

**Ru-Modified Pt(100) Surfaces:  
Effect Of Annealing On The Adsorption Of Co As  
Monitored By Infrared Reflection Absorption  
Spectroscopy (Iras) In Ultrahigh Vacuum**

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**INTRODUCTION**

Bimetallic Pt/Ru surfaces have been shown to display exceptional activity for methanol oxidation,<sup>1</sup> and increased CO tolerance for hydrogen oxidation in electrochemical environments.<sup>2</sup> Experiments have been performed both for Ru-modified Pt<sup>3</sup> and also Pt-modified Ru<sup>4</sup> yielding similar conclusions. A more detailed comparison between the binding of CO to these two types of bimetallic surfaces is of interest in order to determine effects due to the substrate (Pt or Ru). Noteworthy is the ultrahigh vacuum (UHV) work of Schlapka et al<sup>5</sup> which addressed the Pt surface redistribution induced by annealing of Pt-modified Ru(001) using scanning tunneling microscopy (STM), as well as the binding of CO to such surfaces by IRAS. Previous work performed in our laboratories focused on CO binding to Ru-modified Pt(100) surfaces as studied by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD).<sup>6</sup> The present contribution explores the effects of sequential annealing of Ru-modified Pt(100) surfaces on CO adsorption, as monitored by IRAS in UHV.

**EXPERIMENTAL**

A Pt(100) single crystal was mounted on a liquid nitrogen cooled cryostat in a UHV chamber equipped with IRAS and XPS for characterization of Pt single crystals and bimetallic Ru-modified Pt surfaces. The latter were prepared by first cleaning the Pt(100) crystal with cycles of Ar<sup>+</sup> sputtering and annealing to 1073K in an O<sub>2</sub> atmosphere (ca. 1 x 10<sup>-8</sup> torr). The Pt(100) crystal was characterized by XPS and then cooled to 140K before exposure to trisruthenium dodecacarbonyl, Ru<sub>3</sub>(CO)<sub>12</sub>, vapors using procedures developed in our laboratory.<sup>6</sup> After deposition, the Ru<sub>3</sub>(CO)<sub>12</sub> was decomposed by irradiating the sample with X-rays while simultaneously heating the sample to ca. 650K. The X-ray source was then turned off and the sample annealed at 650K in an oxygen atmosphere (ca. 10<sup>-8</sup> torr) for 2-3 min, and XPS spectra recorded. Specimens prepared in this specific fashion will be referred to hereafter as *initial*.

Carbon monoxide is delivered to the chamber through a gas leak valve (Varian) allowing for control of the partial pressure of CO in the mid 10<sup>-10</sup> torr range. The CO adsorption onto the bimetallic Ru-Pt surface is monitored by IRAS. After each CO adsorption experiment, the bimetallic Ru-Pt surface was annealed at ca. 650K for 2.5 h, including 6 min at ca. 650K in an O<sub>2</sub> atmosphere (1 x 10<sup>-8</sup> torr) to remove residual carbon. The CO adsorption experiments on annealed Ru-Pt surfaces monitored by IRAS are performed in an identical manner to that for the initial Ru-Pt surface.

**RESULTS AND DISCUSSION**

The IRAS spectrum of the *initial* Ru-modified Pt(100) ( $\theta_{\text{Ru}} = 0.52$ ) surfaces following CO saturation exposure is shown in curve a, Fig. 1. Curves b through d were collected after individual annealing steps at 650 K for 2.5 in sequence. h. The peak centered at 2092 cm<sup>-1</sup> in curves a-d is attributed to CO adsorption on Ru-modified sites, whereas that at 2100 cm<sup>-1</sup> corresponds to CO adsorption on Pt(100), as evidenced from data obtained on Ru-free Pt(100) (see curve in Fig. 1). Statistical analyses of IRAS spectra recorded in experiments in which a Ru( $\theta_{\text{Ru}}$  ca. 0.52)/Pt(100) surface was annealed sequentially to 650 K for ca. 2.5 h prior to a saturation exposure of CO revealed changes in the relative intensities of the two peaks with a clearly identifiable isosbestic point, characteristic of a quantitative conversion of one type of species into another. This behavior has been attributed to a thermally-induced surface incorporation of Ru into Pt, as inferred from low energy ion scattering spectroscopy (LEIS) for other Ru-modified low index single crystal Pt surfaces, which effectively enriches the surface with Pt, while reducing the Ru coverage.<sup>7, 8</sup>

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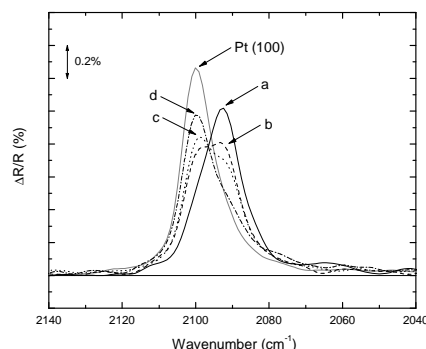


Fig. 1. IRAS spectra for the *initial* Ru-modified Pt(100) ( $\theta_{\text{Ru}} = 0.52$ ) exposed to saturation CO at 130 K (curve a). The corresponding spectra for annealing/saturation CO exposure experiments run in sequence for the same Ru/Pt surface (see text) are given in order in curves b through d. Also shown in this figure is the spectrum of CO on pristine Pt(100).