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The Adsorption and Desorption of Hydrogen and Carbon Monoxide on Bimetallic Re-Pt(111) Surfaces

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Abstract

Bimetallic surfaces of rhenium on Pt(111) were prepared by vapor depositing rhenium on Pt(111). The adsorption and desorption behavior of CO and H₂ on bimetallic Pt-Re surfaces were studied using temperature programmed desorption, and compared to the behavior of CO and H₂ on the monometallic Pt(111) and Re(0001) counterparts.

Depositing rhenium on a Pt(111) surface decreased the activation energy of desorption of hydrogen, and a surface composed of 0.37 monolayers of rhenium on Pt(111) showed an activation energy of hydrogen desorption that was 2.5 kcal/mole less than the 19 kcal/mole displayed by the monometallic Pt(111) surface. In contrast, the activation energy of desorption of CO from bimetallic surfaces depended very little on the bimetallic surface composition, and a value of 27 kcal/mole was observed for low CO coverages.

At saturation exposures of both H₂ and CO, maximum adsorption capacities were obtained for bimetallic surfaces. A surface composed of 0.2 monolayers of rhenium on Pt(111) adsorbed 20% more hydrogen than did Pt(111) alone, while a surface composed of 0.3 monolayers of rhenium on Pt(111) adsorbed 40% more CO than did Pt(111) alone. The results obtained show that surfaces exposing both rhenium and platinum atoms show adsorption/desorption behavior towards hydrogen and CO that is different than the behavior shown by either monometallic platinum or rhenium surfaces. Since the chemisorption behavior cannot be explained as a simple combination of the two metallic components of the surface, it is concluded that an electronic interaction between the two metals at the platinum-rhenium interface modifies the bonding of adsorbates at the mixed metal sites.

1 Introduction

Well characterized bimetallic surfaces composed of platinum and rhenium metals can be prepared, and both platinum films deposited on a rhenium single crystal substrate and rhenium films deposited on a platinum single crystal substrate have been studied [1,2]. It was found that rhenium grows layer by layer on Pt(111) forming a hexagonal close-packed film exposing the (0001) face. In this paper the adsorption and desorption of two small molecules, H_2 and CO, on bimetallic Re-Pt(111) surfaces are discussed.

The behavior of chemisorption systems on the bimetallic Pt-Re surface is important for a number of reasons. Titration techniques using small molecules (mainly H_2 , O_2 , and CO) are routinely used for the determination of the metallic surface area and dispersion on supported metallic catalysts. Materials used as supports, such as alumina and silica, do not reversibly adsorb these gases, so titration with them is a technique thought to reliably measure the metallic surface areas [3]. This is true to a large extent for monometallic catalysts.

When a second metal is introduced, titration techniques become more complicated and less reproducible [4]. One problem for the platinum-rhenium system is that each of these metals alone have different hydrogen chemisorption capacities, about 1 H atom per Pt surface atom, and 0.4 H atoms per Re surface atom as determined by chemisorption techniques [5,6]. When these two metals are codeposited on a support, measurements of the metallic surface area using hydrogen and CO chemisorption sometimes give unreliable results such as a metallic dispersion in excess of 100% [7]. One reason for this is that the chemisorption of hydrogen and CO on bimetallic Pt-Re surfaces is not a linear function of the metallic surface composition, as will be shown in this paper. In addition, evidence suggesting the

existence of a cooperative or electronic effect between platinum and rhenium is presented, and one consequence of this phenomenon is an enhanced adsorption capacity for both CO and hydrogen on bimetallic surfaces at the mixed metal sites that are present on the surface.

Understanding the behavior of the bimetallic surface toward hydrogen is important for another reason. Several investigators have implicated hydrogen as a key in the enhanced activity maintenance demonstrated by platinum-rhenium catalysts compared to monometallic platinum catalysts. For example, Barbier *et al.* found that hydrogen adsorption is enhanced on an alumina supported catalyst when rhenium and platinum have been codeposited compared to a monometallic Pt/Al₂O₃ catalyst [7], and Margitfalvi *et al.* found that the presence of rhenium increases the hydrogen available for hydrodepolymerization reactions that are important for removing deactivating carbonaceous deposits [8]. Pacheco and Petersen report that the presence of both rhenium and sulfur changes the hydrogen pressure dependence for fouling reactions on the bimetallic Pt-Re catalyst [9,10].

2 Experimental

Temperature programmed desorption (TPD) experiments were performed in a stainless steel ultra high vacuum (UHV) system pumped with a liquid nitrogen trapped diffusion pump; the base pressure obtained was 5×10^{-10} Torr after bake-out. The system was equipped with a four grid retarding field analyzer used for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), an ion gun for argon ion sputtering, and a quadrupole mass spectrometer for TPD.

Platinum single crystals were cut to within 1° of the (111) orientation and both sides were polished using standard techniques. The area of the disk was about 1 cm² with a thickness of 0.5 mm. The crystal was spot welded to platinum

wires (0.020 in.) that were spot welded to gold support rods (0.062 in.) affixed to a liquid nitrogen cooled block at the bottom of the manipulator. Resistive heating was used and the temperature monitored with 0.005 inch chromel/alumel thermocouple wires spot welded to the edge of the crystal.

The crystal was cleaned by cycles of heating in 3×10^{-7} Torr of oxygen followed by argon ion sputtering with 1×10^{-4} Torr of argon at 1000 K and a 1 keV beam energy, and annealing at 1300 K until no impurities (mainly Re, S, Ca, C, O) could be detected by AES. Following crystal cleaning, it was verified that a sharp LEED pattern was obtained corresponding to a (1×1) surface structure. Rhenium was removed by prolonged argon ion sputtering at room temperature and a 2 keV primary beam energy after carbon had been removed in 3×10^{-7} Torr oxygen at 900 K. Rhenium metal was deposited from a 0.5 mm. diameter rhenium wire heated resistively to 2000 K which gave a deposition rate of between 1–5 minutes/monolayer. The preparation of the bimetallic platinum–rhenium surface is discussed in detail elsewhere [1,2]. The rhenium wire was obtained from Gallard–Schlesinger and was 99.99% pure. The Pt(111) crystal was held at room temperature during rhenium deposition, and was flashed to 700 K periodically to remove any adsorbed CO and CO₂ that was generated by the rhenium source. The prepared bimetallic surface was cooled to 150 K before hydrogen temperature programmed desorption (TPD) experiments.

Research purity hydrogen, carbon monoxide, and oxygen were obtained from Matheson and used as supplied. For temperature programmed desorption experiments, prepared substrates were dosed with hydrogen and CO in a pressure range of 1×10^{-9} Torr to 1×10^{-7} Torr using precision calibrated leak valves. Hydrogen was dosed at 150 K while CO was dosed at room temperature. The crystal heating rate for TPD experiments was 30 K/sec; the temperatures scanned were between

150–800 K for hydrogen TPD and 300–800 K for CO TPD.

3 Results

3.1 Hydrogen TPD from the Re–Pt(111) System

Hydrogen adsorption with temperature programmed desorption was studied on the Re–Pt(111) system. The monolayer rhenium coverage is defined as one rhenium atom per platinum atom. Representative spectra for a low hydrogen exposure, 0.02 Langmuirs (L) are shown in Figure 1. To compare the behavior of the different bimetallic surfaces towards hydrogen adsorption and desorption, the position of the desorption maximum (T_{max}) extrapolated to zero coverage of hydrogen was determined (T_{max}°). The extrapolation was possible because the position of T_{max} decreased linearly with increasing hydrogen exposure at low exposures (Figure 2). T_{max}° from H_2 TPD obtained from a clean Re(0001) surface was found to be higher than from a clean Pt(111) surface as can be seen in Figures 1 and 2 (460 and 410 K respectively). This is in agreement with previous TPD results reported for Re(0001) [11,12], and for thick rhenium overlayers deposited on Pt(111) [13,14]. For bimetallic surfaces, the position of T_{max}° versus θ_{Re} was found to be decreasing through at least 1.3 monolayers (ML) of rhenium (Table 1), and these results show that submonolayer coverages of rhenium on Pt(111) desorb H_2 at lower temperatures than either Re(0001) or Pt(111).

A high temperature shoulder was observed on the clean Pt(111) spectrum near 480 K after a 0.02 L hydrogen dose, probably due to hydrogen desorbing from defect sites on the platinum surface (Figure 1). At 0.19 ML of rhenium, the high temperature shoulder was not observed, and was also absent at higher rhenium coverages. The hydrogen desorption area did not change with the disappearance

of this shoulder, rather the area was found to incorporate into the main peak when the rhenium coverage was less than one monolayer. The disappearance of the high temperature shoulder suggests that the first adsorbing rhenium atoms populate platinum defect sites that are responsible for the 480 K desorption feature on clean Pt(111). The hydrogen TPD obtained from a Re(0001) surface is shown for reference in Figure 1.

With a linear crystal heating rate and high pumping speed, the desorption peak area is proportional to the hydrogen that desorbed during TPD [15]. At 0.02 L of hydrogen, the hydrogen peak areas were equivalent for all rhenium coverages where $0 \leq \theta_{Re} < 1$ as shown by the lower curve of Figure 3. At hydrogen exposures greater than 0.1 L the hydrogen uptake curves diverged for different rhenium coverages. With saturation hydrogen exposures, the surface containing 0.19 ML of rhenium bound the most hydrogen, 20% more than the clean platinum surface, and the surface with 0.37 ML of rhenium bound 10% more hydrogen than the clean platinum surface. The surface containing 1.3 ML of rhenium bound about half as much hydrogen as clean Pt(111). These results are shown in Table 1 and Figure 3. The behavior towards hydrogen desorption is also shown to depend on the rhenium coverage in Figure 4 where the temperature of the desorption maximum is plotted versus the hydrogen desorption area.

3.2 Activation energy for H_2 desorbing from bimetallic surfaces

Assuming a second order desorption, the activation energy of desorption (E_{des}^a) can be calculated for the desorption of hydrogen from bimetallic platinum-rhenium surfaces using the experimental data and the method of Redhead [15,16]. The

activation energy of desorption is calculated using the relation from reference [15].

$$\frac{E_{des}^a}{RT_{max}^2} = \frac{n_o \nu_2}{\beta} \exp(-E_{des}^a/RT_{max}) \quad (1)$$

Rearrangement yields

$$\ln(n_o T_{max}^2) = \frac{E_{des}^a}{RT_{max}} + \ln\left(\frac{E_{des}^a}{R}\right) - \ln\left(\frac{\nu_2}{\beta}\right) \quad (2)$$

A plot of $\ln(n_o T_{max}^2)$ versus $1/T_{max}$ should give a straight line with a slope of E_{des}^a/R , where E_{des}^a is the activation energy of desorption, R is the gas constant, T_{max} is the temperature of the desorption maximum, ν_2 is the second order pre-exponential factor, β is the heating rate, and n_o is the number of hydrogen atoms adsorbed on the surface before desorption. The value of n_o was estimated by comparing the area of the desorption peak obtained to the area obtained for a saturated clean Pt(111) surface. The clean Pt(111) surface was assumed to adsorb one H atom per Pt atom at saturation, or 1.5×10^{15} H atoms/cm². TPD traces for hydrogen from clean Pt(111) are shown in Figure 5, and the corresponding activation energy plot obtained is shown in Figure 6.

Plots similar to the one shown in Figure 5 were obtained for hydrogen desorption from the bimetallic surfaces studied. The main difference between the plots was that the temperature maxima were lower on surfaces with a larger rhenium coverage for a given hydrogen dose. Activation energy plots were also similar for the bimetallic surfaces (Figure 6); the difference here was that the slopes of the curves at low hydrogen doses were different as tabulated in Table 1. With a hydrogen dose of less than 0.06 L, E_{des}^a was 19 ± 2 kcal/mole for clean Pt(111). At higher hydrogen exposures, the activation energy decrease observed (Figure 6) is probably due to hydrogen desorbing from a second, less strongly bound, adsorption site. For low hydrogen exposures, it can be seen that the activation energy of

desorption decreases with increasing rhenium coverage for all the surfaces tested. The activation energy of hydrogen desorption from Re(0001) was reported to be 20 kcal/mole by Ducros and coworkers and Kelly [12,17].

3.3 CO TPD from Re-Pt(111)

CO TPD experiments with variable CO exposures were performed on bimetallic surfaces of Re-Pt(111) with coverages of $\theta_{Re} \sim 0, 0.3$, and 0.55 ML. Spectra obtained for a CO exposure of 0.1 L on these bimetallic surfaces are shown in Figure 7. The high temperature feature observed was probably due to desorption from defect sites on the surface [18]. The attenuation of the high temperature shoulder with an increase in the intensity of the main peak when rhenium was evaporated onto the surface is indicative of preferential adsorption, or migration following desorption, of rhenium onto defect sites on the platinum surface. This was also observed for hydrogen TPD from Re-Pt(111) surfaces. Additional desorption features were never introduced by the deposition of rhenium onto Pt(111) as was also the case for hydrogen TPD.

Assuming a first order desorption, the activation energy of desorption can be calculated by the method of Redhead using

$$\frac{E_{des}^a}{RT_{max}} = \ln \left(\frac{\nu_1 T_{max}}{\beta} \right) - 3.64. \quad (3)$$

Here E_{des}^a is the activation energy of desorption, T_{max} is the temperature of the desorption maximum, ν_1 is the first order preexponential factor and was estimated to be $1 \times 10^{13} \text{sec}^{-1}$, and β is the heating rate [15]. The activation energy that was calculated from these spectra was 27 ± 1 kcal/mole for the three surfaces $\theta_{Re} = 0, 0.3$, and 0.55 ML. The position of T_{max} and of E_{des}^a for CO was not very different for these three surfaces. CO coverage dependence was also observed for all three surfaces.

As in the case with hydrogen on bimetallic surfaces, CO desorption from these three surfaces displayed similar desorption areas until higher CO exposures were reached. Surfaces exposing both platinum and rhenium atoms were found to adsorb more CO than did clean Pt(111) or thick rhenium films. At CO saturation, the $\theta_{Re} = 0.3$ ML surface bound 40% more CO than clean Pt(111). The $\theta_{Re} = 0.55$ ML surface bound 20% more CO than Pt(111).

Experiments were also performed on platinum surfaces with higher rhenium coverages at saturation exposures of CO (36 L). The results of these experiments are shown in Figure 8. The position of T_{max} for these surfaces reflects the surface composition in that the surface displays both platinum-like and rhenium-like behavior. This means that desorption from clean Pt(111) gives rise to a single desorption peak around 440 K while the two desorption states reported by Ducros *et al.* result in a single broad peak between 385 and 410 K in these experiments [11,12,19,20].

The CO desorption areas were also determined for these experiments, and it was found that rhenium-covered Pt(111) does not adsorb as much CO as does clean platinum. With rhenium coverages of 0.8, 3, and 3 ML oxidized, the surfaces bound less CO: 25%, 50%, and 75% less respectively. Only the 3 ML epitaxial rhenium surface displayed evidence for dissociative chemisorption, as shown by the peak near 730 K in Figure 8c. The relative saturation CO desorption area vs. rhenium coverage is shown for all the surfaces studied in Figure 9, and it can be seen that the surface with a rhenium coverage of $\theta_{Re} = 0.3$ ML adsorbed the most CO.

4 Discussion

4.1 Hydrogen on the bimetallic Re-Pt(111) surface

The addition of rhenium to a Pt(111) surface was found to effect the adsorption and desorption of hydrogen. When rhenium coverages were less than or equal to 1.3 ML, T_{max} extrapolated to zero hydrogen coverage was found to decrease with increasing rhenium coverage. T_{max} for the H_2 desorption peak from clean Pt(111) was about 50 K lower than it was from a Re(0001) surface (Figure 1) or from multilayers of rhenium on Pt(111) (reference [13]). In order to explain the shifting to lower temperatures of the hydrogen desorption peaks, several possibilities must be considered. First, an electronic effect may be operating between the platinum and rhenium metals. The evidence supporting this argument is: 1) The first layer of rhenium on the Pt(111) surface caused a shift to lower temperatures and not to higher temperatures for the hydrogen desorption maximum as would be expected if there was only an additive effect; 2) Low coverages of rhenium on Pt(111) resulted in a surface that bound more hydrogen than either clean Pt(111) or Re(0001) alone.

Additional evidence supporting the existence of an electronic interaction between the two metals was presented previously [1]. Chemical shifts were observed towards higher binding energies compared to the unalloyed metals for both the platinum and rhenium 4f peaks using XPS indicating that a surface alloy was formed at 700 K. Furthermore, rhenium was found to grow layer by layer on platinum indicating that the bonding of rhenium to platinum is strong enough to overcome differences in surface free energies, which otherwise should have resulted in three dimensional growth [1,2].

The behavior and position of the hydrogen desorption peak is discussed first.

Multiple desorption peaks were never observed as might be expected due to the introduction of defects by depositing rhenium metal onto the platinum surface. Kinks and defects in the surface of clean platinum single crystals are known to be sites of higher temperature hydrogen desorption states [21]. One explanation for the absence of multiple desorption peaks for submonolayer rhenium coverages is as follows. Stepped and kinked platinum surfaces are known to desorb hydrogen at higher temperatures than do flat terraces [21,22]. In fact, rhenium apparently migrates to and covers defect sites on the Pt(111) surface thereby eliminating the high temperature shoulder observed from clean Pt(111). But structural defects were not found to yield high temperature shoulders on stepped and kinked rhenium surfaces with terraces in the (0001) orientation by Ducros *et al.* [11]. This indicates that rhenium defects do not introduce hydrogen desorption features to a clean Re(0001) surface, and apparently not to a Pt(111) surface either.

Interesting new studies have been reported regarding the behavior of metallic monolayers on other metals that support electronic modification of the surface. The band structure of a single monolayer of a metallic adsorbate on a second metal does not resemble the bulk metal band structure in some systems. Pan *et al.* showed that 1 monolayer of platinum on niobium did not chemisorb CO even though both metals alone do so readily [23]. As for hydrogen desorption, additional hydrogen desorption peaks were not introduced by depositing gold on platinum films nor for copper on Ru(0001) [24,25].

A second possibility that may explain the shifting to lower temperatures of the hydrogen desorption peak is that surface contamination altered the adsorption/desorption behavior of the surface. Every effort was made to minimize surface contamination; however, traces of carbon and oxygen were sometimes found on the surface after operating the rhenium source. For chemisorption studies, con-

tamination levels no higher than 0.05 and 0.02 ML for carbon and for oxygen were tolerated. However, impurities might change the position of T_{max} in two ways. Non-metallic surface impurities may cause different desorption kinetics through an electronic effect. It seems unlikely that trace carbon and oxygen impurities would cause such a large temperature shift when the surface impurity level is dominated by the presence of relatively large amounts of rhenium. In addition, carbon and oxygen impurities are more likely to block sites rather than enhance the hydrogen adsorption capacity as was observed in these experiments [14,26]. In addition, if hydrogen is unable to occupy some parts of the surface due to the presence of the impurities, then the density of hydrogen would be higher than it should be for a given hydrogen dose. Hydrogen follows second order desorption kinetics and a higher hydrogen density would result in a lower T_{max} for a given hydrogen dose. This possibility can be excluded since T_{max}^0 was determined by extrapolation to zero hydrogen coverage. If no changes in desorption kinetics occurred with respect to the metallic composition, then all surfaces should converge to the same temperature at zero hydrogen coverage.

In addition to the dependence of T_{max} on the metallic composition of the surface, the dependence of the hydrogen desorption area on the metallic composition of the surface must also be explained. At submonolayer coverages of rhenium it was found that some bimetallic surfaces held more hydrogen than a clean Pt(111) surface at hydrogen saturation (Figure 3). The maximum hydrogen area obtained from the surfaces examined was from a bimetallic surface with a rhenium coverage of $\theta_{Re} = 0.19$ ML, and this surface held 20% more hydrogen at saturation than did clean Pt(111). One possible explanation for the increased capacity of the bimetallic surface towards hydrogen is that a cooperative or electronic interaction between platinum and rhenium was operating. Suppose 0.2 ML of rhenium covers

an equal amount of platinum surface. *In order to account for a 20% greater hydrogen capacity, each of the rhenium atoms or mixed sites would have to adsorb two hydrogen atoms per site.* Perhaps isolated rhenium atoms or small rhenium islands provide sites of enhanced hydrogen adsorption because these rhenium atoms have platinum ligands.

It is possible that an increase in surface roughness is responsible for the increase in the hydrogen desorption area. If the prepared bimetallic surface was not flashed to high enough temperatures to smooth out the surface, then the addition of rhenium to the surface should increase the surface area somewhat. This possibility was not fully explored because during TPD experiments, surfaces were never heated to temperatures high enough to cause bulk diffusion of the metals. But it was found that a rhenium surface adsorbed less hydrogen than a platinum surface (Figure 3), therefore it is not expected that an increase in surface roughness by rhenium atoms would compensate for the loss of platinum adsorption sites.

An activation energy of desorption using the Redhead analysis was calculated using the desorption area and position of T_{max} . Here changes were also observed with changes in the metallic composition of the surface. The activation energy of hydrogen desorption from Pt(111) alone was found to be 19 ± 2 kcal/mole. This is close to values obtained by Lu *et al.* and by McCabe *et al.* who reported values for E_{des}^a for H_2 on Pt(111) of 17.5 and 17 kcal/mole, respectively [27,28]. Christmann *et al.* reported a value of 9.5 kcal/mole which seems to be somewhat low for the low hydrogen coverage desorption [16].

The activation energy of hydrogen desorption was found to decrease from the clean Pt(111) value when rhenium was added to the surface. The change in the activation energy of desorption with the addition of rhenium to the surface is indicative of a change in desorption kinetics, and further evidence for the operation

of an electronic effect between the two metals. Other bimetallic systems also display this phenomenon. For example, Shimizu *et al.* found that T_{max} shifted with changing copper coverage for hydrogen adsorption on Cu-Ru(0001), and that no additional peaks or shoulders appeared due to copper or mixed copper-ruthenium sites [25], similar to the Re-Pt(111) case described here. For copper coverages above $\theta_{Cu} = 0.1$ monolayers, a decrease in E_{des}^a was found.

4.2 CO on Re-Pt(111) surfaces

The study of carbon monoxide is of interest because it had been used successfully as a titrant for other unsupported bimetallic single crystal surfaces in this laboratory. It is also used as a titrant for supported metallic catalysts. Yeates and Sachtler used CO to titrate platinum sites on platinum-copper and platinum-gold bimetallic surfaces [29,30,31]. CO was an excellent titrant for these bimetallics because it does not adsorb on gold or copper. Carbon monoxide does adsorb on rhenium as well as on platinum, but it was hoped that the adsorption/desorption behavior would be sufficiently different on the two metals that separate titration of the platinum and rhenium sites would be possible. This turned out not to be the case.

Temperature programmed desorption studies of carbon monoxide from the Pt(111) and the Re(0001) surfaces are well represented in the literature. The desorption of CO from Pt(111) results in a single peak and is known to occur by first order kinetics with respect to CO coverage; the activation energy of desorption is 26-30 kcal/mole [18,28,32,33,34]. The shift in peak position to lower temperatures with increasing CO coverage occurs because the activation energy of desorption is coverage dependent.

The desorption of CO from the Re(0001) surface is somewhat different. A

single peak was obtained at low CO coverages with the addition of a second lower temperature peak at higher coverages resulting in two α peaks in the temperature range 350–500 K [19]. CO follows first order desorption kinetics on Re(0001) with E_{des}^a independent of coverage [11,12,19,20]. Some CO dissociation also occurs on Re(0001) resulting in a high temperature (800 K) β peak, although this probably occurs on the defect sites instead of the terrace sites. Housley *et al.* reported E_{des}^a for the α peaks of 24 and 27 kcal/mole [19].

Assuming that CO follows first order desorption kinetics and that the T_{max} shift to lower temperatures with increasing CO coverage is a result of a decreasing E_{des}^a with CO coverage, it was found that on the three surfaces tested, 0, 0.3 and 0.55 ML Re–Pt(111), that E_{des}^a is CO coverage dependent. This indicates platinum-like behavior even at $\theta_{Re} = 0.55$ ML. The position of T_{max} was not sufficiently different between the two metals, nor was it different on any of the bimetallic surfaces tested. This means, unfortunately, that the platinum and rhenium sites exposed on the surface cannot be distinguished quantitatively using CO TPD.

Although differences in desorption energetics were not observed with metallic surface composition, differences in adsorption capacity were observed. For the monometallics, the room temperature saturation capacity for CO is twice as much on Pt(111) as it is on Re(0001), about 7.5×10^{14} and 4×10^{14} molecules/cm², respectively [11,18,19]. A comparison of the CO adsorption obtained on clean Pt(111) compared to CO adsorption on 3 ML of rhenium on Pt(111) show that these results are in fairly good agreement with the above results (Figure 8).

With a rhenium coverage of $\theta_{Re} \sim 0.3$ ML, a 40% increase in CO capacity was observed compared to clean Pt(111) (Figure 9). *This indicates that each rhenium atom or mixed site adsorbs 2–2.3 CO molecules.* As in the hydrogen case, the 40% increase in CO chemisorption of the $\theta_{Re} = 0.3$ ML surface could

be due to an electronic interaction at the surface or to the presence of surface roughness. At low rhenium coverages the surface is expected to be somewhat rough compared to a well annealed surface. The problem with this explanation is that the increase in roughness is accomplished with rhenium metal. A Re(0001) surface binds about half as much CO as does Pt(111), and the work of Housley *et al.* has shown that the stepped Re[14(0001) $\times$ (10 $\bar{1}$ 1)] surface has about the same adsorption capacity for the molecular CO state as the Re(0001) surface [19]. This indicates that low coordinated rhenium cannot be responsible for the adsorption of higher amounts of molecular CO. CO dissociation was also not observed on surfaces with submonolayer rhenium coverages. This indicates that rhenium atoms with platinum ligands cannot dissociate CO, but the presence of rhenium on the Pt(111) surface does alter the chemisorption capacity towards CO, suggesting that an electronic effect is responsible for the enhancement of the CO chemisorption capacity. The magnitude of the increase was fairly large, in fact it was found that at room temperature a 0.7 ML coverage of CO was obtained in the presence of 0.3 ML of rhenium. But it is known that the compression structure observed on Pt(111) ($\theta_{CO} \sim 0.7$) is formed only when the platinum surface is cooled to liquid nitrogen temperatures [18]. A geometric factor may have contributed to the increased CO capacity, but if an increase in surface roughness was a factor, it was because rhenium is capable of adsorbing more CO through an electronic effect due to contact with an underlying platinum substrate.

5 Conclusions

Bimetallic surfaces prepared by vapor depositing rhenium onto Pt(111) show interesting adsorption and desorption properties with regards to H₂ and CO. Maximum adsorption capacities towards H₂ and CO at saturation under UHV were observed

on bimetallic surfaces composed of between 0.15–0.3 ML of rhenium on Pt(111) indicating that a cooperative or electronic effect operates between the interfacial region. Hydrogen was also found to desorb at lower temperatures when both platinum and rhenium atoms were exposed on the Pt(111) surface compared to both monometallic Pt(111) and Re(0001) surfaces.

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Table 1: Hydrogen Desorption Parameters for Rhenium Modified Pt(111).

θ_{Re}	T_{max}^a	H ₂ Area ^b	E _{des 1} ^c
0	410	1.0	19.0
0.19	398	1.2	17.5
0.37	392	1.1	16.5
0.66	370	0.9	11.5
0.77	370	0.7	7.0
1.3	336	0.5	7.5
∞^d	460	—	20 ^e

- a.* Extrapolated to 0 exposure of H₂, ± 5 K.
- b.* Maximum relative H₂ desorption area obtained after 10 *L* hydrogen dose and compared to clean Pt(111).
- c.* Activation energy of desorption between 0–0.06 *L* in kcal/mole ± 2 kcal/mole.
- d.* Re(0001).
- e.* References [12,17].

Captions for Figures

Figure 1: Hydrogen temperature programmed desorption spectra from Re modified Pt(111). The H₂ exposure was 0.02 *L* at an adsorption temperature of 150 K; the heating rate was 30 K/sec.

Figure 2: Temperature of the desorption maximum (T_{max}) from H₂ TPD of Re modified Pt(111) as a function of H₂ exposure and Re coverage. H₂ was adsorbed at 150 K; the heating rate was 30 K/sec.

Figure 3: Relative maximum H_2 temperature programmed desorption area as a function of θ_{Re} .

Figure 4: The temperature of the desorption maximum is plotted versus the hydrogen desorption area for several rhenium coverages on Pt(111).

Figure 5: Hydrogen temperature programmed desorption spectra from clean Pt(111). The temperature of adsorption was 150 K with a heating rate of 30 K/sec.

Figure 6: Activation energy plot for H_2 desorption from Pt(111). The temperature of adsorption was 150 K with a heating rate of 30 K/sec.

Figure 7: CO TPD from bimetallic Re-Pt(111) surfaces. The adsorption temperature was 300 K; the heating rate was 30 K/sec. The CO exposure was 0.1 L.

Figure 8: CO TPD spectra obtained from bimetallic Re-Pt(111) surfaces at higher rhenium coverages. Adsorption temperature was 300 K; the heating rate was 30 K/sec. The CO exposure was 36 L on the following surfaces: a) Pt(111). b) 0.8 ML Re. c) 3 ML epitaxial Re. d) 3 ML Re annealed to 1150 K. e) 3 ML Re oxidized at 800 K with 100 L O_2 .

Figure 9: Saturation CO desorption area vs. rhenium coverage for Re-Pt(111) surfaces.

XBL 882-617

Fig. 1

XBL 882-618

Fig. 2

XBL 882-619

Fig. 3

XBL 882-620

Fig. 4

XBL 882-621

Fig. 5

XBL 882-622

Fig. 6

XBL 882-623

Fig. 7

XBL 882-624

Fig. 8

XBL 882-625

Fig. 9

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