Formation and detection of subsurface oxygen at polycrystalline Pd surfaces

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An ion-sputtered, oxygen-exposed, polycrystalline palladium surface has been studied using ion scattering spectroscopy (ISS) before and after exposures to H_2 and CO. A room-temperature exposure to O_2 for 1 min at 1×10^{-7} Torr does not yield chemisorbed oxygen in the outermost layer of atoms according to the ISS data. However, subsequent exposure to H_2 or CO induces subsurface oxygen formed during the O_2 exposure to migrate to the surface under a chemical driving force and populate the outermost atomic layer where it is detected by ISS. This study demonstrates that a reductive treatment can increase the oxygen content of a surface and provides a useful method for examining subsurface oxygen.

Keywords: subsurface oxygen; polycrystalline Pd; ion scattering spectroscopy

1. Introduction

Pd catalysts are active for a number of oxidation reactions including methane oxidation [1–5], CO oxidation [6–13] and alcohol synthesis [14]. The behavior of a particular Pd-based catalyst is strongly dependent upon its surface composition and the chemical states of species present in the near-surface region, which depend upon the preparation and history of the catalyst. Oxygen could be present at these catalyst surfaces in numerous forms including PdO, adsorbed oxygen at various sites, hydroxyl groups and subsurface oxygen. Specific forms of oxygen most likely are responsible for the oxidative properties of these catalysts, and the results presented in this letter suggest that subsurface oxygen is present at these surfaces and may play an active role catalytically. Studying the O–Pd interaction is of importance with regard to gaining a fundamental understanding of how these catalysts function.

The interaction between molecular oxygen and single-crystal Pd(100) [15–19], Pd(111) [20,21] and Pd(110) [22] surfaces have been examined over broad temperature ranges. The coverage dependence and structures formed are quite complex. Simmons et al. [19] have provided a summary of the phases observed by low-energy electron diffraction (LEED) on a Pd(100) surface as a function of O_2 exposure and temperature. They also discuss the surface reconstruction of the surface Pd atoms at higher exposures based on results of high-resolution electron energy loss spectroscopy (HREELS) experiments. Similar reconstructions have also been observed in other studies [15,17,18,20]. In addition to oxygen adsorbed above the outermost Pd layer and incorporated within this layer, Weissman-Wenocur et al. [20] have identified a subsurface oxygen using photoemission spectroscopy (PES) and Auger electron spectroscopy (AES). This is consistent with the LEED and thermal desorption spectroscopy (TDS) results presented by Conrad et al. [23].

In this study the adsorption of oxygen at an ion-sputtered polycrystalline Pd surface has been studied using ion scattering spectroscopy (ISS). ISS is a very important surface characterization technique for examining catalyst surfaces because it provides compositional information only about the outermost atomic layer. This high surface sensitivity arises from the fact that primary ions which penetrate beneath the outermost atomic layer either scatter multiple times and then appear in the broad ion background or are neutralized and not detected. Various factors which affect spectral resolution, elemental sensitivity, experimental factors and quantification of ISS data are discussed in a series of papers by Young, Hoflund and coworkers [24–27].

2. Experimental

The polished, polycrystalline Pd disc (1 cm diameter × 1 mm) was obtained from MaTech with a purity of 99.999 at%. The sample was introduced into an ultrahigh vacuum system (base $P < 10^{-10}$ Torr) where it was sputter cleaned with 2 keV Ar^+ to remove surface contamination according to ISS. The sample was not annealed during these studies. ISS was performed at a scattering angle of 147° using a primary beam energy of either 0.5 or 1 keV He^+ over a spot size of approximately 0.5 cm in diameter, a collection time of 45 or 90 s respectively and primary beam current of 100 nA. These conditions result in a total dose below 5×10^{13} ions/cm^2. The spectra were collected using a double-pass cylindrical mirror analyzer (CMA) (Perkin Elmer PHI model 25-270AR) in the nonretarding mode with pulse-counting detection [28]. Dosing of H_2 and O_2 was carried out at approximately 1×10^{-7} Torr measured with a Perkin-Elmer Digital Gauge Control III.

3. Results and discussion

An ISS spectrum collected after sputter cleaning the air-exposed polycrystalline Pd sample using a 1 : 1 sputter-gas mixture of Ar : He at 1×10^{-5} Torr for 20 min is shown in fig. 1a. The presence of Ar in the sputter gas increases the sputter rate but does not affect the resulting ISS spectra because the ISS features due to Ar^+ are negligible compared to those due to He^+ [26]. The predominant peak present in the spectrum at an E/E_0 of 0.85 is due to Pd. The expanded portion (×5) of the spectrum indicates that a small amount of oxygen (E/E_0 of 0.39) is present on the surface. Furthermore, the negligible background is characteristic of a highly conductive metallic surface. In a previous study of O_2-exposed polycrystalline Ag [29], an ISS calibration experiment was performed and the O/Ag sensitivity factor ratio was determined to be about 0.05. Since the cross sections of the ISS features increase monotonically with mass and the mass of Pd is similar to that of Ag, the O/Pd and O/Ag cross-section ratios are assumed to be similar. Based on this ratio the oxygen content of the surface shown in fig. 1a is about 0.2 at%. The sample was then exposed to 1×10^{-7} Torr of O_2 for 60 s before collecting the ISS spectrum shown in fig. 1b. Again the predominant component of the outermost layer is Pd. Unexpectedly, there is now less oxygen present on the surface than before the oxygen exposure. After exposing the Pd to $^{16}O_2$, it was exposed to $^{18}O_2$ at 1×10^{-7} Torr for 60 s and an identical oxygen-free spectrum was collected (not shown). A subsequent H_2 exposure of 10^{-7} Torr for 60 s was performed, and the spectrum shown in fig. 1c was obtained. There is a large increase in the outermost atomic layer oxygen content to about 30 at% after this reductive treatment. This indicates that oxygen penetrates beneath the Pd surface during an O_2 exposure to form subsurface oxygen. Furthermore, under these conditions oxygen does not adsorb above the Pd surface and is not incorporated within the outermost Pd layer because these forms of oxygen would be detected by ISS if they were present. This differs from the adsorption results obtained in the single-crystal surface studies. The difference may result from structural differences between the polycrystalline surface and the single-crystal surfaces, the fact that the techniques used in the single-crystal surface studies are not as surface sensitive as ISS or the fact that the polycrystalline Pd surface was sputtered and not annealed before O_2 exposure. The presence of hydrogen causes the subsurface oxygen to migrate to the outermost atomic layer under a chemical-induced driving potential where it is detected by ISS. This behavior implies that the reductive treatment results in an enrichment of oxygen in the near-surface region contrary to anticipated behavior. This type of behavior has been observed previously during the reduction of a $TiO_2(001)$ surface [30]. The first O_2 exposure results in the small amount of oxygen present in the outermost atomic layer to move beneath the Pd surface. This may be due to a surface reconstruction caused by the oxygen exposure which then allows all of the oxygen to migrate beneath the surface.

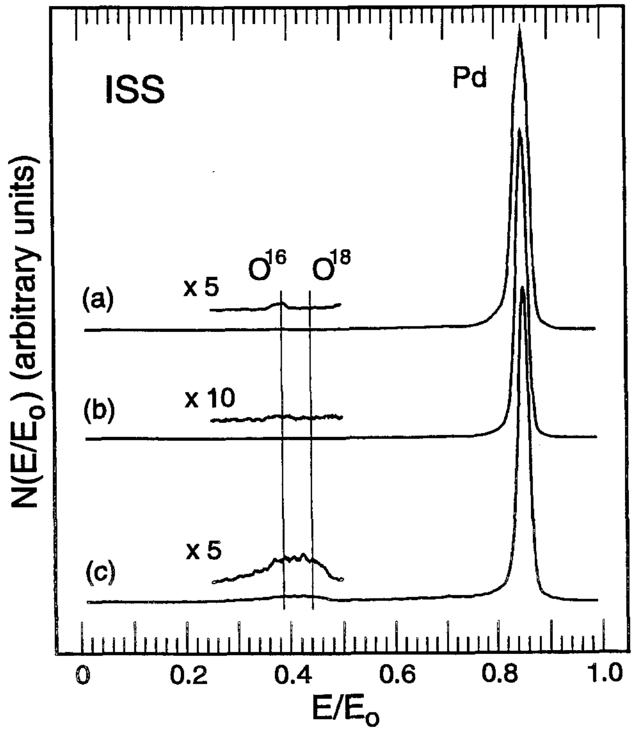

Fig. 1. ISS spectra obtained from the polycrystalline Pd sample after (a) sputter cleaning, (b) exposure to 1×10^{-7} Torr of O_2 for 60 s and (c) exposure to 1×10^{-7} Torr of H_2 for 60 s.

The reactions between surface oxygen and hydrogen or CO to form gaseous reaction products is another important consideration because the amount of surface oxygen present at any time is determined by the relative rates of migration of subsurface oxygen to the surface and loss of surface oxygen as gaseous reaction products. This is illustrated by the data shown in figs. 2 and 3. The sample was sputter cleaned for about 10 min with the

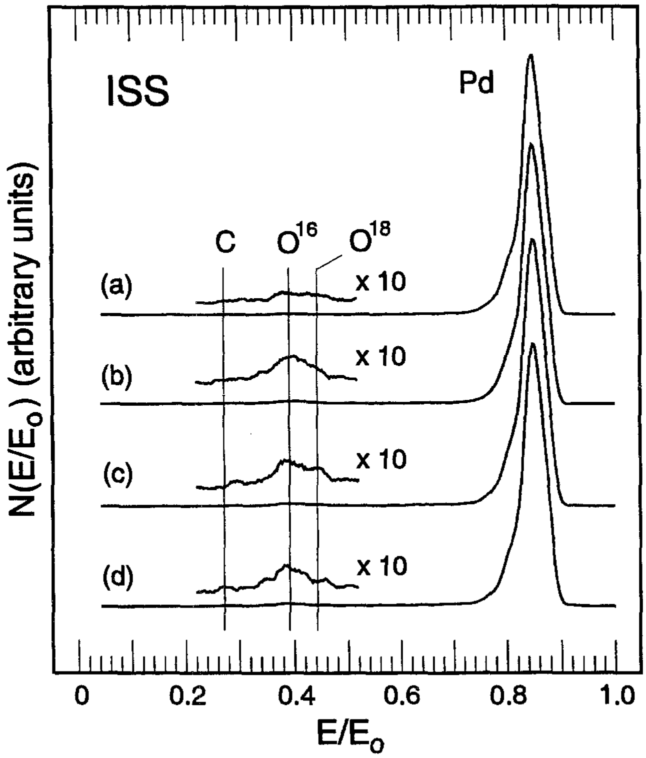

Fig. 2. ISS spectra obtained from the polycrystalline Pd sample after (a) sputter cleaning, (b) exposure to 1×10^{-7} Torr of CO for 120 s and sputtering with He^+ ions for (c) 45 s and (d) 135 s.

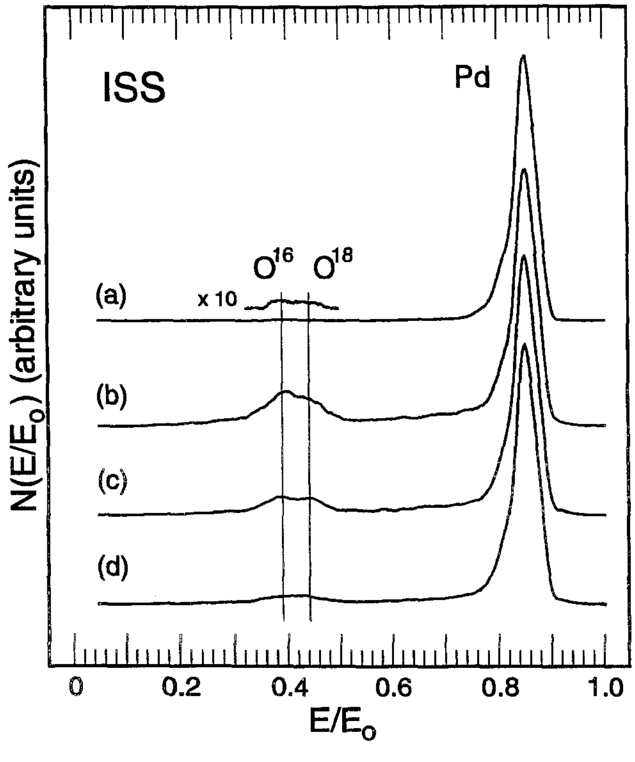

Fig. 3. ISS spectra obtained from the polycrystalline Pd sample after (a) sputter cleaning, (b) exposure to 1×10^{-7} Torr of CO for 60 s and sputtering with He^+ ions for (c) 45 s and (d) 135 s.

Ar/He mixture to remove oxygen from the outermost atomic layer (fig. 2a) and dosed with $^{18}O_2$ at 1×10^{-7} Torr for 4.75 min and then dosed with CO at 1×10^{-7} Torr for 2 min before collecting the ISS spectrum shown in fig. 2b. Small features due to ^{16}O and ^{18}O but not C are apparent. After sputtering this surface for 45 and 135 s while repeatedly collecting ISS spectra with 0.5 keV He^+ (100 nA over a 5 mm diameter area), the spectra shown in fig. 2c and 2d respectively were obtained. This light sputtering results in loss of some of the surface oxygen and appearance of a small C peak at an E/E_0 of 0.27. This indicates that CO adsorbs on this surface and is dissociated during the mild sputtering. Dissociation of CO adsorbed on a polycrystalline Pt surface by ion sputtering has also been observed [31]. The fact that the C feature is not apparent before sputtering indicates that the CO bonds to the Pd vertically through the C atom exposing the ^{16}O atom to the ISS probe.

The sample was then sputter cleaned again to remove the ^{16}O and ^{18}O in the outermost atomic layer (fig. 3a) and then exposed to 1×10^{-7} Torr CO for only 1 min. The ISS spectrum obtained from this surface is shown in fig. 3b. It exhibits large ^{16}O and ^{18}O features indicating that a significant amount of subsurface oxygen migrates to the surface even without further dosing of O_2. Based on the oxygen and Pd peak areas, the outermost atomic layer contains about 85 at% oxygen. Therefore, the difference in sizes of the oxygen features between the spectra shown in figs. 2b and 3b is due to the clean-off reaction between CO and surface oxygen. During the longer CO exposure, more of the surface oxygen reacts with the CO forming CO_2 and then CO adsorbs on the bare Pd sites. ISS spectra were also collected after He^+ sputtering for 45 and 135 s (100 nA over a 5 mm diameter spot), and they are shown in fig. 3c and 3d. Sputter removal of oxygen is apparent. In this case there is no apparent C feature indicating that significant amounts of CO do not adsorb on an oxygen-covered Pd surface.

4. Summary

Exposure of an ion-sputtered, polycrystalline Pd surface to O_2 at room temperature results in adsorption of oxygen and formation of subsurface oxygen. Exposure to H_2 or CO produces a chemical driving force which induces migration of subsurface oxygen to the outermost atomic layer where it is detected by ISS. The outermost layer oxygen concentration depends upon both the rate of subsurface oxygen migration to the surface and the rate of reaction of surface oxygen with H_2 or CO to form gaseous products.

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