Pd–Sn bimetallic model catalysts were prepared as alloy films on a Rh(100) substrate via physical vapor deposition. The surface composition, structure, and chemisorption properties were studied by low energy ion scattering spectroscopy (LEIS), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), infrared reflection adsorption spectroscopy (IRAS), and temperature programmed desorption (TPD). The ordered surface alloy of c(2 × 2) was formed after annealing the Pd–Sn mixtures to 700 K as evidenced by LEED and LEIS showing a 50% surface concentration of Pd. This ordered surface arrangement was further confirmed by IRAS, LEED, and TPD studies using CO as a probe molecule, in which the surface Pd atoms are completely isolated by Sn atoms. The surface Pd composition was determined to be 0.5 monolayers (ML). The catalytic properties of this Pd–Sn surface were tested with respect to vinyl acetate (VA) synthesis by ethylene acetoxylation that showed a maximum in the VA formation rate at a surface Pd coverage of 0.5 ML, i.e., a c(2 × 2) surface arrangement. This is consistent with our previous proposal that a pair of suitably spaced, isolated Pd monomers is the more efficient site for VA synthesis.

1. Introduction

Fundamental surface science studies of bimetallic alloy systems are important to many industrial applications some of which include metallurgy, catalysis, electrochemistry, magnetic materials, and microelectronics fabrication.1 Particularly in heterogeneous catalysis, the addition of a second metal often greatly enhances the reaction activity, selectivity, and stability.2–4 Further optimization of the catalytic performance requires a thorough understanding of the reaction mechanism at the atomic level, for which model surface science studies on well-defined surfaces can provide critical information. The preparation of ordered Pt–Sn surface alloys was first demonstrated by depositing Sn on Pt(111) or Pt(100) followed by annealing to elevated temperatures.5–8 These well-characterized surface templates were used for extensive catalytic reaction studies.3,9–13 These model studies have provided a more in depth understanding of the chemistry observed on ordered alloy surfaces including the relative importance of ensemble and ligand effects.

Only a limited number of model studies on Pd–Sn bimetallic systems have been performed despite the importance of Pd-based industrial catalysts.14–17 Hamm et al.14 and Lee et al.15 studied the formation of two ordered Pd–Sn surface alloys by thermal treatment of vapor deposited Sn films on a Pd(111) single crystal. Depending on the preparation conditions, two surface periodicities, p(2 × 2) and (√3 × √3)R30°, were observed with surface stoichiometries of Pd3Sn and Pd2Sn, respectively.14,15 On the Pd(110) single crystal, two ordered structures, c(2 × 2) and (3 × 1), were also reported corresponding to 0.5 monolayer (ML) and 0.67 ML of Sn in the surface layer.17 In both cases, a strong chemical interaction between Sn and Pd was deduced based on core level binding energy shifts (CLS) and attenuation of the CO adsorption energy in TPD data.15,17 However, no detailed investigations concerning Pd–Sn alloy formation on <100> oriented substrates have been reported. Previously, we had studied disordered Pd–Au model alloy surfaces2,18–22 where Pd atoms were found to be isolated by Au atoms at low surface Pd coverage.2,18–22 A pair of these Pd monomers has been proposed to serve as the active site for vinyl acetate synthesis.2,18

In the present work, Pd–Sn alloy films on a Rh(100) were used as model surfaces. Compared with Sn/Pd(100) model systems, bimetallic films provide more flexibility in controlling desired surface metal concentrations.22 The surface composition, the extent of alloying, and the electronic properties in this system were studied, as well as their catalytic activities for vinyl acetate synthesis. In contrast to Pd–Au, Pd–Sn form ordered surface alloys where the surface Pd atoms are isolated by Sn atoms, maximizing the fraction of surface isolated Pd monomer pairs.

2. Experimental Section

The experiments were carried out in several ultrahigh vacuum (UHV) chambers equipped with XPS, LEIS, IRAS, XPS, and a cell for reaction kinetic studies. Each chamber was also equipped with LEED, AES, and TPD. The base operating pressure for each system was ∼2 × 10⁻¹⁰ Torr. XPS and LEIS spectra were collected using a concentric hemispherical analyzer (PHI, SCA 10–360) and Ne⁺ ions (0.75 keV) with an ion beam scattering angle of ∼45° with respect to the surface normal. A Mattson Cygnus 100 FTIR spectrometer was used for the IRAS measurements. The IR spectra were acquired using 4 cm⁻¹ resolution and 512 scans in the single reflection mode at an incident angle of 84° with respect to the surface normal. The Rh(100) single crystal was mounted on a transferable probe capable of liquid nitrogen cooling to 80 K and resistive heating to 1500 K. The sample temperature was monitored with a W-5% Re/W-26% Re (type C) thermocouple spot-welded to the back of the Rh(100) single crystal. A heating ramp of 5K/s was used for the TPD measurements. These experimental systems have been described in detail elsewhere.24,25

The Rh(100) single crystal was cleaned by Ar⁺-sputtering, oxidation (1200 K, 5 × 10⁻⁷ Torr O₂) and vacuum annealing (1400 K) cycles until no carbon and oxygen were detected in AES and a sharp (1 × 1) LEED pattern observed. The Pd doser
consisted of a tungsten filament about which a high purity Pd wire was wound. The Sn doser was similarly constructed with the Sn wire source housed in a ceramic tube. Impurities in the evaporators were removed thoroughly by degassing prior to use. All metal depositions were performed with the sample at room temperature and the dosing rates calibrated by the break points in the LEIS, XPS, or AES data as a function of coverage. Carbon monoxide and oxygen (99.99%, Matheson Gas Products) were further purified by storage in a liquid-nitrogen reservoir prior to transfer to glass bulbs attached to the gas manifold.

The VA synthesis experiments were carried out in a combined elevated-pressure reactor-UHV XPS chamber. After preparation and characterization in the UHV chamber, the Pd−Sn/Rh(100) sample was transferred in situ into the reaction chamber through a double-stage, differentially pumped Teflon sliding seal. Glacial acetic acid (CH₃COOH) was further purified by triple distillation; research-grade ethylene (C₂H₄) and ultrahigh purity O₂ were used as received. A CH₃COOH:C₂H₄:O₂ (2:4:1) mixture with a total pressure of 14 Torr was used for the vinyl acetate product was analyzed by gas chromatography using a flame ionization detector (FID).

The influence of annealing temperature on surface concentration is plotted in Figure 1b. A decrease in Sn surface concentration (C_{Sn}) and an increase of Pd surface concentration (C_{Pd}) was apparent with an increase in the annealing temperature to 700 K. At 700 K, the surface concentrations of Sn and Pd were ca. 47% and 53%, respectively. At a temperature above 700 K, the surface composition of Pd and Sn is constant and consistent with a stable Pd/Sn surface alloy with a ratio of ~1:1.

LEED was used to further characterize the Pd−Sn alloy surface structure. Figure 2 displays the LEED pictures from (a) the clean Rh(100) substrate, (b) the 4 ML Pd/Rh(100) surface, and (c) the 1 ML Sn/4 ML Pd/Rh(100) surface. Both of the Pd and Pd−Sn alloy films were annealed at 700 K for 1 min before photographing. The 4 ML Pd film exhibited a clear (1 × 1) LEED pattern (Figure 1b), even though the spots were more diffused and the background was brighter compared with the clean Rh surface. This indicates that the Pd film grows pseudomorphic overlayers on Rh(100), adopting a substrate-like <100> orientation. Because of the small lattice difference between Pd and Rh, it is not surprising that the 4 ML Pd film surface is not as ordered as the substrate Rh(100) surface. After deposition of 1 ML Sn onto this Pd film and annealing the sample surface to 700 K, a new LEED pattern of c(2 × 2) was clearly observed (Figure 2c). A checkerboard-like, ordered c(2 × 2) Pd−Sn alloy surface structure has been proposed by Logan et al. for the Sn/Pd(100) system. A series of studies have concluded that a similar, planar c(2 × 2) Pt−Sn alloy structure is formed after annealing the alloy surface to 700−750 K. From the above LEIS results, the surface concentrations of Pd and Sn in the 1 ML Sn/4 ML Pd/Rh(100) surface are close to 50% after annealing to 700 K. Based on these LEIS and LEED results and the similar studies on the Sn/Pt(100) system, an ordered Pd−Sn alloy structure as depicted in the bottom of Figure 2 is presumed.

In order to probe the proper preparation conditions for ordered Pd−Sn alloy surfaces, LEIS experiments with depositions of different initial Sn coverages on a 4 ML Pd film were carried out. The changes in the surface concentrations of Pd and Sn as a function of dosed Sn based on the LEIS data are shown in Figure 3. It should be noted that each of these alloy surfaces was annealed at 700 K for 1 min prior to acquisition of the
LEIS data. Ideally, 0.5 ML Sn is needed to form a c(2 × 2) ordered Pd–Sn alloy surface assuming limited diffusion of the Sn into the bulk Pd film. Our results indeed show the surface concentrations of the 0.5 ML Sn/4 ML Pd/Rh(100) alloy surface after annealing to 700 K is approximately 1:1 Pd to Sn, specifically 40% Sn and 60% Pd. This is actually expected because the surface free energy of Sn is much smaller than that of Pd, i.e., diffusion of Sn into the bulk Pd film is thermodynamically unfavorable. With the addition of >0.5 ML Sn, the surface concentrations of Pd and Sn remained constant. It is likely that Sn in excess of 0.5 ML diffuses into the bulk leaving the c(2 × 2) ordered structure at the outmost surface layer.

XPS experiments were also carried out to study the electronic structural changes in the process of forming an ordered Pd–Sn alloy surface. In Figure 4a, Sn 3d core level spectra are displayed as a function of the annealing temperature for the 1 ML Sn/4 ML Pd/Rh(100) surface. No obvious peak intensity variations or core level binding energy (CLE) shifts are apparent as the annealing temperature is increased to 700 K. A decrease in the intensity and a slight reduction of the CLE is evident after annealing to 800 K. The Pd 3d core level features measured concomitantly are shown in Figure 4b. The CLE values for the Pd 3d features did not change significantly following the Sn deposition and annealing at different temperatures. The intensities, however, of these peaks are attenuated after annealing the alloy film to temperatures higher than 800 K. The observed small CLBE changes of the Pd and Sn 3d features observed after annealing correlate very well with results found previously for Sn/Pd(111).15

IRAS and TPD. The chemisorptive properties of Pd-Sn alloy surfaces were studied by IRAS and TPD using CO as a probe. Control experiments of CO adsorbed on a 4 ML Pd film were first carried out. Figure 5a displays a series of IRAS spectra acquired in 1 × 10⁻⁷ Torr CO background as a function of sample temperature. Only one feature was observed in this series of spectra. This feature appears as a broad peak at 1908 cm⁻¹ at 500 K, then gradually blue shifts to 1985 cm⁻¹ upon cooling the sample to 250 K. At CO saturation coverage, this feature reaches 2001 cm⁻¹ and becomes much sharper. The spectral features and the temperature dependent frequency shift are essentially identical in the corresponding data found in CO-IRAS spectra acquired for Pd(100) under similar conditions.27–29 These data are entirely consistent with the above LEED results and support the conclusion that the 4 ML Pd film on Rh(100) adopts a <100>-like orientation. Based on the TPD and LEED studies carried out for CO on Pd(100),27–29 this CO-IR feature is assigned to CO adsorption on 2-fold bridging Pd sites.

IRAS spectra for CO adsorption on 1 ML Sn/4 ML Pd/Rh(100) surface as a function of sample temperature are shown in Figure 5b; the alloy surface was annealed at 700 K for 1 min, and all of the spectra were collected in 1 × 10⁻⁷ Torr CO background. Only a single IR feature around 2094 cm⁻¹ is apparent in this series of spectra. Comparing with the single feature observed on 4 ML Pd film surface at 2001 cm⁻¹, this IR result clearly shows that totally different adsorption sites
are formed on the Pd–Sn alloy surfaces. The frequency of this feature corresponds to CO adsorption on atop Pd sites. Moreover, this IR feature attenuates between 150 and 200 K, and completely disappears below 300 K. On a 4 ML Pd film surface, a CO-IRAS feature can be seen up to 500 K. The contrast in these spectra shows that CO adsorbs differently on the Pd–Sn alloy surface. The lower desorption temperature indicates weaker CO-substrate bonding, paralleling the conclusion that CO adsorbs on atop Pd sites. It is also noteworthy that the IR frequency for isolated Pd sites on Pd–Au alloy surface is 2088 cm⁻¹, and this isolated Pd IR feature for Pd–Au vanishes around 300 K. The similarities in both IR frequency and CO desorption temperature in these two systems suggest that CO occupies identical adsorption sites in both these systems, i.e. CO adsorbs on the isolated Pd sites on the Pd–Sn alloy surface.

A direct comparison of the saturation CO-IRAS spectra from 4 ML Pd film, 4 ML Sn film, and 1 ML Sn/4 ML Pd alloy film further supports the above conclusion. As seen in Figure 6a, no IR feature is observed on 4 ML Sn film surface at 80 K due to the weak interaction between Sn and CO. Based on the above LEIS and LEED results, the 1 ML Sn/4 ML Pd alloy film annealed at 700 K forms a well-ordered c(2 × 2) alloy structure, and that the IR feature observed on Pd–Sn alloy surface arises from CO adsorption on the isolated Pd sites. Furthermore these data show that most of the surface Pd atoms on Pd–Sn alloy surfaces are isolated, consistent with an ordered c(2 × 2) arrangement.

It should be also noted that the IR frequency for the isolated Pd sites in Pd–Sn alloy systems is slightly higher than that in Pd–Au systems (2094 cm⁻¹ vs 2088 cm⁻¹). This may be due to the difference in the surface orientation (Pd–Sn(100) vs Pd–Au(111)). Also an electronic effect, e.g., charge transfer between Pd and Sn or Au, may contribute to this difference. Further investigations regarding this issue are warranted. Moreover, a blue shift is observed in Figure 5 when the surface
CO coverage is increased on the Pd–Sn alloy surface. In the Pd–Au alloy system, the IR frequency for the isolated Pd sites is not shifted with a change in the surface CO coverage. This may be caused by the fact that the saturation CO coverage on the Pd–Sn alloy surface is higher than that of the Pd–Au surface. Dipole–dipole interactions from neighboring CO molecules may induce this shift to higher frequencies, however further experiments are also required to confirm this conclusion.

CO TPD was also used to further study the CO adsorption behavior on Pd–Sn alloy surfaces. In particular, the CO adsorption/desorption properties of the c(2 × 2) ordered Pd–Sn alloy surface were examined and compared with that of clean Rh(100) substrate, 4 ML Pd, and 4 ML Sn films. In Figure 6b, saturation CO TPD spectra for all these surfaces are presented. The clean Rh(100) substrate gives a broad desorption feature ranging from 250 to 500 K. Upon deposition of 4 ML Pd on Rh(100), this broad peak is completely quenched and replaced by a feature in the range 300 to 450 K, indicating the 4 ML Pd film wets the surface effectively. With respect to the desorption temperature and spectral shape, the CO TPD spectrum from the 4 ML Pd film is almost identical with that from a Pd(100) single crystal.27–29 This confirms the above LEED and CO-IRAS results showing that the 4 ML Pd film has a c(2 × 2)-like surface orientation. As was pointed out in earlier discussions of CO-IRAS and TPD studies on different facets of Pd single crystal surfaces,27–29 this feature can be assigned to the CO adsorption on Pd bridging sites. For a clean Rh(100) or Sn/Rh(100) surface, no VA formation was observed. On a Pd(4 ML)/Rh(100), a turnover frequency (TOF) of 1 × 10^{-5} s^{-1} was observed for a 3 h reaction, consistent with Pd being an active catalyst for VA synthesis.2,18 Subsequently various amounts of Sn were deposited on a Pd(4 ML)/Rh(100) film followed by an anneal at 600 K for 1 min. Each surface was then in situ transferred into the reaction cell for VA reaction for 3 h. The results are shown in Figure 7. The reaction rates were computed based on the concentration of surface Pd assuming that only Pd is active for VA synthesis. The VA formation rate increases with increasing Sn coverage, maximizing at a Sn coverage of 0.5 ML. The VA rate decreases with a further increase in Sn coverage up to 1 ML. The rate at 0.5 ML Sn coverage is significantly higher compared to Pd-alone on Rh(100). As discussed in the previous section, a c(2 × 2) ordered surface arrangement was formed at a Sn coverage of 0.5 ML. For this c(2 × 2) structure, all surface Pd atoms are isolated by Sn with a maximum number of isolated Pd pairs. Such isolated pairs have been demonstrated previously to be a more efficient active sites for VA synthesis than for contiguous Pd sites.2,18 These data then are consistent with isolated Pd pairs serving as the catalytic active site for VA synthesis.2,18
synthesis. In the Pd–Au alloy system, an ensemble effect was assumed to be the dominant factor for the enhanced VA reactivity, whereas a ligand (or electronic) effect was considered to be insignificant due to the limited chemical interaction between Pd and Au. In the Pd–Sn system, the chemical interaction between Pd and Sn is much stronger. Therefore, it is difficult to assess the influence of a ligand (electronic) effect on the VA reactivity without further detailed investigations. The fact that the VA reactivity decreases as the Sn coverage is increased from 0.5 to 1 ML may indicate that a ligand effect plays a significant role. Even though the surface Pd concentration remains at 50% during the Sn coverage between 0.5 to 1 ML, the extra Sn that diffuses into the second or deeper layers may affect the chemisorptive behavior of the surface Pd atoms, which may result in a diminution of the VA rate within this Sn coverage range.

However, it is emphasized that the rate obtained for the Pd–Sn surface over a three-hour-average is much smaller than that for a Pd–Au surface. This lower rate may be due to oxidation of Sn under VA synthesis reaction conditions as indicated by XPS after reaction. Such oxidation of Sn will result in dealloying of Sn–Pd and phase separation of Pd and SnOx. Furthermore, the SnOx residue on the surface serves to block the Pd active sites. Noting the time dependent rate, of greater significance is the initial reaction rate of the Pd–Sn catalyst as shown in Figure 8 for a 0.5 ML Sn/Pd(4 ML)/Rh(100) surface. The VA formation rate indeed decreases very rapidly as the reaction proceeds. After 10 h of reaction, the activity is in fact much less than for Pd alone. An initial rate of $5 \times 10^{-4}$ molecules/(per site per second) was obtained by extrapolating the rate data to zero time, a rate some fifty times higher than that found for Pd alone.

4. Conclusions

Pd–Sn bimetal thin films were synthesized on Rh(001). A 4 ML Pd on Rh(100) exhibits similar properties as Pd(100). Upon deposition of Sn onto Pd/Rh(100) and following an annealing at 600 K, an ordered surface arrangement of c(2 × 2) was formed at a Sn coverages greater than 0.5 ML. LEIS and IRAS using CO as a probe confirmed a surface structure containing equal amounts of Sn and Pd with isolated Pd and Sn atoms. This checkerboard arrangement showed a maximum catalytic performance for VA synthesis. This alloy system demonstrates that a pair of isolated Pd monomers serves as an active site for VA synthesis as previously proposed.2,18

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References and Notes