

Ligand Effects for CO and H₂ Chemisorption on a Polycrystalline Pt₃Ti Surface

The Pt-Ti bimetallic system is interesting for several reasons, but most particularly as an example of an "Engel-Brewer" type intermetallic (1). The highly exothermic enthalpy of formation of these alloys has been interpreted in terms of strong bonding interaction of electrons in the *d* bands of both metals. In principle, such a strong interaction is likely to modify the electronic properties of the metals and cause changes in the chemical properties that are often called ligand effects. Ligand effects have been considered as a possible cause for the increased catalytic activity, as compared to pure Pt, of the Pt₃Ti intermetallic in the electrolytic reduction of oxygen to water in acid fuel cells (2). Also a ligand effect caused by the Pt-Ti bond is considered to be related to the strong metal-support interaction (SMSI) which is observed when Pt supported on TiO₂ is reduced in hydrogen at elevated temperature (3, 4). Because of these changes in the catalytic properties of platinum in the presence of Ti, we have undertaken a study of the surface properties of the ordered Pt₃Ti intermetallic compound, which has the most exothermic heat of formation in the Pt-Ti system (5). In this paper we report the results of a study of carbon monoxide and hydrogen chemisorption, which we used as chemical probes to test the presence of ligand effects.

The Pt₃Ti compound was prepared by arc melting the metals in an argon atmosphere. The Pt/Ti atomic ratio was checked after melting by X-ray emission spectroscopy. X-Ray diffraction indicated that the alloy bulk structure was the fcc AuCu₃ type (Pt₃Ti can also exist in the cubic β-W and hexagonal TiNi₃ type structures (5)) with

lattice parameter 3.906 Å. Disk shaped samples about 1 mm thick and 5 mm diameter were mounted in a UHV system equipped with a single pass CMA with grazing incidence electron gun for Auger electron spectroscopy (AES), a mass spectrometer for thermal desorption spectroscopy of adsorbates (TDS), and a sputter gun for surface cleaning. The sample could be annealed up to about 1200 K by resistive heating through the supporting Ta wires. The system was also equipped with an electron beam evaporator located in a separate chamber. The purpose of this evaporator was to coat the sample with a pure Pt film in order to be able to compare the alloy and pure metal properties in TDS experiments. In this way we insured that the surface area, geometry, and heating rate were exactly the same.

The AES spectrum after argon ion bombardment of the sample is shown in Fig. 1. A quantitative analysis of the spectrum using the elemental sensitivity factors reported in (6) indicates that a Ti(387 eV)/Pt(237 eV) Auger peak ratio of 3.8 corresponds to a Pt/Ti atomic ratio of 3.5. We do not consider that the Pt/Ti atomic ratio of 3.5 calculated from the elemental sensitivity factors accurately represents the surface composition. Other observations, such as the AES spectrum of the air-exposed surface (mostly Ti and O peaks) and the chemisorptive behavior of oxygen on the ion-bombarded surface, indicated to us that the ion-bombarded surface was actually titanium rich, i.e., the Ti(387 eV)/Pt(237 eV) Auger peak ratio of 3.8 actually corresponds to a Pt/Ti ratio less than 3.0. The residual carbon and oxygen in the AES

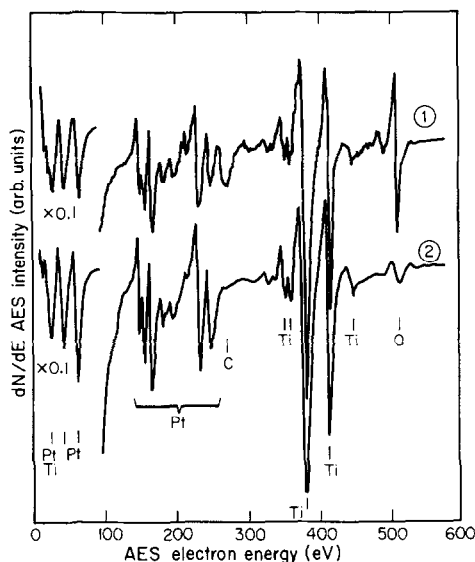


FIG. 1. AES spectrum of the Pt_3Ti surface. 2Vpp modulation. Curve 1, surface after ion bombardment; curve 2, surface after annealing at 923 K.

spectrum were apparently bulk impurities, since they could not be eliminated by ion-bombardment alone. To investigate that problem further, some samples were analyzed using spatially resolved AES, i.e., scanning Auger electron microscopy (SAM). This analysis indicated that arc melting the pure elements can result in a grainy structure with substantial TiO_2 inclusions in the grain boundaries. Such inclusions would not be removed by continuous ion bombardment. It was nevertheless possible to obtain a nearly oxygen-free surface by means of a thermal treatment. As shown in Fig. 1, annealing the sample at 923 K in vacuum was sufficient to remove all the carbon and most of the oxygen. We determined by mass spectrometry that carbon and oxygen were desorbed from the surface as CO_2 during annealing. Samples prepared from different melts had different amounts of bulk carbon and oxygen and for some crystals the residual after annealing was carbon rather than oxygen. Residual carbon could be eliminated by oxygen dosing at 600–700 K, and the oxygen left on the surface after the dosing was removed by flash-

ing the crystal to 1000 K. As shown in Fig. 1, the effect of the annealing was also to reduce the value of the $\text{Ti}(387 \text{ eV})/\text{Pt}(237 \text{ eV})$ AES ratio from 3.8 to 1.9, indicating that surface segregation of Pt occurred. The Ti/Pt AES ratio after annealing remained unchanged upon cooling and showed very little dependency on the annealing temperature. All the AES results reported in this paper are for the clean surface obtained after annealing. Once the surface was cleaned and annealed, reaction with oxygen was observed only at high temperature and/or high oxygen pressure. At room temperature the surface did not react detectably with oxygen for pressures up to 10^{-5} Torr. In contrast, the bombarded surface reacted with oxygen in the 10^{-8} Torr range.

Figure 2 shows the AES results after room temperature CO adsorption on the clean Pt_3Ti surface. The carbon AES peak after CO saturation on the surface shows the double peak characteristic of the undissociated molecule (7). No residual carbon was detectable after CO flash desorption, indicating that dissociation did not occur during desorption. When the clean surface was dosed with O_2 at 573 K (10^{-6} Torr, 100), CO adsorption was greatly reduced, as seen by the carbon AES peak in Fig. 2. Figure 3, curve 2 shows the result for CO

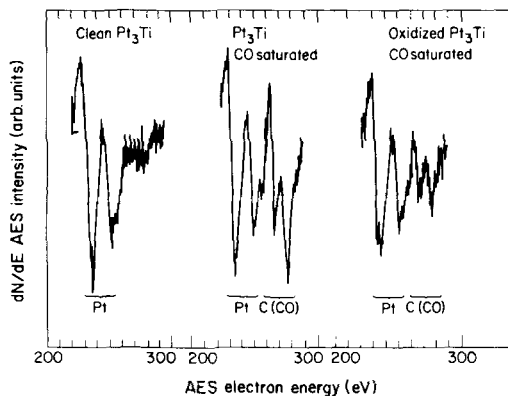


FIG. 2. AES of the Pt_3Ti surface showing the carbon (CO) features for the clean surface, the clean surface after SA turnover with CO and the oxidized surface after saturation with CO 2Vpp modulation.

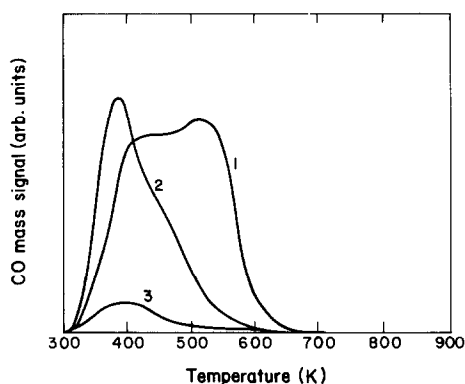


FIG. 3. CO thermal desorption from: Curve 1, polycrystalline Pt; curve 2, polycrystalline Pt₃Ti (clean); curve 3, polycrystalline Pt₃Ti (oxidized).

thermal desorption from the Pt₃Ti clean surface and curve 1 the result with a pure Pt surface. The surface was cleaned as described above, saturated with CO at room temperature (10 liter dose) and flashed at a rate of 44 K s⁻¹. For the pure Pt result, the Pt₃Ti surface was covered with Pt by evaporation until the Ti AES peaks were undetectable and then annealed at 700 K (higher temperature caused Ti diffusion through the Pt film). After a 10 liter dose of CO at room temperature, the TDS peak was recorded in the same manner as for the clean Pt₃Ti surface. In curve 3 we show the CO TDS peak after Pt₃Ti had been dosed with 5×10^{-6} Torr O₂ at 1000 K. The results on the clean polycrystalline Pt surface found here are comparable to those reported in the literature (8–10). Two desorption states were observed, which are usually interpreted as adsorption on the two different low index facets, (111) and (100), that normally occur on annealed polycrystalline Pt. CO on the Pt(100) facet has the lower desorption temperature, and according to work on single crystals (11), the saturation coverages on the two facets would differ only slightly. A similar poisoning of CO and H₂ adsorption on Ni₃Ti by oxygen dosing was reported by Fischer *et al.* (19). As pointed out in their study, the Ti–O interaction is sufficiently strong that it overrides the intermetallic bond and caused oxygen induced enrich-

ment of the Ni₃Ti surface in oxidized titanium. The same mechanism of poisoning by oxygen probably applies in the case of Pt₃Ti as well.

In comparison with the pure Pt, the CO TDS curve for Pt₃Ti shows two important differences: smaller area, indicating lower total CO coverage; a shift of the peak toward lower temperatures. The suppression of the high binding energy state has also been observed with a Au-rich Pt/Au alloy, but no shift in the peak temperature for the low binding energy state was reported (12). Since the X-ray diffraction analysis of the Pt₃Ti did not indicate any preferred orientation in this crystal, the peak shift probably did not arise from the absence of (100) facets in the intermetallic surface, but rather represents a real difference in adsorption energy. Furthermore, we have conducted a few CO adsorption experiments on Pt₃Ti (100) and (111) single crystals, and these gave single TDS peaks displaced to lower temperatures than for either Pt (100) or (111) surfaces. If we estimate the adsorption energy from the temperature at which the first-order desorption rate is maximum (13), the two adsorption states on Pt correspond to 32 and 25 kcal/mol, and the state on Pt₃Ti to 21 kcal/mol, at least a 4 kcal/mol decrease in adsorption energy.

In Fig. 4, we report the thermal desorption of hydrogen following room temperature dosing at 10⁻⁶ Torr. As in the CO desorption experiments, the results for the Pt₃Ti surface were compared to those on a pure Pt surface obtained by evaporation onto the intermetallic crystal. In comparison with pure Pt, the very small hydrogen signal observed from the intermetallic surface can be taken as indicative of essentially no chemisorption of hydrogen on this surface *at room temperature*. Unfortunately, our holder was not equipped with any cooling capability, so we could not look for retention of hydrogen by the surface at lower temperature. The absence of hydrogen chemisorption could not be attributed to artefacts like surface contamination, as

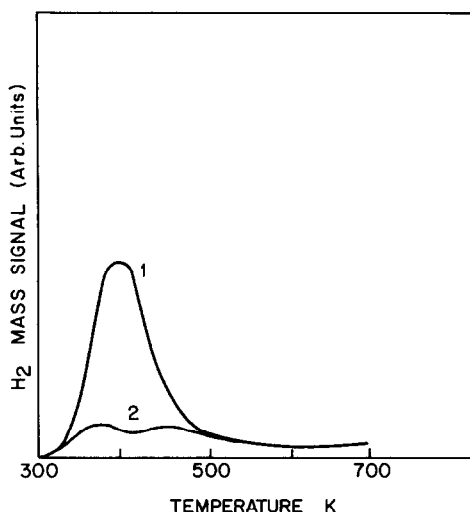


FIG. 4. H₂ thermal desorption from: curve 1, polycrystalline Pt; curve 2, polycrystalline Pt₃Ti.

AES indicated the surface was clean, or CO competitive adsorption (no significant CO signal seen by mass spectrometer during the flash) or oxygen "clean-off" (no significant oxygen signal in mass spectrometer during or following hydrogen dosing). Also, the same surface was observed to chemisorb CO, as shown in Fig. 3, and artefacts like contamination and oxygen "clean-off" would have suppressed CO adsorption as well. The suppression of hydrogen chemisorption and the reduced bond energy for adsorbed carbon monoxide appear to be genuine effects of the presence of Ti in the Pt surface.

An interpretation of these results must first consider the bimetallic surface structure and composition. The AES signal reflects contributions from several surface layers and therefore the value of the Ti/Pt AES ratio alone cannot provide an unambiguous determination of the outermost layer composition. However, use of the elemental sensitivity factors (6), inelastic mean-free paths (14), and the usual relations for escape depths of Auger electrons (15) enable certain extreme cases of surface composition to be eliminated. In analogy with the Pt/Sn exothermic alloy (16, 17), we assume, for this approximate calculation,

that enrichment would occur through an exchange of atoms in the first two atomic layers (17). If we define an enrichment factor f , as

$$f = (\text{Ti/Pt})_{\text{surf}}/(\text{Ti/Pt})_{\text{bulk}}$$

so that $f > 1$ is enrichment by Ti, and $f < 1$ is enrichment by Pt, then it can be shown that the observed Ti/Pt AES ratio indicate that $0.5 < f < 1.5$, i.e., pure Pt or pure Ti overlayers are totally inconsistent with the AES data. Beyond these extreme cases of enrichment that do not seem to occur, it is not possible to draw definitive conclusions about the surface composition from just the AES data. The chemistry of this system and general concepts (17) of surface segregation permit us to make qualitative arguments concerning the most likely surface composition. It seems unlikely that the bombarded bimetallic surface had the bulk composition, since the reactivity of this surface with oxygen at room temperature suggest a Ti rich surface. This would mean that the Pt segregation observed on annealing probably represents restoration of the bombarded surface to the bulk composition. Theoretical considerations (17) of the driving forces for surface enrichment indicate that in very exothermic alloy systems, where there is strong intermetallic bonding, the strong bulk-type bonding predominates over surface-specific forces and termination at the surface in the bulk composition and structure is to be expected. While not definitive, the present AES data are at least consistent with this expectation.

The data presented here indicate the effect of Ti on CO adsorption is most probably a ligand effect, i.e., a modification of the Pt chemical properties caused by charge redistribution upon forming the Pt-Ti bonds. The CO-metal bond is very sensitive to variations in the electron distribution on the metal atoms. This bond has been described in terms of both a σ -type bond, where the 5σ molecular orbital donates electrons to the empty metal orbitals, and a π -type bond, where the metal donates elec-

trons to the π^* antibonding orbitals of the CO molecule (18) which weakens the C=O bond but strengthens the metal-C bond. In the Engel-Brewer intermetallic bonding concept (1), the Pt rehybridizes from the metallic electronic configuration ($d^9s \rightarrow d^7 sp^3$) in order to maximize the number of d -bonds it can form with Ti. The Pt-Ti bonding maximizes use of the Pt d -orbitals for the intermetallic bond, and would leave only sp orbitals available for adsorbate bonding. One would expect then from the Engel-Brewer model that CO bonded to Pt in Pt₃Ti would have less bonding to the CO π^* orbitals than in the case of pure Pt, resulting in a weaker Pt-carbon adsorptive bond.

The SMSI effect for Pt dispersed on titanium oxide that was subsequently heated in hydrogen involved complete suppression of H₂ and CO adsorption at room temperature. Tauster *et al.* (3) considered the possibility of Pt₃Ti formation and showed that under their conditions of reduction at 500°C it was at least thermodynamically possible. However, our results indicate that intermetallic formation would not account entirely for the SMSI effect described by these workers. In our experiments, hydrogen adsorption was absent on the intermetallic but CO adsorption was completely suppressed only when TiO₂ segregated to the surface upon heating the Pt₃Ti in oxygen at elevated temperature. However, the trends of the effect of Pt-Ti intermetallic bonding on H₂ and CO chemisorption are clearly the same as the effect of strong reduction of Pt/TiO₂, and it would seem that strong intermetallic bonding is implicated in the SMSI effect. It may be that the Pt/TiO₂ system has structural constraints or anomalies that complement the intermetallic bonding effect. Further studies are in progress in order to elucidate the characteristics of the Pt-Ti bond by electron spectroscopy (XPS, UPS), and to make definitive determinations of the composition and structure of the intermetallic surface using LEED and single crystals.

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