Applied Surface Science 256 (2010) 4517–4521

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Carbon monoxide adsorption on Co deposited Pt(1 0 0)-hex: IRRAS and LEED investigations

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ARTICLE INFO

Article history:
Received 29 September 2009
Received in revised form 8 February 2010
Accepted 12 February 2010
Available online 18 February 2010

Keywords:
Infrared absorption spectroscopy
Low-energy electron diffraction
Carbon monoxide
Platinum
Cobalt
Hex reconstruction
Surface alloy

ABSTRACT

Infrared reflection absorption spectroscopy (IRRAS) was used to investigate carbon monoxide (CO) adsorption on Pt(1 0 0) surfaces deposited with Co layers with different thicknesses. Pt(1 0 0) surfaces cleaned in ultrahigh vacuum showed surface reconstruction, i.e., Pt(1 0 0)-hex: two absorption bands ascribable to adsorbed CO on the 1 × 1 surface and hex domains emerge at 2086 and 2074 cm^{-1}, respectively, after 1.0 L CO exposure. Deposition of a 0.3-nm-thick-Co layer on Pt(1 0 0)-hex at 333 K changes the low-energy electron diffraction (LEED) pattern from hex to p(1 × 1), indicating that the deposited Co lifts the reconstruction. The IRRAS spectrum for 1.0-L-CO-exposed $Co_{0.3\,nm}$/Pt(1 0 0)-hex fabricated at 333 K yields a single absorption band at 2059 cm^{-1}. For $Co_{0.3\,nm}$/Pt(1 0 0)-hex fabricated at 693 K, the LEED pattern shows a less-contrasted hex and the pattern remains nearly unchanged even after CO exposure of 11 L, although only 1.0 L CO exposure to Pt(1 0 0)-hex lifts the surface reconstruction. A $Co_{0.3\,nm}$/Pt(1 0 0)-hex surface fabricated at 753 K exhibits an absorption band at 2077 cm^{-1}, which is considered to originate from CO adsorbed on the Pt-enriched surface alloy. $Co_{0.3\,nm}$/Pt(1 0 0)-hex surfaces fabricated above 773 K show a clear hex-reconstructed LEED pattern, and the frequencies of the adsorbed CO bands are comparable to those of Pt(1 0 0)-hex, indicating that the deposited Co atoms are diffused near the surface region. The outermost surface of the 3.0-nm-thick-Co-deposited Pt(1 0 0)-hex is composed of Pt–Co alloy domains even at a deposition temperature of 873 K. Based on the LEED and IRRAS results, the outermost surface structures of Co_x/Pt(1 0 0)-hex are discussed.

1. Introduction

To develop highly efficient and low-cost electrode catalysts for use in fuel cells, Pt-based alloy surfaces have been investigated extensively [1–5]. Stamenkovic et al. clearly show a volcano-type relationship between the surface electronic structure (the d-band center) and the oxygen reduction reaction (ORR) activities for Pt_3M (M = Ni, Co, Fe, Ti, V), where Pt_3Co was the most active in the ORR [1,2]. They also show that the ORR activities strongly depend on the single-crystal indices of the substrates, and the topmost pure Pt atomic layer (called the Pt skin) was found to improve the catalytic activities. Moreover, it is noteworthy that electrochemically fabricated Pt core-shell structures, in which non-Pt nano-sized particles are covered by a monolayer of Pt, reveal superior ORR activities compared to pure platinum particles [6,7]. Improvements in the catalytic activity by alloying can be attributed to the "ensemble" and "ligand" effects [8], and the previous results clearly demonstrate that the atomic design of an alloy's outermost surface plays a significant role in the development of new Pt-based alloy catalysts. In situ observation of the molecular behavior of the outermost alloy surfaces is thus indispensable to elucidating the mechanisms of electrode catalysis.

Vacuum deposition of metal onto different single-crystal metal substrates is one way to construct well-defined surface templates that are suitable to study the surface molecular behavior of alloys [9–15]. For example, molecular beam epitaxy (MBE) and ultrahigh-vacuum (UHV) techniques are successful in achieving well-defined bimetallic surfaces. Detailed experimental conditions of Pt skin generation for well-defined bimetallic surfaces give us a clue to the fabrication of Pt core-shell structures by thermal annealing of Pt-based alloy particles. From the above-mentioned perspectives, we conducted infrared reflection absorption spectroscopic (IRRAS) investigations of carbon monoxide (CO) adsorption on Fe_x/Pt(1 1 1) [16,17], and the outermost surface structures have been discussed based on the C-O stretch frequencies of adsorbed CO bands. The results reveal that an outermost Pt skin generated by 0.5-monolayer (ML)-thick-Fe deposition at 473 K yields a very sharp single absorption band of linearly bonded CO–Pt at 2060 cm^{-1}—30 cm^{-1} lower than that for clean Pt(1 1 1). Comparative study has been conducted for CO adsorption on Fe_x/Pt(1 0 0)-hex [18], where Fe deposition lifts the surface reconstructions, resulting in the topmost Fe–Pt alloy surface, even

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doi:10.1016/j.apsusc.2010.02.039

for deposition at 343 K. For well-defined Pt–Co alloy surfaces, Al-Shamery et al. have investigated the adsorption and desorption behaviors of CO on annealed 0.9-nm-thick-Co-deposited Pt(1 1 1) using IRRAS and temperature-programmed desorption, and demonstrated the ligand effect of Pt–Co alloys [19,20]. Our research group has also discussed the outermost surface structures for Co_x/Pt(1 1 1) fabricated at various Co deposition temperatures using low-energy electron diffraction (LEED) and IRRAS [21], where Co deposition on Pt(1 1 1) at about 773 K generates a Pt skin.

Investigating the molecular behavior of Co_x/Pt(1 1 1) as well as Co_x/Pt(1 0 0) on alloy surfaces is essential to understand the improvement in ORR activity by alloying Pt with Co. The surface cleaning process of Pt(1 0 0) in UHV leads to surface reconstruction (the so-called “hex”) [22]. This paper describes LEED and IRRAS investigations of the outermost surface structures for Co_x/Pt(1 0 0)-hex (x = 0.15, 0.3, 0.6, and 3.0 nm) fabricated by vacuum deposition of Co onto Pt(1 0 0)-hex at elevated substrate temperatures. We focus on the dependence of the deposition temperature on the outermost surface structures.

2. Experimental

The experimental equipment used in this study has been described elsewhere [23]. Briefly, the system is equipped with several facilities including IRRAS, LEED, quadruple mass spectrometer (Q-mass), and electron-beam evaporator. The Pt(1 0 0) (<1° miscut) crystal surface was cleaned by repeated Ar^+ sputtering and annealing at 1000 K under UHV. Heating of the sample is performed using pyrolytic graphite heater and the sample temperatures are monitored by an alumel-chromel thermocouple. The surface crystallographic order is verified by LEED (OCI BDL400), and the LEED pattern of the resulting Pt(1 0 0) shows 5 × 20 surface reconstruction (Pt(1 0 0)-hex). Co (99.99% in purity) is deposited onto the Pt(1 0 0)-hex using an electron-beam evaporator (Beamtron). The Co deposition rate is fixed at 0.1 nm min^{-1}; it was estimated by a flux monitor installed in the evaporator and calibrated separately by a quartz microbalance. The sample temperature during the Co deposition is kept constant (less than ±0.5 K) by using a proportional–integral–derivative (PID) controller (CHINO DB1000). The UHV chamber base pressure is 3×10^{-8} Pa and the pressure during Co deposition is less than 1×10^{-7} Pa. Exposure of CO to the resultant surfaces is conducted at approximately 5×10^{-7} Pa. IRRAS spectra are recorded at 2 cm^{-1} resolution with an average of 100 scans using an FT-IR spectrophotometer (Bomem MB100) equipped with a liquid-N_2-cooled HgCdTe detector. Each spectrum is presented as a ratio of spectra recorded before and after CO exposure.

3. Results and discussion

3.1. IRRAS spectra for adsorbed CO on $Co_{0.3\,nm}$/Pt(1 0 0)-hex fabricated at elevated substrate temperatures

We measured IRRAS spectra for adsorbed CO on $Co_{0.3\,nm}$/Pt(1 0 0)-hex fabricated at elevated substrate temperatures. Fig. 1 shows the IRRAS spectra for the corresponding surfaces recorded at about 300 K after 1.0-L CO exposure (1 L = 1.0×10^{-6} Torr s). For comparison, CO-IRRAS spectrum for clean Pt(1 0 0)-hex is also presented. In addition, the corresponding LEED patterns for the surfaces before CO exposure are shown on the right. In the IRRAS spectrum of 1.0-L-CO-exposed Pt(1 0 0)-hex (top), we observed prominent absorption bands at 2086 and 2076 cm^{-1}, accompanied by weak absorption at 1868 cm^{-1}. It is well known that surface cleaning of Pt(1 0 0) in UHV causes LEED patterns with 5 × 20 surface reconstruction (called Pt(1 0 0)-hex), where the topmost surface is composed of hexagonal closely packed domains on an original 1 × 1 surface [22]. With regard to clean Pt(1 1 1), CO adsorption yields IRRAS bands at 2093 and 1855 cm^{-1} [24,25]. In contrast, CO-adsorption behavior on Pt(1 0 0)-hex is rather complicated. The surface reconstruction is lifted by CO exposure [26,27], and the linearly bonded CO on the 1 × 1 surface and the reconstructed hex domains of Pt(1 0 0)-hex give rise to absorption bands at around 2080–2090 and 2070–2085 cm^{-1}, respectively. Based on the published results described above, the two bands at 2086 and 2074 cm^{-1} can be assigned to C–O stretch vibrations of the linearly bonded CO on the 1 × 1 and hex domains of Pt(1 0 0)-hex, respectively; the weak absorption at 1868 cm^{-1} is ascribable to the bridge-bonded CO on the surface.

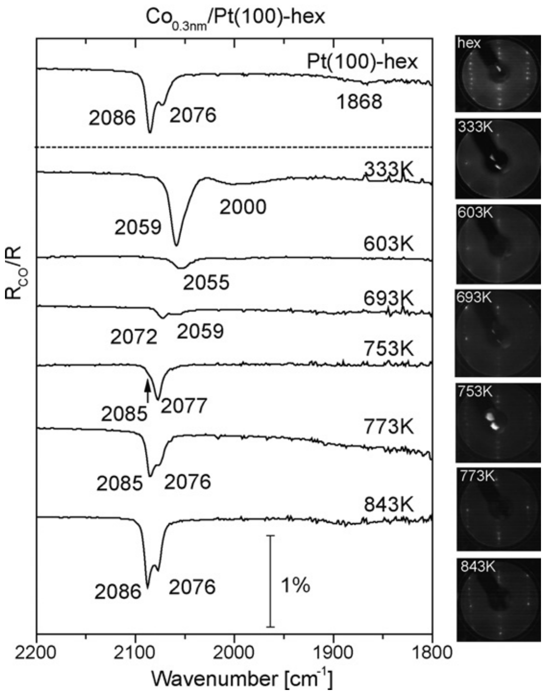

Fig. 1. IRRAS spectra of 1.0-L-CO-exposed $Co_{0.3\,nm}$/Pt(1 0 0) surfaces fabricated within the temperature range 328–843 K. Corresponding LEED patterns are shown on the right.

Co depositions of 0.3-nm thickness on Pt(1 0 0)-hex below 603 K make the LEED sub-spots almost disappear, leaving the less-contrasted p(1 × 1) (Fig. 1). Lifting of the hex reconstruction for Ag_x/Pt(1 0 0)-hex is also shown by Strüber et al. [28], where the Ag depositions lift the surface reconstruction. The $Co_{0.3\,nm}$/Pt(1 0 0)-hex fabricated at 333 K shows a CO band at 2059 cm^{-1}, accompanied by a weak absorption at around 2000 cm^{-1}. The 603-K-fabricated surface also exhibits a band at 2055 cm^{-1} in addition to a faint absorption band at around 2000 cm^{-1}. Several authors [29,30] reported CO adsorption on clean Co(0 0 0 1) by IRRAS, in which linearly bonded CO bands appear at around 2000–2050 cm^{-1}: the frequencies depend on CO ambient pressures. Therefore, the weak absorption at 2000 cm^{-1} can be ascribed to the adsorbed CO at the surface Co domains grown epitaxially on Pt(1 0 0)-hex.

The spectral features of the CO adsorptions are sensitive to the Co deposition temperatures. For example, a band at 2077 cm^{-1} dominates the spectrum for a 753-K-fabricated surface. The results suggest a change in the alloy compositions and structures at the topmost surfaces. We have previously reported CO adsorption of Fe_x/Pt(1 0 0)-hex [18]: C–O stretch bands shift from 2049 cm^{-1} for 343-K-fabricated $Fe_{0.5ML}$/Pt(1 0 0)-hex to 2073 cm^{-1} for 873-K-