Infrared reflection absorption study of carbon monoxide adsorption on Fe-deposited Pt(111) surface

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Abstract. Infrared reflection absorption spectroscopy (IRRAS) was used to investigate carbon monoxide (CO) adsorption on sub-monolayer (ML)-thick Fe deposited Pt(111). The CO exposure to a clean Pt(111) surface at room temperature yielded linear-bonded and bridge-bonded CO-Pt bands at 2090 and 1850 cm⁻¹. The CO-Pt band intensities decreased steeply with increasing Fe thickness. For a 1-ML-thick-Fe/Pt surface, the bridge-bonded CO-Fe band at 1950 cm⁻¹ dominated the spectra. Furthermore, the Fe depositions showed a new absorption band at around 2060 cm⁻¹. The IRRAS spectrum for CO adsorption on the 3-Å-thick-Pt-covered a 1-ML-Fe/Pt(111) surface showed a single absorption at 2070 cm⁻¹. Based on the IRRAS results, we discuss CO adsorption behavior on sub-ML-thick Fe/Pt(111) surfaces.

1. Introduction
Pt-based bimetallic surfaces have been particularly subjected to research. For example, precise control of the Pt/Fe hetero-structures is indispensable to develop novel magnetic-information-storage devices [1,2,3]. Furthermore, alloying of Pt with Fe improves the carbon monoxide (CO) tolerance of the electrode catalyst for fuel cells [4]. Fabrication of well-defined alloy surfaces through vacuum deposition of a metal onto different single-crystal metal substrates has been investigated for designing new materials showing unique surface properties that are not available in a single metal [5,6]. These approaches for constructing specific surface lattice structures are crucial not only for investigating physical, chemical, and electronic properties of alloys but also for innovating industrial processes, particularly in the fields of magnetic devices and heterogeneous catalysis.

To date, numerous studies for Pt-based alloys have been carried out for developing CO-tolerant electrode materials [4,7]. Molecular characterizations of CO on well-defined alloy surfaces would provide us important clues to understand CO tolerance and produce an essential guide for development of inexpensive electrode materials for fuel cells. Koel and co-workers investigated the vicinal surface structures of as-deposited and 500-K-annealed Fe/Pt(111) by ion scattering and X-ray photoelectron spectroscopic measurements [8]. Nevertheless, few studies have specifically examined surface chemistry for well-defined Pt/Fe surface alloys. We have reported infrared reflection absorption spectroscopic (IRRAS) results for molecular adsorptions on several bimetallic surfaces [6,9,10,11]. For the present study, we carried out IRRAS measurements for CO on the Pt/Fe bimetallic surfaces fabricated by vacuum-depositions of Fe on a clean Pt(111) held at 340 K under ultra-high vacuum (UHV) conditions: the results are briefly reported.
2. Experimental
Details of the experimental equipment and procedures have been described elsewhere [6,9,10,11]. Briefly, a Pt(111) crystal was used as the substrate for Fe deposition. Repeated Ar⁺ sputtering and annealing at 1500 K under UHV conditions cleaned the Pt(111) surface. Using a Knudsen cell, Fe of 99.999% purity was deposited onto the Pt substrate surfaces held at 340 K. The Fe thicknesses in monolayer (ML) units were estimated based on the deposition time and the number of regular oscillations in the RHEED intensity observed during the fcc-Fe/Cu(100) epitaxial growth [9]. The deposition rate was approximately 0.3 ML/min. Using an electron-beam evaporation method, Pt (99.99% purity) was deposited onto the 1 ML-thick-Fe deposited Pt(111) to fabricate a Pt/Fe/Pt hetero-structure. The Pt thickness was determined using a quartz oscillator. The reflection high-energy electron diffraction (RHEED) measurements were made using a 10 keV electron beam incidence. The diffraction images were analyzed quantitatively via detection of light emitted from the fluorescent screen using a computer-controlled CCD video camera and a data acquisition system (KSA 400). Exposures of CO to the resulting Fe/Pt(111) and Pt/Fe/Pt(111) surfaces were carried out at approximately 7×10⁻¹⁰ Torr. The IRRAS spectra of adsorbed CO were recorded at 2 cm⁻¹ resolution as an average of 300 scans using an FT-IR spectrophotometer equipped with a liquid-N₂-cooled HgCdTe detector. Each spectrum is presented as a ratio with the spectrum recorded before CO exposure.

3. Results and Discussion

Figure 1 shows IRRAS spectral changes of adsorbed CO on the 0.5-ML-thick Fe/Pt(111) surface with CO exposure. Three absorption bands appear at 2080, 2045, and 1920 cm⁻¹ at CO exposure of 0.1 L (1 L=1.0×10⁻⁶ Torr·s). Because of the dipole-dipole interaction of the adsorbed CO molecules, the bands increase in intensity and shift to higher frequencies with increasing CO exposure [13]. At saturation CO coverage (1.0 L), the highest and lowest frequency bands are located at 2090 and 1955 cm⁻¹. On the clean Pt(111), the strong band at 2093 cm⁻¹, which is ascribable to the linear-bonded CO adsorption, dominated the IRRAS spectrum for CO adsorption at saturation coverage [14,15]. Actually, the clean Pt(111) surface shows the linear-bonded and bridge-bonded CO bands at 2093 and 1870 cm⁻¹ (Fig. 3). Furthermore, our previous study of the fcc-Fe on Cu single crystal substrates showed that the
bridge-bonded CO on the fcc-Fe arose the IRRAS bands at around 1950 cm$^{-1}$ [6,9]. Consequently, the 2090 and 1955 cm$^{-1}$ bands for the spectrum of the 1.0L-CO-exposure can be assigned respectively to the linear CO-Pt and the bridge CO-Fe bonds. The origin of the 2060 cm$^{-1}$ band (indicated by an arrow) will be discussed later.

![Figure 2](image1.png) ![Figure 3](image2.png)

**Figure 2.** IRRAS spectral changes of adsorbed CO on the 0.5-ML-thick-Fe/Pt(111).

**Figure 3.** IRRAS spectra of saturated CO on various thicknesses of Fe/Pt(111). Inset: Pt-CO peak intensity vs. Fe thickness.

Figure 3 depicts the IRRAS spectra for saturated CO adsorptions on the clean surface and from 0.25-ML-thick to 1.0 ML-thick-Fe deposited Pt(111) surfaces. For the spectrum of the 0.25-ML-thick-Fe/Pt(111) surface, the most intense band appeared at 2090 cm$^{-1}$, concomitant with the bridge-bonded CO-Fe band at 1950 cm$^{-1}$. With increasing Fe thickness, the linear CO-Pt band (indicated by an asterisk) markedly decreases in intensity, as is clearly visible in the inset. For thickness greater than 0.75 ML, no bands caused by CO adsorbed on the clean Pt(111) surface; the bands caused by CO adsorptions on the deposited Fe dominate the spectra. Those results suggest that the Pt(111) surface is almost covered by the 1-ML-thick-Fe deposition. Taking the previous RHEED results (Fig. 1) into account, the fcc-Fe(111) grows in a layer-by-layer manner on the Pt(111).

It is worth pointing out that the sub-ML-thick Fe depositions create weak bands around 2060 cm$^{-1}$ (indicated by arrows). The arriving Fe atoms might eject substrate Pt to form a cluster at the outermost growing surface. The cluster atoms might diffuse on the surface by thermal energy of the sample and are trapped by the step-edge of the original Pt surface to form an outermost layer of Pt atoms. In the light of scanning tunnelling microscopic (STM) observations for Co growth on Pt(111) [16], misfit dislocations in the Fe layer might also contribute to the formation of the outermost Pt layer. Hannon et al. reported a similar surface layer including the substrate atoms for the Pd depositions on the Cu(100) at 473 K [17]. Furthermore, Koel and co-workers investigated the surface structures of the Fe-deposited Pt(111) and reported that the outermost surface included Pt even after the 500-K-annealing of the Fe/Pt(111) [8]. Therefore, new bands at around 2060 cm$^{-1}$ might be assigned to CO adsorption on the outermost Pt layer formed through the Fe deposition process at 340 K. In order to verify the influence of the under-laid Fe on the IRRAS frequency of CO adsorbed on the outermost Pt layer, a Pt/Fe/Pt(111) structure was fabricated by the 3-Å-thick-Pt deposition on the 1-ML-thick-Fe/Pt(111). The RHEED image for the Pt/Fe/Pt(111) revealed streaks corresponded to the substrate Pt(111) and the streaks due to the Fe (indicated by arrows in Fig. 1) disappeared. At CO saturation coverage, the resulting Pt/Fe/Pt(111) yielded only a single intense band at 2070 cm$^{-1}$ that can be ascribed to the
linearly-bonded CO to Pt. The above-mentioned results clearly indicate that the top surface of the Pt/Fe/Pt(111) should be composed of pure Pt atoms and the IRRAS band position of adsorbed CO on the outermost Pt layer might shift to lower frequency in comparison to that on the clean Pt(111).

As depicted in the inset, the CO-saturated Pt(111) surface raised the intensity of the linear CO-Pt band about 3.3%. In contrast, the 2060 cm\(^{-1}\) band intensity was about 0.3% for the 0.5-ML-thick-Fe deposited surface. If we assume layer-by-layer growth of the fcc-Fe on the Pt(111), the increase in Fe deposition should cause a linear decrease in surface-area of the uncovered Pt, bringing about linear intensity reduction of the Pt-CO band. Nevertheless, the Pt-CO band intensity markedly decreased with increasing Fe thickness. In any event, a very small amount of the deposited Fe causes significant intensity reduction of the Pt-CO band. This might correlate with reduction of CO sticking probability to the Fe/Pt surface, thereby corresponding to the low CO-poisoning of the Pt-Fe alloy electrode in the fuel cell [4,7].

4. Summary

The CO adsorption behaviour on the various-thick Fe/Pt(111) surfaces fabricated by Fe vacuum-depositions on the clean Pt(111) at 340 K are elucidated using IRRAS. The CO-Pt IRRAS band intensities decreased steeply with increasing Fe thickness from 0 to 0.5 ML: a very small amount of the deposited Fe resulted in significant reduction of CO adsorption on the Fe/Pt surfaces. For the 1-ML-thick-Fe/Pt surface, the bridge-bonded CO-Fe band dominated the spectra, accompanied by a new absorption near 2060 cm\(^{-1}\). Furthermore, the IRRAS spectrum for CO adsorption on the 3-Å-thick-Pt-covered 1-ML-Fe/Pt(111) surface showed a single absorption at 2070 cm\(^{-1}\), revealing that adsorbed CO on the outermost Pt layer might show a red-shift in peak frequency. The results suggest that the Pt(111) substrate is almost covered by the 1-ML-thick Fe deposition and that the Fe diffusion into the substrate creates an outermost Pt layer, giving rise to the new band at 2060 cm\(^{-1}\) caused by CO adsorption on the outermost Pt layer.

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