Pd oxidation under UHV in a model Pd/ceria–zirconia catalyst

M.Yu. Smirnov* and G.W. Graham

Ford Research Laboratory, MD3179/SRL, PO Box 2053, Dearborn, MI 48121, USA

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A model planar catalyst was prepared by depositing Pd onto a thick (few μm) film of ceria–zirconia in ultrahigh vacuum (UHV), and the oxidation state of Pd and its support was determined by X-ray photoelectron spectroscopy, following thermal treatments in UHV, oxygen, or carbon monoxide. It was found that Pd could be oxidized simply by heating the catalyst in UHV, indicating that transfer of oxygen from the support to the metal is both thermodynamically favorable and facile.

KEY WORDS: palladium; ceria–zirconia; oxygen storage; automotive exhaust catalyst

1. Introduction

Ceria is used to provide oxygen storage capacity (OSC) in automotive three-way catalysts [1]. That is, under transient conditions in which the exhaust gas develops an excess of reductants relative to oxidants, ceria supplies some of its own lattice oxygen for reaction with gas-phase reductants by undergoing partial reduction. Subsequently, if the exhaust-gas composition changes to an excess of oxidants, ceria removes oxygen from the gas phase by re-oxidation. The way in which ceria supplies oxygen is generally understood to involve oxygen diffusion through the ceria to a contacting precious-metal particle, the free surface of which is covered with adsorbed reductant molecules. Studies of model catalysts clearly demonstrate that oxygen can be extracted from ceria-supported precious-metal particles during temperature-programmed reaction with carbon monoxide preadsorbed on the precious-metal particles, for example [2]. Many details of the reaction mechanism are not well understood, however. Structural aspects of the ceria, such as crystallite size, have a strong effect on oxygen availability [2], and the nature of the metal–support interface could well be a controlling factor in oxygen transfer. In fact, transfer of oxygen from ceria to the precious metal particles has not been observed directly as a separate step, raising the question of whether the reaction occurs entirely on the metal or only at its boundary with the ceria [3].

Ceria–zirconia mixed oxides have recently proven to be even better OSC materials than ceria, providing greater accessibility of lattice oxygen [4]. Studies of model catalysts made with these materials are thus of interest since they may shed new light on some of the unresolved matters surrounding the reaction mechanism. In the present work, for example, we have obtained direct evidence that oxygen transfer from ceria–zirconia to supported Pd takes place easily, leading to complete oxidation of the Pd under UHV conditions.

2. Experimental

The ceria–zirconia film was made by a spray-pyrolysis technique [5]. The substrate for the film was a plate of FeCrAlloy (obtained from Sandvik Steel), $1 \times 1 \times 0.065$ cm^3 in size, which had previously been held at 1200 °C for 5 h in air in order to produce an alumina-rich surface-oxide layer. An aqueous solution of approximately 0.020 molar $Ce(NO_3)_3$ and 0.010 molar $ZrO(NO_3)_2$ was sprayed onto the substrate using an airbrush, with N_2 (at a pressure of 25–30 psi) as the carrier gas, at a rate of about 1 ml/min. At the same time, the substrate was maintained at approximately 200 °C by resistively heating FeCrAlloy-foil strips which had been spotwelded to the edges of the FeCrAlloy plate after its oxidation. Six individual spray depositions (10 ml of solution, each) were performed in all, with the substrate held at 350–370 °C in air for about 30 min between depositions. Following the last deposition, the sample was held at 250 °C in air overnight. The final thickness of the ceria–zirconia film was estimated to be a few μm, based on the total amount of solution used, the fraction collected by the substrate, and the oxide density.

The sample was mounted on a conventional manipulator (allowing both heating and cooling) and placed in a Physical Electronics Industries UHV electron spectrometer, which has been described previously [6]. For these experiments, it was only necessary to sputter the sample (1 keV Ar^+), perform thermal treatments in various ambients (UHV or 10^{-7} Torr of either O_2 or CO), deposit Pd (using a thermal evaporation source), and perform X-ray photoelectron spectroscopy (XPS) measurements. (The flux of O_2 or CO onto the sample surface was actually somewhat higher than that based on the system pressure since the gases were admitted a few cm in front of the sample through a small tube (~2 mm i.d.) connected to the leak valve.) A Shirley-type background subtraction was applied to the raw photoemission spectra, and quantitative results were obtained using Physical Electronics Industries sensitivity factors appropriate for the double-pass cylindrical mirror analyzer [7]. The bind-

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* Permanent address: Boreskov Insitute of Catalysis, 630090 Novosibirsk, Russia.

ing energy (BE) scale was referenced to the Ce 3d lines [8]. X-ray diffraction (XRD) patterns were obtained from the sample after the XPS measurements using a Scintag X2 diffractometer with Cu Kα radiation.

3. Results

Initial examination of the ceria–zirconia film revealed only adventitious C contamination, which was removed by a few minutes of sputtering with Ar^+. Sputtering of the film also led to reduction of Ce^{4+} to Ce^{3+} (due to preferential removal of the lighter O atoms), as judged from both the appearance of their characteristic lines in the Ce 3d region (figure 1) and the attenuation of the so-called u$'''$ line with BE $\approx$ 917 eV (figure 1), characteristic of Ce^{4+} [8]. The intensity of u$'''$, relative to all of the Ce 3d lines, is listed in table 1.

The reduced film could be re-oxidized by heating in UHV or oxygen. Both procedures resulted in the disappearance of the characteristic Ce^{3+} lines (figure 2 (A) and (B)) as well as an increase in the relative intensity of the u$'''$ line back to its original value (tables 2 and 3). The re-oxidation was complete at $T \geqslant 150\,^\circ$C in UHV and at $T \geqslant 100\,^\circ$C in oxygen. A substantial degree of re-oxidation of Ce^{3+} occurred in oxygen even at room temperature.

Table 1
The effect of Ar^+ sputtering on the ceria–zirconia film composition and chemical state.

Sputtering time (min)	Ce/Zr	u$'''$ relative intensity
0	2.43	0.116
1	2.51	0.096
2	2.50	0.103
5	2.35	0.090
10	2.31	0.090
20	2.41	0.087

The Ce : Zr ratio, evaluated from XPS measurements of the clean and re-oxidized film, is approximately 7 : 3, and the (Ce + Zr) : O ratio is close to 1 : 2. Thus, the surface composition of the ceria–zirconia film prepared by spray pyrolysis

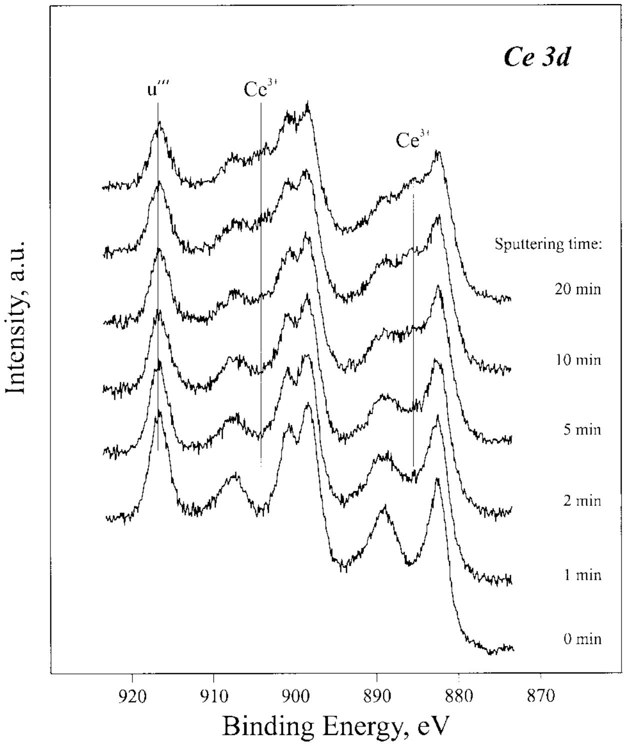

Figure 1. Effect of Ar^+ sputtering time on Ce 3d lines.

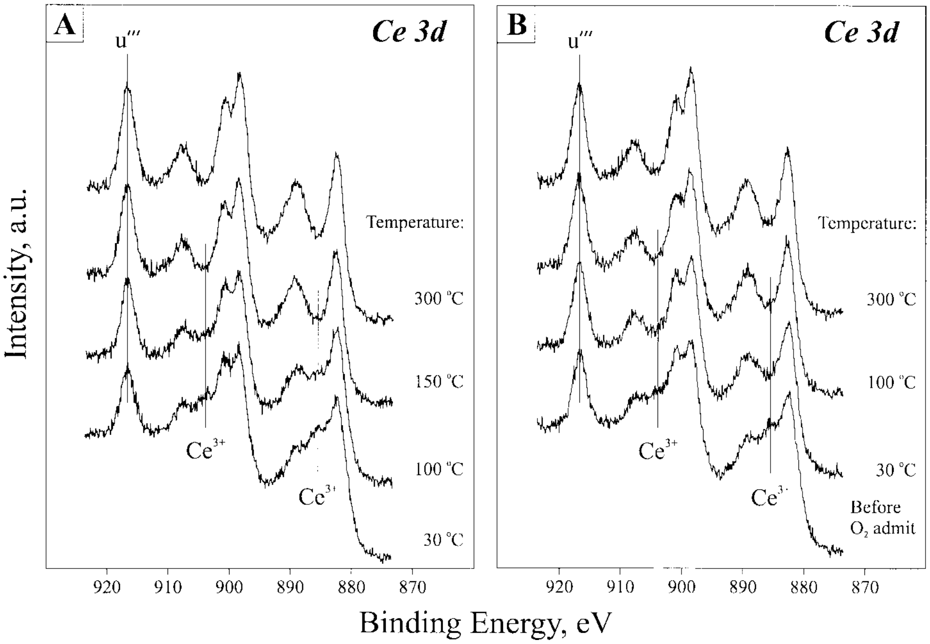

Figure 2. Effect of heating in UHV (A) and in oxygen (B) on Ce 3d lines after sputtering.

is $Ce_{0.7}Zr_{0.3}O_2$. The Ce : Zr ratio was not affected by sputtering (table 1), and it remained constant during re-oxidation (tables 2 and 3).

Survey spectra of the clean and re-oxidized ceria–zirconia film before and after deposition of Pd (always performed with the film at room temperature) are shown in figure 3(A). The amount of Pd deposited corresponds to a few monolayers (based on previous experience with this particular evaporation source [6]). The Pd appears in the metallic state, characterized by a Pd $3d_{5/2}$ line with BE of 335.3 eV (figure 3(B)), though its deposition is accompanied by the reduction of a portion of Ce^{4+} to Ce^{3+} (figure 3(C)). In addition, an apparent change in composition of the film occurs, the Ce : Zr ratio becoming smaller, close to 60 : 40 (table 4). Removal of the Pd, by sputtering, restored the original Ce : Zr ratio.

Table 2
The re-oxidation of the sputtered ceria–zirconia film by heating in UHV at different temperatures.

Temperature (°C)	Ce/Zr	u‴ relative intensity
30	2.41	0.087
100	2.45	0.099
150	2.46	0.114
300	2.54	0.120

Table 3
The re-oxidation of the sputtered ceria–zirconia film by heating in oxygen at different temperatures.

Temperature (°C)	Ce/Zr	u‴ relative intensity
Reduced film	2.42	0.094
30	2.27	0.107
100	2.43	0.117
300	2.51	0.113

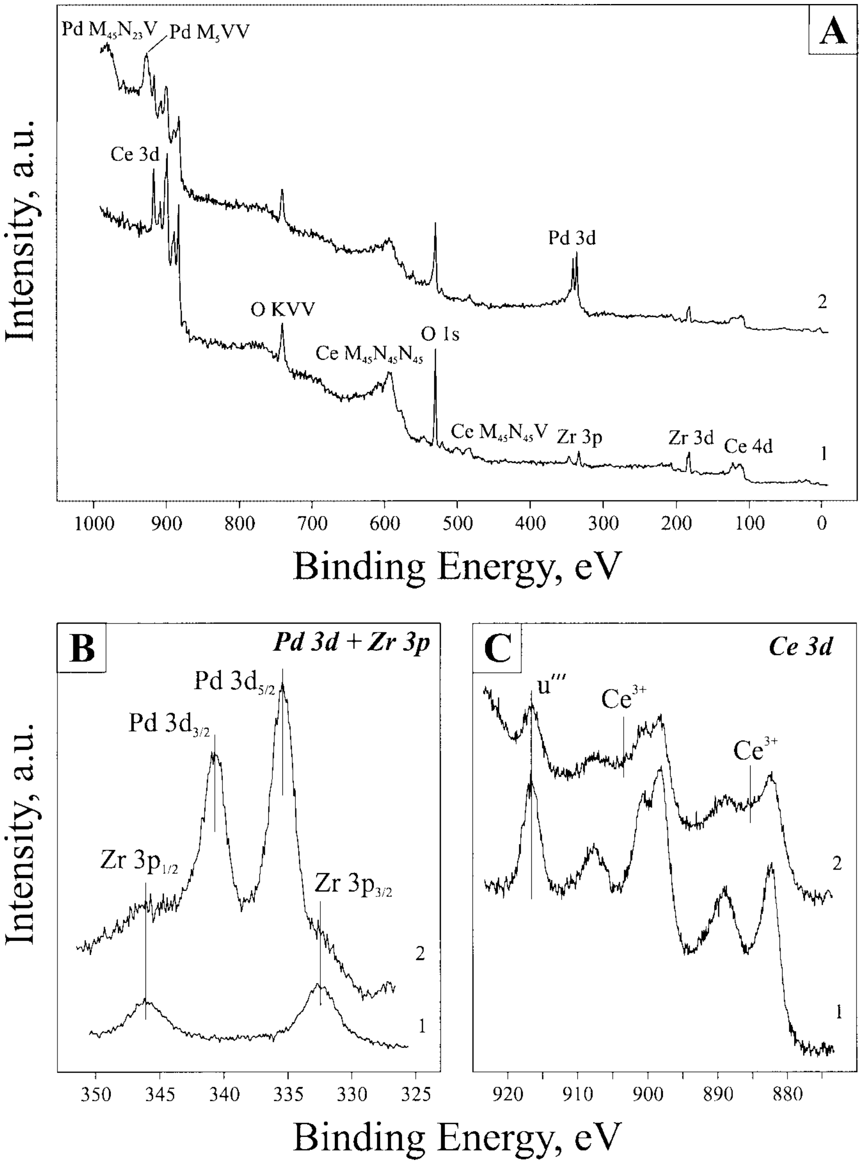

Figure 3. Survey spectra (A), Pd 3d (B), and Ce 3d (C) before (1) and after (2) Pd deposition.

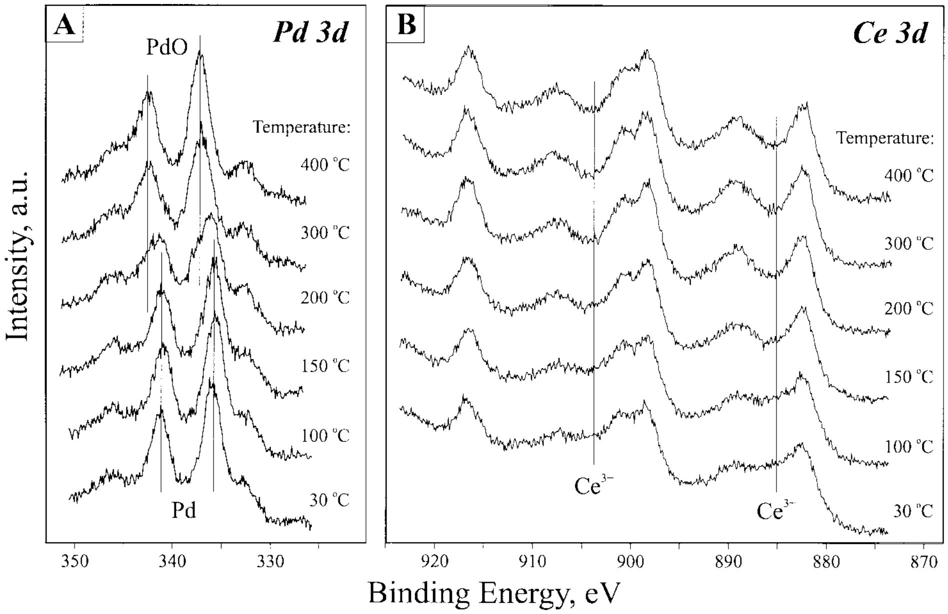

Figure 4. Effect of heating freshly-deposited Pd in UHV on Pd 3d (A) and Ce 3d (B) lines.

Table 4
The effect of heating the ceria–zirconia film with freshly deposited Pd in UHV.

Temperature (°C)	Ce/Zr	Pd/Ce	Pd/Zr	u‴ relative intensity
After Pd deposition	1.49	0.69	1.02	0.115
100	1.45	0.68	0.98	0.117
150	1.56	0.61	0.95	0.125
200	1.43	0.66	0.94	0.123
300	1.82	0.53	0.97	0.130
400	1.53	0.60	0.92	0.125

Table 5
The effect of heating the oxidized ceria–zirconia film with oxidized Pd in CO.

Conditions	Ce/Zr	Pd/Ce	Pd/Zr	u‴ relative intensity
Oxidized film	1.56	1.15	1.79	0.156
100 °C		1.23		0.141
150 °C		1.23		0.134
200 °C		0.84		0.131
250 °C		0.88		0.125
300 °C		0.73		0.119
400 °C		0.86		0.123

When the freshly deposited Pd was heated in UHV, it was observed that Ce^{3+} converts back to Ce^{4+} at $T \geqslant 150\,°C$, similarly to when heating is performed without Pd (figure 4(B) and table 4). (Note that the relative intensities of the u‴ line listed in table 4 are higher than those in tables 1–3. The reason for this is that the background curves subtracted from raw Ce 3d spectra with and without Pd differ in shape due to the presence of a strong Auger line of Pd.) After the temperature reaches 200 °C, Pd begins to oxidize, as evidenced by the growth of a Pd $3d_{5/2}$ line with BE $\approx$ 337 eV at the expense of the line at 335.3 eV (figure 4(A)). The intensity of the Pd 3d lines, relative to the Ce 3d and Zr 3d lines, decreases slightly with increasing temperature (table 4). This effect is clearer for the Pd : Ce ratio than the Pd : Zr ratio.

Heating the re-oxidized ceria–zirconia film with oxidized Pd (freshly prepared, with somewhat more Pd than in table 4) at $T \geqslant 150\,°C$ in carbon monoxide results in the reduction of a small portion of Ce^{4+} to Ce^{3+} (figure 5(B) and table 5). Futhermore, the oxidized Pd also begins to reduce to its metallic state (figure 5(A)). With additional heating in carbon monoxide, to higher temperatures, most of the oxidized Pd reduces to the metallic state, and a further decrease in the Pd : Ce intensity ratio occurs (table 5).

To see whether the intensity of the Pd 3d line changes reversibly under oxidation–reduction cycles, the re-oxidized ceria–zirconia film with another freshly-deposited layer of Pd was heated repeatedly in UHV and CO at 400 °C, and Pd 3d and Zr 3d spectra were acquired after every heating procedure. Figure 6 shows that all the Pd oxidizes upon heating in UHV, and then most of the oxidized Pd converts back into the metallic state upon heating in CO. The following cycle of heating in UHV and CO shows that the oxidation and reduction of Pd is reversible. Also, it was found that the Pd : Zr ratio changes nearly reversibly under the reduction–oxidation cycles. First, the value of Pd/Zr diminished from ca. 2.4 to ca. 2.0 when the ceria–zirconia film with freshly-deposited Pd was oxidized by heating in UHV. The subsequent reduction in CO led to a further decrease of this value to ca. 1.6. The following oxidation restored Pd/Zr nearly to its previous value of ca. 2.0, whereas the subsequent heating in CO returned it to ca. 1.7.

Upon removal of the sample from the electron spectrometer, its powder XRD pattern (figure 7) was obtained. The main, broad, peaks match those of a fluorite structure with

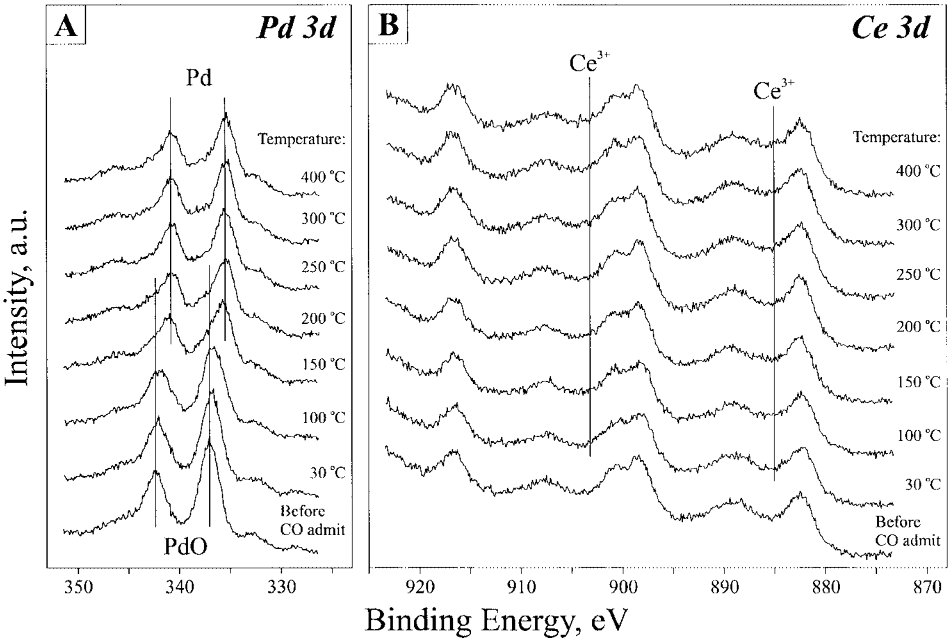

Figure 5. Effect of heating oxidized sample in CO on Pd 3d (A) and Ce 3d (B) lines.

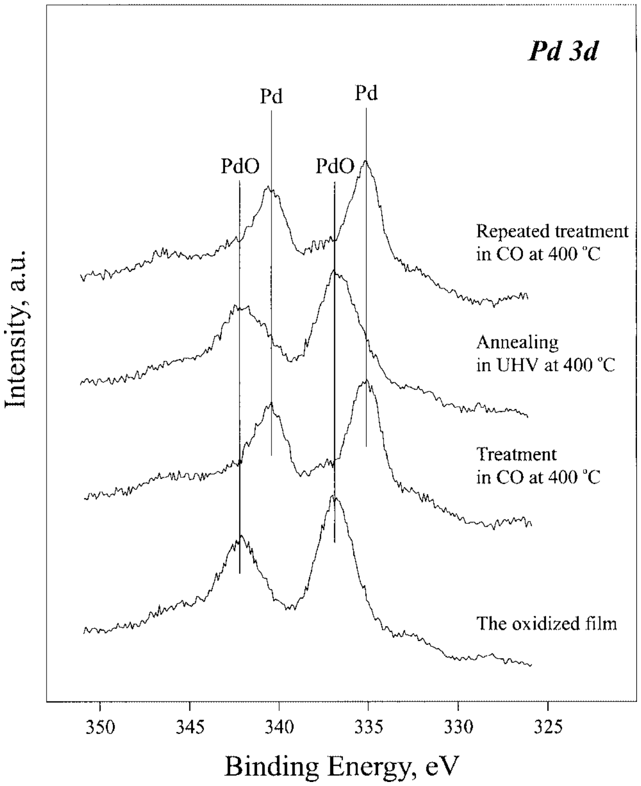

Figure 6. Effect of oxidation–reduction heating cycles on Pd 3d lines.

lattice constant corresponding to $Ce_{0.68}Zr_{0.32}O_2$ [9], and the widths of these peaks correspond to a crystallite size of 5.5 nm. Most of the weak, narrow, peaks are due to the α-Al_2O_3 in the oxide layer on the surface of the FeCrAlloy substrate, but the origin of the stronger peak near 38° is unknown.

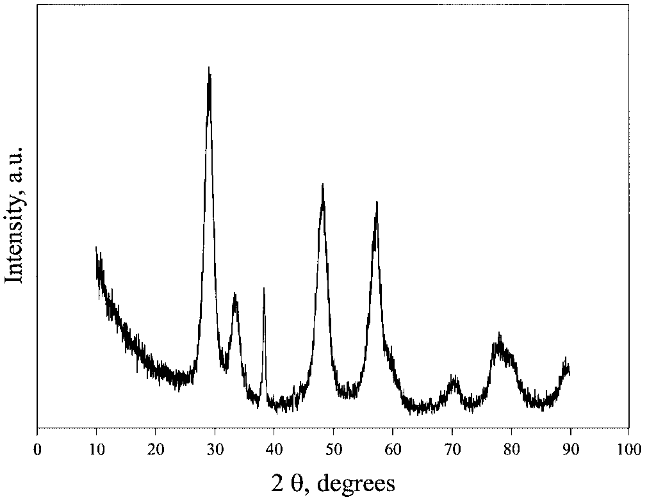

Figure 7. XRD pattern of the ceria–zirconia film.

4. Discussion

XRD indicates that the ceria–zirconia film is a solid solution of ceria and zirconia with bulk composition nearly equal to that of its surface, as deduced by XPS. The effect of Pd deposition on the apparent surface composition of the ceria–zirconia film is thus most likely the result of different attenuation of the Ce 3d and Zr 3d lines produced by the Pd deposit, due to the difference in the inelastic electron mean free paths (1.5 nm for Ce 3d and 2.5 nm for Zr 3d [7]). For a uniform Pd deposit, this would produce a definite, monotonic relation between decreasing Ce : Zr ratio and increasing Pd thickness. For a nonuniform deposit (e.g., Pd particles), however, this relation might also depend on other factors (e.g., particle shape and nucleation density). Deposits with larger Pd : Ce and Pd : Zr ratios thus may not produce the expected smaller Ce : Zr ratio if the deposits are nonuniform.

Typically, heating leads to the sintering of supported metal particles. In these experiments, heating freshly-deposited Pd in UHV results in a decrease in Pd : Ce and Pd : Zr ratios, which is consistent with sintering of the Pd particles. At the same time, however, Pd becomes oxidized, the BE of the Pd 3d lines shifting by an amount corresponding to the conversion of Pd to PdO [7]. Since PdO particles would be larger than the Pd particles from which they were formed, further heating in CO, resulting in the conversion of PdO particles to Pd particles, would result in a further decrease in Pd : Ce and Pd : Zr ratios, as observed. Subsequent oxidation–reduction cycles would be expected to alter the size of the Pd particles and thereby affect the Pd : Zr ratio in just the way observed.

Although heating in CO does reduce most of the oxidized Pd to metallic Pd, relatively little Ce^{4+} is reduced to Ce^{3+}. This simply reflects the ease with which oxygen from the bulk of the ceria–zirconia film moves to the surface under mild heating, at temperatures $\sim$150 °C. Indeed, this flux of oxygen is apparently sufficient to convert the Pd particles to PdO particles at slightly higher temperatures in UHV, a feat which is difficult to accomplish with gas-phase oxygen at pressures typically used in conjunction with UHV. The facile transfer of oxygen from the ceria–zirconia film to the Pd particles, as clearly evidenced by the PdO formation upon mild heating in UHV, is perhaps an essential step, allowing such an OSC material to so effectively promote the CO-oxidation reaction.

Note added in proof

Another paper in this issue, entitled “A calorimetric study of oxygen-storage in Pd/ceria and Pd/ceria–zirconia catalysts”, by L. Yang, O. Kresnawahjuesa, and R.J. Gorte, nicely complements this work.

Acknowledgement

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