Surface Science 603 (2009) 455–461

Contents lists available at ScienceDirect

Surface Science

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

An IRAS study of CO bonding on Sn/Pt(1 1 1) surface alloys at maximal pressures of 10 Torr

Adrian Hightower [a,*], M. Dolores Perez [b], Bruce E. Koel [c]

[a] Occidental College, Physics, 1600 Campus Road, Los Angeles, CA 90041, USA
[b] University of Southern California, Los Angeles, CA 90089, USA
[c] Lehigh University, Bethlehem, PA 18015, USA

ARTICLE INFO

Article history:
Received 9 September 2008
Accepted for publication 21 November 2008
Available online 3 December 2008

Keywords:
Carbon-monoxide
Pt(1 1 1)
Platinum
Catalyst
Pt_3Sn
Sn–Pt alloy
FTIR
IRAS

ABSTRACT

The adsorption of CO on Pt(1 1 1), (2 × 2) and ($\sqrt{3} \times \sqrt{3}$)R30° Sn/Pt(1 1 1) surface alloys has been studied using temperature programmed desorption (TPD), low energy electron diffraction (LEED) and infrared reflection adsorption spectroscopy (IRAS). The presence of Sn in the surface layer of Pt(1 1 1) reduces the binding energy of CO by a few kcal/mol. IRAS data show two C–O stretching frequencies, ~2100 and ~1860 cm^{-1}, corresponding to atop and bridge bonded species, respectively. Bridge bonded stretching frequencies are only observed for Pt(1 1 1) and (2 × 2) Sn/Pt(1 1 1) alloy surfaces. A slight coverage dependence of the vibrational frequencies is observed for the three surfaces. High pressure IRAS experiments over a broad temperature range show no indication of bridge bonded CO on any of the three surfaces. Direct CO adsorption on Sn sites is not observed over the measured temperature and pressure ranges.

1. Introduction

The wide use of bimetallic catalysts has motivated extensive studies of well-defined surface alloys [1–3]. In particular, CO has been widely studied on bimetallic platinum surfaces as a prototypical molecule to investigate the influence of site-blocking and electronic phenomena on reaction kinetics [4–9]. There is also special interest in CO behavior as a poison and/or intermediate in the mechanism of low temperature hydrocarbon oxidation [10–13]. The drive to better correlate the performance of bimetallic heterogeneous catalysts with ultrahigh vacuum (UHV) surface science studies has lead to numerous high pressure surface studies on single crystals [14–18]. This work presents results of high pressure vibrational studies of CO on Sn/Pt(1 1 1) alloys to better understand the so-called “pressure-gap”.

Sn/Pt(1 1 1) alloys are known to form two ordered surfaces, (2 × 2) Sn/Pt(1 1 1) and ($\sqrt{3} \times \sqrt{3}$)R30° Sn/Pt(1 1 1) by vapor deposition of Sn on Pt(1 1 1) single crystals followed by careful annealing under high vacuum conditions [5,19]. Low energy ion scattering spectroscopy (LEISS) and depth profiling by Auger electron spectroscopy (AES) indicate this procedure yields surface alloys with Sn atoms localized to the top two surface layers [20]. Fig. 1 displays the proposed alloy surfaces and corresponding LEED patterns. Sn atoms protrude 0.02 nm above the surface-Pt plane for both surfaces [21]. For the (2 × 2) structure, pure-Pt threefold sites are present, but no adjacent pure-Pt threefold sites exist. All pure-Pt threefold sites are eliminated in ($\sqrt{3} \times \sqrt{3}$)R30° structure. For brevity throughout this paper, (2 × 2) Sn/Pt(1 1 1) and ($\sqrt{3} \times \sqrt{3}$)R30° Sn/Pt(1 1 1) surface alloys will be referred as (2 × 2) and $\sqrt{3}$ alloys, respectively.

The bonding and structure of CO on clean Pt(1 1 1) has been well-studied by TPD and high resolution electron energy loss spectroscopy (HREELS). CO is chemisorbed perpendicular to the surface with carbon bonding directly to metal atoms. CO initially populates atop sites at low coverage and then populates bridges sites form a c(4 × 2) structure at $\theta_{CO} = 0.5$ (θ_{CO} is defined as the ratio of CO molecules to surface atoms) [22,23]. These results have been supported by density-functional theory (DFT) calculations [24,25]. Dense CO adlayers forming “linear domain-wall” c($\sqrt{3} \times 7$) structures at $\theta_{CO} = 0.71$ coverage have also been reported on Pt(1 1 1) [26].

A thorough inspection of the CO adsorption on these alloy surfaces concluded that alloying with Sn causes only slight decreases in the CO binding energy to the surface compared to Pt(1 1 1) [4]. At low temperatures (~100 K) and saturation coverage, CO was found to chemisorb to atop and bridge sites on the Pt(111), (2 × 2) and $\sqrt{3}$ surfaces. Xu et al. proved the existence of a modifier precursor state and used this to explain how Sn influences CO chemisorption kinetics in a manner other than that predicted by a

---

[*] Corresponding author. Tel.: +1 323 259 2826; fax: +1 323 341 4858.
E-mail address: hightower@oxy.edu (A. Hightower).

0039-6028/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2008.11.020

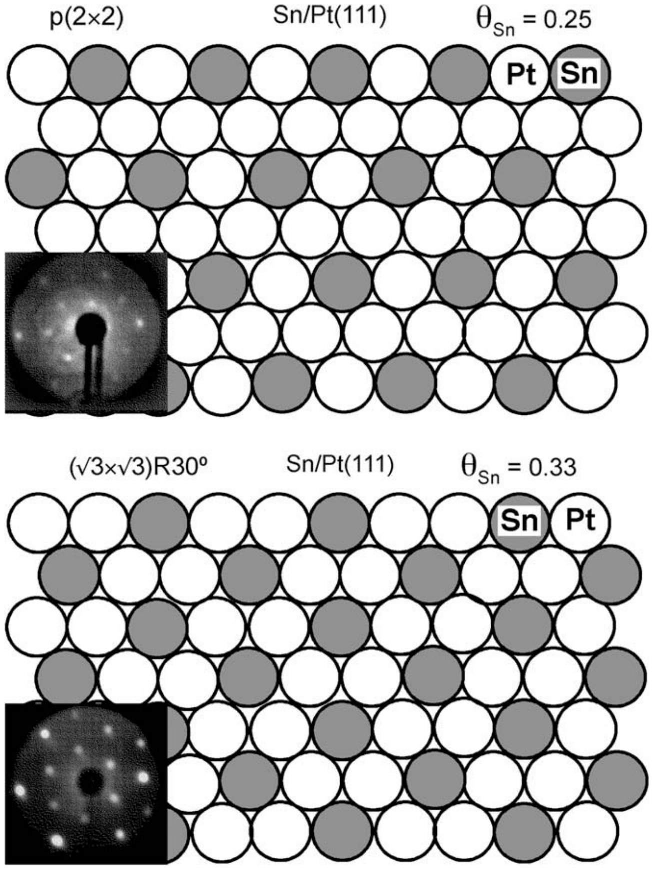

Fig. 1. Schematics diagrams and corresponding LEED patterns of the two ordered Sn/Pt(1 1 1) surface alloys that were investigated.

simple site-blocking model [5]. Previous LEED studies report a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure for CO adlayers at saturation coverage on the (2×2) surface while no ordered CO adlayers were observed on the $\sqrt{3}$ surface [4]. The same study utilized HREELS to observe CO populating both atop and bridge sites for Pt(1 1 1), (2×2) and $\sqrt{3}$ alloy surfaces at saturation coverage. Yet the limited resolution of HREELS measurements leaves questions regarding the coordination of CO relative to Sn sites on surface alloys.

Recent surface studies and DFT calculations on the (1 1 1) surface of bulk Pt_3Sn alloys have provided valuable insight into the activity of CO oxidation on Pt–Sn surfaces [27,28]. HREELS studies by Dupont et al. [9] on the (2×2) $Pt_3Sn(1 1 1)$ bulk alloy surface have found CO populating both atop and bridge sites similar to the HREELS measurements on the (2×2) surface alloy [4]. High pressure polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) studies on $Pt_3Sn(1 1 1)$ bulk alloys exposed to CO followed by O_2 at room temperature found more efficient CO desorption from the $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface than from the (2×2) [18]. It is important to note that surface studies on bulk alloy must contend with segregation of Sn to the surface [29]. In contrast, the surface alloys studied in this work are extremely thin (less than two monolayers) and are thought to be less susceptible to surface segregation. Indeed an important advantage of studying surface alloys over bulk alloy surfaces is the opportunity to exploit Gibbsian surface segregation to achieve a desired surface rather than fight against it [30].

In the present work we use infrared reflection adsorption spectroscopy (IRAS) to gain further insight on the interaction of CO on two ordered Sn/Pt(1 1 1) surface alloys. The high resolution of infrared (IR) spectroscopy makes it well-suited to study the C–O stretching modes of CO on Pt surfaces [31]. Care must be taken when using IRAS to assign CO populations to atop, bridge, and threefold hollow sites of Pt(1 1 1). Dynamic dipole–dipole coupling in dense CO adlayers is known to influence IRAS spectra by “intensity transfer” phenomena by which higher frequency bands gain intensity at the expense of lower frequency bands [32]. Nevertheless, the high resolution of IRAS measurements should provide insight into the interaction of CO and Sn on alloy surfaces.

Here we present IRAS studies at varying CO coverage on the Pt(1 1 1) and two alloys surfaces at pressures ranging from 10^{-10} to 10 Torr. Despite background features in the high pressures IRAS spectra, we can draw some conclusions on CO adsorption and packing on the Pt(1 1 1), (2×2) and $\sqrt{3}$ surfaces.

2. Experimental methods

Experiments were performed in a stainless steel UHV chamber equipped for Auger electron spectroscopy (AES), low energy electron diffraction (LEED), temperature programmed desorption (TPD) and Fourier-transform infrared (FTIR) spectroscopy. The chamber had a base pressure of 2×10^{-10} Torr. The Pt(1 1 1) crystal was resistively heated to 1200 K and cooled to 87 K by direct contact of the copper block of the sample holder with liquid-nitrogen. A chromel–alumel, type K thermocouple was spot welded directly to the edge of the crystal. The Pt(1 1 1) surface was cleaned by cycles of Ar^+-ion sputtering with the sample held at 800 K followed by exposure to 1×10^{-7}-Torr of O_2 at 800 K and annealing the crystal at 1200 K for 10 s. The cleanliness and long-range order of the surfaces were checked by AES and LEED.

TPD measurements were made using a UTI 100C quadrupole mass spectrometer in line-of-sight with the sample surface and using a linear heating rate of ~4 K/s. The crystal was located at 2 mm in front of the entrance of a shielded aperture.

IRAS was carried out at a grazing incidence angle of 86° from the surface normal. An Infinity® 60 M FTIR spectrometer and a medium-band, liquid-nitrogen cooled, mercury cadmium telluride (MCT) detector was used for collecting the IR spectra. Typically, spectra were taken at a spectrometer resolution of $4\ cm^{-1}$ and by averaging 1000 scans taken over 8 min. Samples were dosed CO at 87 K and then heated to desorb CO in a controlled fashion to study a range of CO surface coverages. The samples were then allowed to cool down for the acquisition of each spectrum. All of the spectra reported were taken with the sample at a temperature of 87–90 K and ratioed against the clean surface spectrum as a background.

CO (Matheson, 99.5%) was dosed using leak valves. The exposures are given in units of Langmuir ($1\ L = 10^{-6}$ Torr s) uncorrected for the dozer enhancement factor and ion gauge sensitivity. Adsorbate coverages in this paper are referenced to the Pt(1 1 1) surface atom density, i.e., $\theta = 1.0$ corresponds to 1.505×10^{15} atoms/cm^{-2}.

The (2×2) and $\sqrt{3}$ surfaces were prepared by evaporating Sn on the clean Pt(1 1 1) crystal surface and subsequently annealing the sample to 1000 K for 10 s. Depending on the initial deposited Sn coverage, the annealed surface exhibited either (2×2) or $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern [30].

3. Results and discussion

3.1. CO adsorption

TPD spectra of CO adsorption on the Pt(1 1 1) and the two alloy surfaces for saturation coverage are displayed in Fig. 2. These results are in agreement with previous reports [4,33] presenting broad desorption peaks for the three surfaces. Peaks shift to lower temperatures with increasing Sn which indicates that the binding energy of CO on the surface alloys is reduced by a few kcal/mol compared to the Pt(1 1 1) surface. No evidence of dissociative CO desorption was observed on any of the surfaces. A visible shoulder