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## Probing the modifier precursor state: adsorption of CO on Sn/Pt(111) surface alloys

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### Abstract

The presence of a second, inert metal component in an alloy surface can have a dramatic effect on the adsorption kinetics compared to that predicted from simple site-blocking. This is due to the important role that is often played by the *modifier precursor state* [Xu and Koel, J. Chem. Phys., in press]. In order to more clearly reveal details concerning this state, the adsorption kinetics and thermodynamics of CO on Pt(111) and two ordered Sn/Pt(111) surface alloys have been studied. The thermodynamics of CO adsorption on Pt(111) is only slightly influenced by the presence of Sn. In contrast to the adsorption thermodynamics, the nature of the adsorption kinetics depends strongly on the presence of Sn. This difference can be explained by the fact that the thermodynamics of strong chemisorption is mainly determined by chemical bonding forces, while the adsorption kinetics can be determined by physisorption forces because of their influence on precursor states.

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### 1. Introduction

The importance of bimetallic catalysts has motivated extensive studies on well-defined bimetallic surfaces using surface science techniques [1,2]. A great amount of information has been gathered during the past few years [3–5]. However, most studies have concentrated on the thermodynamic properties of bimetallic surfaces. Very little is known about adsorption kinetics on bimetallic surfaces. The importance of this elementary step in reactions on bimetallic surfaces requires a better appreciation of the influence of surface modi-

fiers on adsorption kinetics prior to an improved understanding of surface chemistry and catalysis.

In this paper we report on our studies of CO adsorption kinetics on well-defined Sn/Pt(111) surface alloys. Our results show that the presence of a second element at the surface can strongly change the adsorption kinetics (over that expected from simple site blocking), even in cases where the thermodynamic properties are not significantly influenced by the presence of the second element. This is due to the fact that the alloy surface thermodynamic properties are mainly determined by the chemisorption forces present at the reactive metal sites. Because of the presence of precursor states, the inert metal component can play an important role in the adsorption kinetics via physisorption forces.

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## 2. Experimental methods

The experiments were performed in an ultra-high vacuum chamber equipped for Auger electron spectroscopy (AES), low energy electron diffraction (LEED), temperature programmed desorption (TPD) and directed beam dosing for making sticking coefficient measurements. The system base pressure was  $6 \times 10^{-11}$  Torr. 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  $\sim 4$  K/s. The mass spectrometer was equipped with a shield having a small (6 mm diameter) entry hole and the crystal was always placed very close ( $\sim 1$  mm) to the entry hole in front of the QMS when performing TPD measurements. The UPS data were taken using a double-pass cylindrical mirror analyzer and a high pressure discharge lamp using He. The resolution in UPS was 0.24 and 0.40 eV for the He I and He II regions, respectively.

The Pt(111) crystal was cooled down to 95 K using liquid nitrogen or resistively heated to 1200 K. The temperature was measured by a chromel–alumel thermocouple spot-welded to the side of the crystal. The Pt(111) crystal was cleaned using the procedure found in Ref. [6]. The  $(2 \times 2)$ Sn/Pt(111) and  $(\sqrt{3} \times \sqrt{3})$ R30°Sn/Pt(111) surfaces were prepared by evaporating Sn on the clean Pt(111) surface and subsequently annealing to 1000 K for 10 s. Depending upon the initial Sn coverage (0.25–0.4 ML), the annealed surface exhibited a  $p(2 \times 2)$  or  $(\sqrt{3} \times \sqrt{3})$ R30° LEED pattern. The structure for these patterns was originally assigned to the (111) face of Pt<sub>3</sub>Sn and a substitutional surface alloy of composition Pt<sub>2</sub>Sn [7] as shown in Fig. 1, and this has now been confirmed [8,9]. Angle-dependent low energy ion scattering spectroscopy (LEISS) measurements using 500–1000 eV Li<sup>+</sup> [8] and dynamic LEED studies [9] show that surface alloys (rather than Sn adatoms) are produced and that Sn atoms are almost coplanar with the Pt atoms at the surface; Sn only protrudes  $\sim 0.022 \pm 0.005$  nm above the surface. Furthermore, Sn was not detected in the second or deeper layers. For brevity in this paper, the  $(\sqrt{3} \times \sqrt{3})$ R30°Sn/Pt(111) surface alloy and

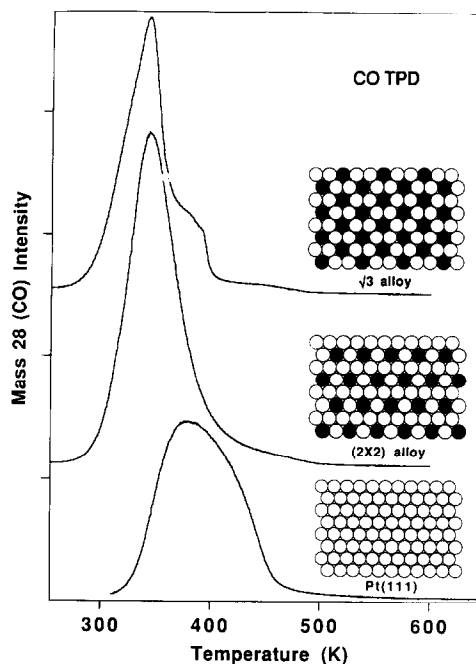


Fig. 1. CO TPD spectra after saturation exposures of CO on the Pt(111) surface and the  $(2 \times 2)$  and  $\sqrt{3}$  surface alloys.

the  $(2 \times 2)$ Sn/Pt(111) surface alloy will be referred to as the  $\sqrt{3}$  alloy and  $(2 \times 2)$  alloy, respectively.

The sticking coefficient was determined using a simple kinetic uptake method, similar to that of King and Wells [10], as described previously [10–12].

## 3. Results and discussion

The adsorption of CO on Pt(111) and the two Sn/Pt(111) surface alloys has been investigated previously by means of LEED, AES, HREELS and TPD [13]. In comparing Pt(111) to the Sn/Pt(111) surface alloys, the binding energy of CO is only slightly decreased (a few kcal/mol) as indicated by the small decrease in the desorption temperature. TPD spectra after saturation CO exposures on Pt(111) and the  $(2 \times 2)$  and  $\sqrt{3}$  surface alloy are provided in Fig. 1. Our spectra are in qualitative agreement with the previous results [13]. It is seen in Fig. 1 that the desorption

peaks on the two surface alloys are much narrower than on Pt(111). Since the presence of Sn on the surface introduces a new kind of precursor state, a modifier precursor, on top of Sn (see below), this precursor state will certainly also contribute to the desorption kinetics by introducing a new pathway. The pre-exponential factor,  $\nu$ , is likely to be increased by the new pathway. An increase of the pre-exponential factor will cause both narrowing of the desorption peak and a decrease in the desorption temperature. Therefore, the decrease observed in Fig. 1 for the peak desorption temperature from the alloys must at least partially have a kinetic origin. From HREELS results, CO is bound still on atop and bridge sites on both Sn/Pt(111) surface alloys. The deduced population ratio of atop and bridge sites for CO adsorbed on the Pt(111) surface and the  $(2 \times 2)$  and  $\sqrt{3}$  surface alloys are consistent with the individual site ratios available on the three surfaces [13].

In order to get some information about the electronic structure of CO adsorbed on the Sn/Pt(111) surface alloys, UPS spectra have been taken after saturation CO coverage on the Pt(111) and the  $(2 \times 2)$  and  $\sqrt{3}$  alloy surfaces. The results are provided in Fig. 2; no attempt has been made to normalize the intensity. UPS spectra taken with He I are shown on the right-hand side and UPS spectra taken with He II are shown on the

left-hand side. Our UPS spectra on the CO-covered Pt(111) surface are in good agreement with previous results [14,15]. The peaks at 8.8, 9.4 and 11.9 eV can be assigned to emission from  $1\pi$ ,  $5\sigma$  and  $4\sigma$  orbitals, respectively. Emission from the  $1\pi$  orbital can be seen better in the He I spectra where emission from  $\sigma$  orbitals have smaller cross sections. Comparing the Sn/Pt(111) surfaces to Pt(111), there are almost no changes in the UPS spectra except a small shift of all three peaks to higher binding energy by 0.1–0.3 eV. Since the  $4\sigma$  orbital has non-bonding character in the CO–metal bond, the small shift of all the orbitals is due to different final state screening by the three surfaces. This indicates that the electronic structure of CO on the Sn/Pt(111) surface alloys remains essentially the same as on clean Pt(111). In Fig. 2, a CO-induced peak near 2 eV is also seen. Such peaks have also been previously observed on Ni(100), Ni(110), Ni(111) [16,17], Cu(111) [18] and Cu(100) [19] with UPS and on Ni(111) [20], Pd(111) [21] and Mo(110) [22] with surface Penning ionization electron spectroscopy (SPIES). This state has been assigned usually to a  $2\pi^*$  orbital containing electrons from the metal via backdonation. In contrast, Miranda et al. [23] assigned a peak at 2 eV on CO/Pd(111) to a shifted Pd surface state. A recent careful investigation of such a state on CO/Ni(110) by Kuhlbeck et al. [24] using ARUPS and synchrotron light has identified this state unambiguously to be the  $2\pi^*$ -d surface band. Accordingly, we tentatively assign the peak at 2 eV in Fig. 2 to the  $2\pi^*$  state. A definitive assignment would require careful ARUPS measurements. In any case, this CO-induced peak at 2 eV does not change significantly from Pt(111) to the Sn/Pt(111) surface alloys.

Summarizing the TPD, HREELS [13], and UPS results, we can say that the thermodynamic properties of CO chemisorbed on Pt(111) have *not* been changed significantly by the alloying of Pt(111) with Sn.

Now we turn to the adsorption kinetics of CO on these surfaces. In Fig. 3, the dependence of the CO initial sticking coefficient on the surface temperature of Pt(111) and the  $(2 \times 2)$  and  $\sqrt{3}$  alloys is shown. On the clean Pt(111) surface, the

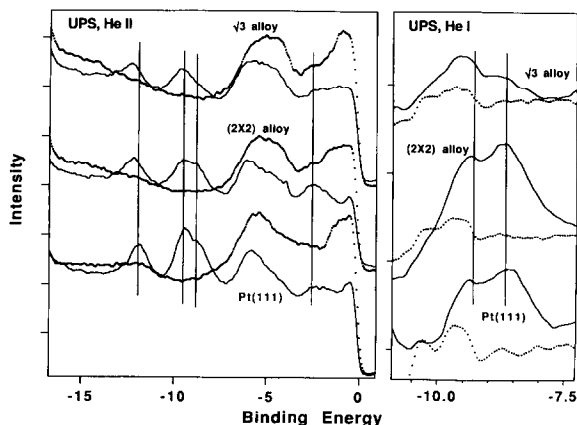


Fig. 2. He I and He II UPS spectra of CO saturation coverages on the Pt(111) surface and the  $(2 \times 2)$  and  $\sqrt{3}$  surface alloys.

initial sticking coefficient is independent of the surface temperature between 100 and 300 K, consistent with previous results [6,12,25,26]. This situation has been attributed to the very high probability of converting CO in an intrinsic precursor state to chemisorbed CO [4,26–30]. Both Sn/Pt(111) surface alloys, however, show a *strong temperature-dependent initial sticking coefficient of CO*: the initial sticking coefficient decreases almost linearly with increasing surface temperature.

The strong decrease of the CO initial sticking coefficient cannot be due to CO desorption at the higher temperatures on the Sn/Pt(111) alloy surfaces. Fig. 4 shows this point. TPD are provided after dosing CO onto the  $\sqrt{3}$  alloy surface at 100 K (a and d) or 200 K (b), or after annealing a CO-saturated surface to 200 K (c). Dosing at 200 K or annealing to 200 K does not cause CO desorption from the Sn/Pt(111) alloy surfaces. Therefore, the presence of Sn in the surface of Pt(111) induces a dramatic change of the temperature dependence of the initial sticking coefficient, in contrast to the almost unchanged thermodynamics of CO adsorption on Pt(111).

The dependence of the initial sticking coefficient on the concentration of Sn in the surface at a substrate temperature of 130 K is shown in Fig. 3. Increasing the Sn concentration from  $\theta_{\text{Sn}} = 0$  on Pt(111) to  $\theta_{\text{Sn}} = 0.25$  on the  $(2 \times 2)$  alloy causes

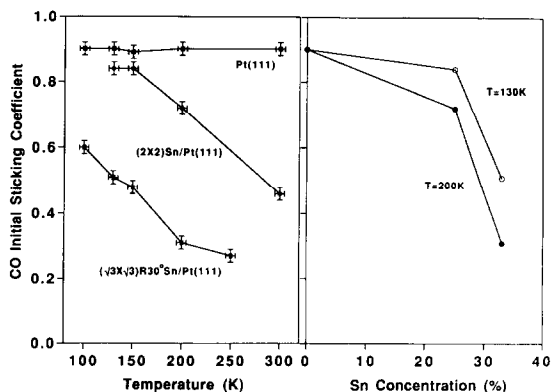


Fig. 3. The influence of surface temperature (left) and Sn concentration in the surface layer (right) on the initial sticking coefficient of CO on Pt(111) and two ordered Pt-Sn surface alloys.

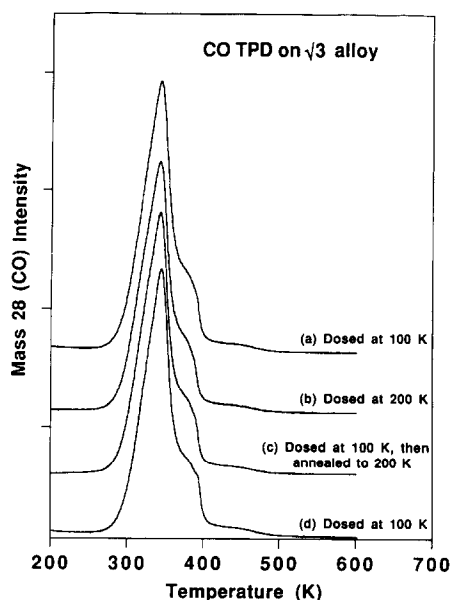


Fig. 4. CO TPD spectra from the  $\sqrt{3}$  surface alloy for several different conditions.

only a slight decrease in the initial sticking coefficient. The  $\sqrt{3}$  alloy with  $\theta_{\text{Sn}} = 0.33$ , however, shows a much smaller CO initial sticking coefficient. Similar results have been obtained on these systems at 200 K and, indeed, for adsorption on many bimetallic and modified surfaces [4,12,31–38]. For instance, the initial sticking coefficient of CO has been found to be independent of the modifier coverage also on K/Pt(111) [12], K/Pd(100) [38], Bi/Ni(100) [32], S/Ni(100) [33], O/Pt(111) [12,34], S/Pt(111) and Se/Pt(111) [35–37] up to 0.25–0.35 ML of the modifier. These results clearly demonstrate that the dependence of the initial sticking coefficient on the modifier coverage cannot be described always by the commonly used Langmuir isotherm  $S_M = S(1 - m\theta_M)$ . In this equation,  $S$  and  $S_M$  are the sticking coefficients on the clean surface and on the surface precovered with a modifier (second component), respectively,  $\theta_M$  is the modifier coverage, and  $m$  is a parameter describing how many sites are blocked by one adatom of the modifier.

The failure of this simple site blocking equation is due to the presence of the so-called “modifier precursor” state as we have discussed previ-

ously [30]. The physical origin is as follows: If one assumes the presence of an extrinsic precursor state on top of an adsorbate to explain the coverage independence of the sticking coefficient at small adsorbate coverage, it is also reasonable to assume that a similar, but energetically different, precursor state will also exist on top of a modifier atom which we have called a “modifier precursor” state [30]. A mathematical description of the adsorption kinetics of molecules on chemically modified or bimetallic surfaces incorporating this state has been derived previously based on Kisliuk’s statistical model [30]. We will use this theory to explain the results in Fig. 3. For our case, where the CO coverage is zero, the original equation [30] can be reduced to:

$$S_0(\theta_M)/S_0 = \left(1 + \frac{m\theta_M}{1 - m\theta_M} K''\right)^{-1}, \quad (1)$$

with

$$K'' = \frac{P_b}{P_a + P_b}.$$

Eq. (1) describes the dependence of the CO initial sticking coefficient on the Sn concentration in the surface layer of Pt(111).  $P_a$  and  $P_b$  represent the probability that a physisorbed (trapped) molecule above an empty site becomes chemisorbed or desorbs, while  $P_b''$  is the probability that a physisorbed (trapped) molecule above a filled site occupied by a surface modifier adatom desorbs. Eq. (1) is very similar to the original Kisliuk equation. The principal difference between these two equations is that the adsorbate coverage  $\theta$  is replaced by the modifier coverage  $\theta_M$ , and the probability of desorption from the extrinsic precursor on top of an adsorbate is replaced by the probability of desorption from the modifier precursor on top of the modifier. Physically, this means that the precursor on top of the modifier prevents a linear decrease of  $S_0(\theta_M)$  with increasing modifier coverage just as in the case of a clean surface where the extrinsic precursor prevents a linear decrease of the sticking coefficient with increasing adsorbate coverage.

The strong temperature dependence of the initial sticking coefficient of CO on Sn/Pt(111) surface alloys can also be satisfactorily explained by the presence and influence of the modifier precursor state. To simplify the development, we will first make some approximations. The adsorption kinetics of CO on Pt(111) has been extensively studied by various groups [4,6,12,25–27]. Every trapped CO molecule is converted to chemisorbed CO with a trapping coefficient  $\alpha = 0.9$ . For a physisorbed (trapped) molecule above an empty site, the probability of becoming chemisorbed is therefore much larger than that for desorbing, namely  $P_a = \nu_a e^{-E_a/kT} \gg P_b = \nu_b e^{-E_b/kT}$ . Since the adsorption energy of CO molecules on the Sn/Pt(111) surface is essentially the same as on Pt(111), it is reasonable to assume that most of the CO trapped on top of Pt atoms will be converted to chemisorbed CO. Impinging on the surface, CO can be (i) trapped on top of the Pt atoms with a trapping coefficient  $\alpha$  and then become chemisorbed or (ii) trapped on top of the Sn atoms with a trapping coefficient  $\alpha''$ . The CO molecule trapped on top of Sn can either desorb or diffuse to a neighboring atom with a probability  $P_c''$ . Since the nearest-neighbor of any Sn atom is always Pt, these CO molecules also will become chemisorbed. Thus, the initial sticking coefficient can be described with the following equation:

$$\begin{aligned} S_0 &= \alpha(1 - \theta_{Sn}) + \alpha''\theta_{Sn}P_c'' \\ &= \alpha(1 - \theta_{Sn}) + \alpha''\theta_{Sn} \\ &\quad \times \frac{\nu_c'' \exp(-E_c''/kT)}{\nu_b'' \exp(-E_b''/kT) + \nu_c'' \exp(-E_c''/kT)} \\ &= \alpha(1 - \theta_{Sn}) + \alpha''\theta_{Sn} \\ &\quad \times \frac{1}{1 + (\nu_b''/\nu_c'') \exp[-(E_b'' - E_c'')/kT]}, \end{aligned} \quad (2)$$

where  $\nu_i$  and  $E_i$  are the pre-exponential factors and activation energies for the individual processes. Since the trapping coefficients are often temperature independent [39], the last term is the

only temperature-dependent factor. The temperature dependence is determined by the difference in activation energies for migration and desorption of the precursor on top of a Sn atom. Typical physisorption energies of CO are between 7 kJ/mol (the condensation energy of CO [40]) and 19 kJ/mol (on Ag [41]) and the migration activation energy of the precursor is expected to be about 30% of its binding energy (equal to the physisorption energy) or less. Therefore,  $(E_b'' - E_c'')$  is a few kJ and a strong temperature dependence of the first term is expected between 100 and 300 K ( $kT = 0.83\text{--}2.5$  kJ/mol). From Eq. (2) it is also seen that  $S_0$  decreases with increasing surface temperature.

In summary, Sn influences CO chemisorption kinetics in a dramatically different manner than that predicted from a simple site-blocking perspective. This occurs even though Sn could easily be justified (with regard to CO chemisorption) to be a simple site-blocking modifier in the Pt–Sn surface alloy, since CO does not chemisorb on Sn and the presence of Sn has little effect on the chemisorption thermodynamics or bonding sites on Sn/Pt(111) surface alloys compared to Pt(111). The influence of Sn on the CO adsorption kinetics is manifested by a weak dependence of the CO initial sticking coefficient on the amount of Sn in the surface layer and by a strong temperature dependence of the CO initial sticking coefficient on the Pt–Sn surface alloys (in contrast to the temperature independence of this parameter on Pt(111)). These effects can be understood when one considers the important role played by a modifier precursor state. It has been known for a long time that catalytic reactions can be altered strongly by adding a simple site-blocker to the surface. A better (e.g., more quantitative) understanding of the chemistry and catalysis of chemically modified or bimetallic surfaces should result by explicitly accounting for the important role played by the modifier precursor state in adsorption and reaction kinetics. This was illustrated here in CO chemisorption experiments, but also should be rather clearly revealed in more complex catalytic reactions if the adsorption step is a factor in the rate-limiting process for the reaction.

#### 4. Acknowledgments

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