ratio.

The results of experiments to assess the effects of changing the nature of the oxide substrate are illustrated in Fig. 3. Samples having a CeO_2 substrate were heat treated for 16 hr in 20 kPa oxygen and the results, normalized by the Pd/Pt ratio at the lowest temperature, showed a somewhat slower decrease in concentration of palladium with temperature than seen in the air experiment where the substrate was Al_2O_3 (cf. Fig. 1).

It is well known that at high temperatures, and in oxygen environments, noble metals can be lost by the formation and volatilization of their oxides, which tend to be more volatile than the metals themselves (*9*). Palladium is an exception in that the metal possesses a higher vapor pressure than the oxide. Hence, in the past, when loss of palladium from bulk samples has been observed and measured at temperatures of 1000°C and above, it has generally been ascribed to volatilization of the metal (*9–13*). In the present work, free evaporation cannot be invoked as the mechanism of palladium loss, as the samples were sealed in silica capsules, specifically in order to suppress that type of loss. Furthermore, palladium loss was observed only under oxidizing conditions, indicating that the mechanism of palladium loss was inoperative under conditions where palladium was present either in solid metallic (alloy) form or as the metallic vapor. While solid PdO is unstable with respect to a mixture of the metal and oxygen gas, at temperatures above ~800°C, a finite partial pressure of PdO will always exist in the vapor above the samples in the presence of O_2 (*9*). Therefore, we conclude that the mechanism of loss must require that palladium be present in the form of PdO, and that some sink for PdO be available within the sealed capsule system. Indeed, it is reasonable to expect that palladium should be able to interact more readily with the oxides in the capsule (namely, SiO_2 and Al_2O_3 or CeO_2) by the formation of either solid solutions or mixed oxides, when it is present in the oxidized form.

There is, however, no conclusive evidence which positively identifies the sink for the palladium. Diffusion of PdO into the 10-nm-thick Al_2O_3 or CeO_2 substrates directly in contact with the alloy particles is ruled out, because the XES technique would have detected any palladium in these thin films. The only tenable hypothesis is that the PdO dissolves into (or forms mixed

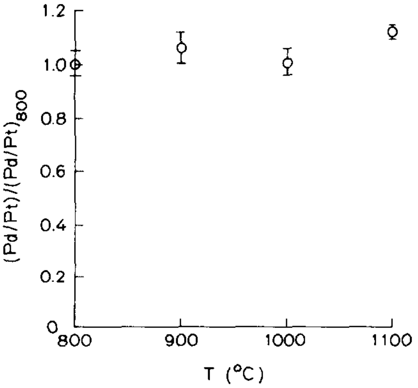

FIG. 2. Results of experiments using Pt-Pd crystallites on Al_2O_3 substrates in vacuum environment.

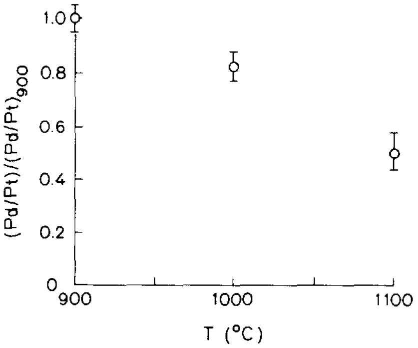

FIG. 3. Results of experiments using Pt-Pd crystallites on CeO_2 substrates in air environment.

oxides with) the silica present in the system as capsule material and as mechanical supports for the substrates. In this case the average concentration of palladium in silica would be so low (on the order 0.01 ppm), that it would be difficult, if not impossible, to detect. Hence, this remains only a hypothesis at this time.

The results of experiments using CeO_2 substrates, under oxidizing conditions, suggest that PdO interacts somewhat more strongly with CeO_2 than with Al_2O_3, but not strongly enough to prevent loss of Pd to the silica in the system.

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