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Formation of and CO adsorption on an inert La-Pt(111) surface alloy

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Thin La overlayers (up to ≈3 ML) have been deposited onto a Pt(111) surface. We find that an ordered interface alloy is formed when the system is annealed above 800 K. A 2×2 overlayer structure was observed by low-energy electron diffraction. Photoemission reveals a substantial increase in the density of states near the Fermi level as a result of the alloying reaction. When the as-deposited La-on-Pt(111) system was exposed to CO, and subsequently annealed, a desorption peak was observed to coincide with the alloying transition. The signature of this desorption peak was that of zeroth-order desorption. Thermal-desorption studies showed that CO is more weakly adsorbed on the La-Pt surface alloy as compared to the pure Pt(111) surface. A desorption energy $E_d=0.9\pm0.1$ eV was estimated for CO on the surface alloy in the limit of zero CO coverage. The desorption measurements are discussed in view of recent Monte Carlo simulations as well as calculations using the transfer-matrix method. [S0163-1829(99)03223-3]

I. INTRODUCTION

Electronic promoters play an important role in heterogeneous catalysis.[1,2] The platinum (111) surface doped by low work-function elements like, e.g., rare-earth metals, may constitute an important system for studying catalytic promotion.[3] The presence of a low work-function element at the surface has the effect of lowering the electrostatic potential and thus affecting the bonding of gas molecules and thereby altering the catalytic activity. However, an overall description of a given catalytic reaction is made complicated due to the fact that a substantial number of other properties of the catalyst may also have been changed by the adsorbate, e.g., adsorption sites and the surface mobility of adsorbed species, the structure and electronic structure of the catalyst, the number of active sites, etc.

Rare earths are well suited to be used as dopants in catalysts since they have low surface free energies.[4] They therefore have a tendency to be located at or near the surface in an actual catalytic system, and will thus directly influence adsorption and desorption of various gas molecules. Frequently, simple model systems may give useful insight into real catalytic processes as well as fundamentals of adsorption and desorption of various gas molecules. In this work, La overlayers on a Pt(111) crystal have been studied by photoelectron and thermal-desorption spectroscopies. The motivation for this study was to modify electronic and structural properties of the Pt(111) surface to change its reactivity. The formation of an ordered surface alloy, as well as adsorption of CO and O_2 on the surface alloy, have been investigated. Previous experiments have shown that solid-state reactions occur when rare earths are deposited on a variety of metallic substrates even at ambient temperatures.[5–7] We find that the La-Pt alloy is more inert to adsorption of CO and O_2 than the pure Pt(111) surface at ambient temperatures. Similar to the present case, previous work on the Ce on Pt(111) system showed that a surface alloy formed that was relatively inert to adsorption of oxygen.[8]

II. EXPERIMENT

Photoemission measurements were recorded using an HA-50 hemispherical electron energy analyzer from Vacuum Science Workshop (VSW). The exciting radiation was from a twin-anode x-ray source from VSW for the x-ray photoelectron spectroscopy (XPS), and a homemade rare-gas discharge lamp for the ultraviolet photoelectron spectroscopy (UPS). Total-energy resolutions were ≈1 eV and ≈0.2 eV for XPS and UPS, respectively. Temperature-programmed desorption (TPD) spectra were recorded by using a Transpector H100M quadropole mass spectrometer from Leybold-Inficon that was interfaced to a personal computer. The tip of the mass spectrometer was shielded to minimize contributions from the edges and back side of the sample as well as the sample support. Some of the initial TPD measurements were performed without this shield. The TPD measurements were performed using a heating rate of 2 K/s. The temperature was varied by use of a Eurotherm temperature controller. The sample was cooled by liquid nitrogen in order to enable measurements below ambient temperature.

The Pt(111) crystal was cleaned by repeated cycles of Ar-ion sputtering (30 min at room temperature, and 15 min at 1100 K), oxygen annealing at 1×10^{-8} torr at 1000 K, and annealing to 1500 K for 5 min. The cleanliness of the surface was verified by measuring C 1*s* and O 1 *s* core levels by XPS and by UPS from the valence-band region, and the structure was checked by low-energy electron diffraction (LEED). The work function of the sample was measured by subtracting the width of the UPS from the photon energy ($h\nu=21.2$ eV). La was deposited from a water-cooled evaporation source that consisted of a thermally heated tungsten basket, and that was thoroughly outgassed prior to use. The effective La coverage was estimated from core-level intensity measurements. The La-Pt(111) surface alloy was produced by heating the sample to 900 K at a rate of 2 K/s.

III. RESULTS AND DISCUSSION

First the formation of the La-Pt(111) surface alloy will be considered. The alloy formation has been studied by use of

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XPS, UPS, and as TPD. It is observed that when CO is adsorbed on the as-deposited La-on-Pt(111) sample, some remaining CO will in fact desorb at the temperature of the alloy transformation.

The main emphasis in this paper will be placed on the ordered La-Pt(111) surface alloy and thermal desorption of CO from this sample. The observed relative inertness to adsorption of CO and O_2 on this system at room temperature is remarkable in view of the expected high reactivity of rare earth metals.

A. Surface alloy formation

When an effective La coverage of near 1 ML was deposited on the Pt(111) substrate and subsequently annealed to 900 K, a 2×2 superstructure was observed by LEED. Previous work on the Ce-Pt(111) system showed similar results, and presented speculations that the surface was Pt terminated in that case.[8] More recently, a comprehensive study of the Ce-Pt(111) system by Baddeley *et al.*[9] concluded that the structure of the interface was an *ABAB* layered arrangement of Pt_2Ce and Kagomé nets of Pt atoms, where either type of layer could appear at the surface as the terminating structure. It was argued that observed low reactivity to ambient gases was caused by a termination by a Kagomé net of Pt atoms.[9] Recent work on La-Pt(111) by Garnier *et al.*[10] showed that a surface alloy was formed that was stable against contamination, when a ≈10-Å La overlayer on Pt(111) was annealed at 900 K for about 10 min. A 2×2 LEED pattern was observed. The electronic structure of this alloy was found to be similar to the Ce-Pt(111) alloy. Similar conclusions regarding the electronic and geometric structure were also found by Pillo *et al.*[11] Substantial changes were observed in the photoemission from the valence-band region when a surface alloy was formed by annealing. In Fig. 1 we show valence-band photoelectron spectra that were recorded near normal emission. A large increase in the 5*d* emission near the Fermi level is seen for the heated sample as compared to both the as-deposited La-on-Pt(111) sample and the pure Pt(111) sample.

As may be expected when a low work-function material like La ($\phi \approx 3.5$ eV) is deposited on the surface of a high work-function material like Pt ($\phi \approx 5.7$ eV), a substantial decrease in the work function is observed. This is shown in Fig. 2 for various amounts of La on the Pt(111) surface. An increase in the work function is observed after formation of a surface alloy upon heating to 900 K. The resulting work function of the alloy, however, is in the order of 1 eV lower than that of pure Pt(111). We note that changes in work function are small for coverages below 0.5 ML, i.e., in a coverage region where surface alloying was not observed, as discussed below. The errorbars in Fig. 2 in the estimates of relative work functions are of the order 0.3 eV, due partly to uncertainties in coverage estimates and partly to uncertainties in the measurements of the work function itself.

The formation of a La-Pt(111) surface alloy was found to depend critically on the amount of La that was deposited on the Pt substrate before annealing the sample. In Fig. 3 we show TPD spectra from a La-on-Pt(111) sample that has been exposed to sufficient doses of CO to saturate the surface. These La-Pt samples were not annealed prior to the desorption measurements. The structure between temperatures 400 and 500 K corresponds to the usual desorption of CO that is observed from a Pt(111) crystal (bottom spectrum). The shoulder near 500 K is an artifact due to desorption from the edges, back side, and sample support, since the quadropole mass spectrometer was not shielded for these measurements. Such a shoulder may also be observed for stepped surfaces; however, this explanation may be ruled out in the present case since the shoulder was strongly attenuated when the mass spectrometer was later shielded. The main attention should focus on the structure above 800 K in these

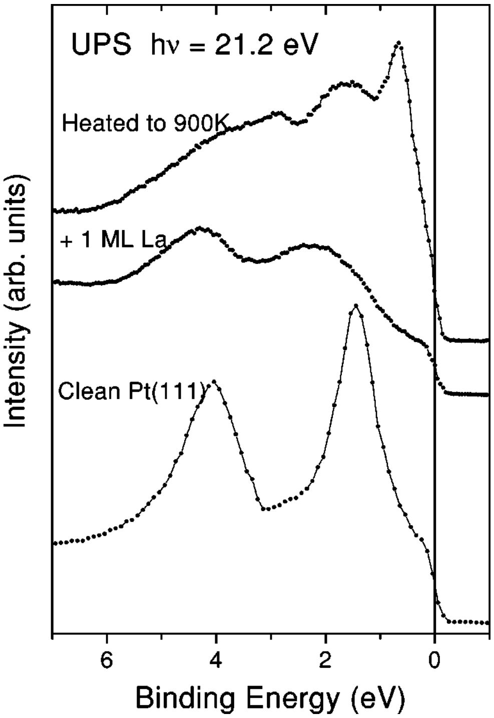

FIG. 1. Valence-band photoemission spectra ($h\nu = 21.2$ eV) from pure Pt(111) (bottom curve), as-deposited 1-ML La-on-Pt(111), and annealed 1-ML La-on-Pt(111) (top curve). The spectra were recorded near normal emission. The top spectrum corresponds to the ordered La-Pt(111) surface alloy.

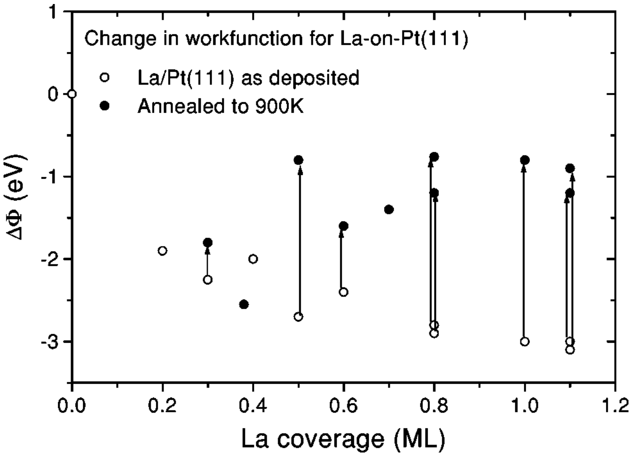

FIG. 2. Changes in work function $\Delta\phi$ for various amounts of La on Pt(111). The vertical arrows show changes that are induced by heating the sample to 900 K. All values of $\Delta\phi$ are measured relative to the value for clean Pt(111).

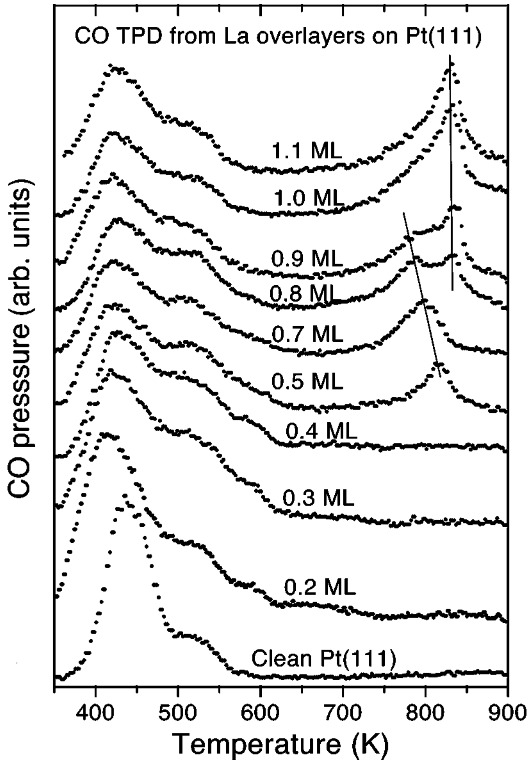

FIG. 3. TPD spectra from as-deposited La on Pt(111). The samples have been dosed to saturation with CO. The effective La coverage is given in the figure. The feature near 400–450 K is the usual desorption of CO from Pt, whereas the features above 800 K is associated with the formation of the surface alloy. The shoulder near 500 K is an artifact that results from desorption from the sample mount and edges and the back side of the crystal.

spectra. For effective La coverages below 0.4 ML no high-temperature CO desorption structure was observed. Whereas only small changes were observed in the work function or in the UPS for La coverages below 0.4 ML, significant changes were observed for La coverages above 0.5 ML. The high-temperature desorption feature also emerges at a La coverage of 0.5 ML. At first a single peak is observed. Subsequently, for coverages slightly less than 1 ML, two peaks are clearly resolved. Finally, for coverages near and above 1 ML, one single peak is observed.

The signature of the CO desorption peak above 800 K is of zeroth-order desorption, which usually is associated with desorption from a multilayer or desorption due to decomposition of a larger species. In the present case, the latter mechanism is most likely to be in effect. The desorption of CO results simultaneously with the formation of the surface alloy. The bimodal peak observed above 800 K in the desorption spectrum for some La coverages is thought to originate from C and O that are bound in different local environments. The nature of a possible C-O-La-Pt complex remains undetermined.

Carbon monoxide is not adsorbed in its molecular form on the as-deposited La-Pt surface. This is indicated by the absence of molecular CO orbitals in the UPS, as shown in the middle curve in Fig. 4, and by the large change in the oxygen 1*s* XPS as shown in Fig. 5. The top curve of Fig. 4 confirms previous reports of molecular adsorption on the Pt(111) surface.[12,13] The bottom curve of Fig. 4 shows that molecular adsorption also occurs on the annealed La-Pt surface alloy. The main O 1*s* peak is observed near a binding energy of 533 eV in the case of CO on Pt(111) (bottom curve, Fig. 5). A lower binding energy of about 530 eV was

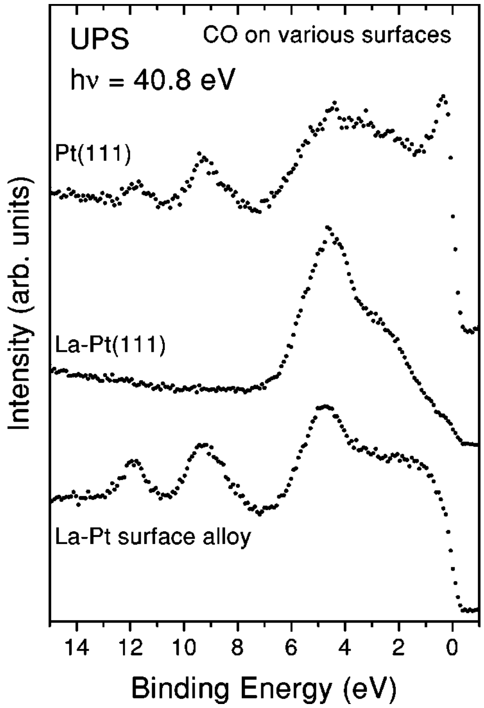

FIG. 4. UPS using the He II line at 40.8 eV. The molecular CO orbitals are observed for the CO/Pt and CO/surface alloy cases.

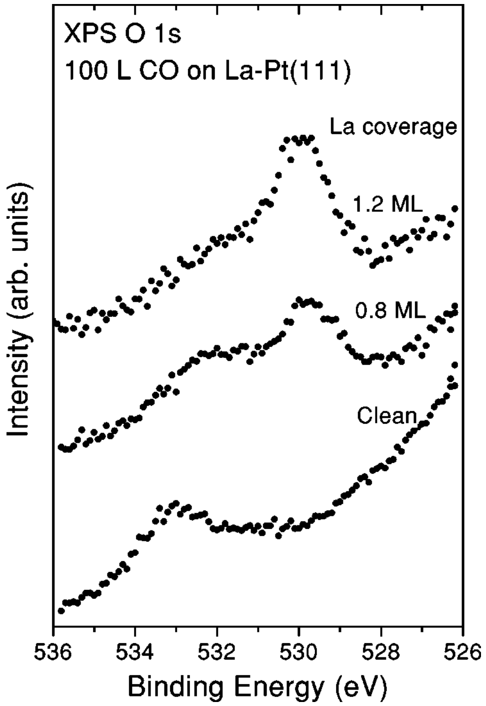

FIG. 5. Oxygen 1*s* XPS after exposure to 100-L CO to Pt(111), 0.8-ML La on Pt(111), and 1.2-ML La on Pt(111), as indicated in the figure. The spectra were recorded prior to annealing and surface alloy formation.

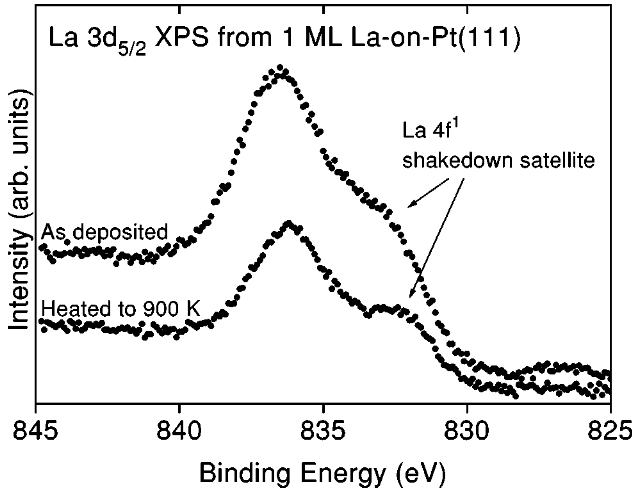

FIG. 6. La $3d_{5/2}$ XPS showing the $3d^9 4f^1$ shakedown satellite at the low-binding-energy side of the main peak, before and after annealing of 1-ML La-on-Pt(111).

observed for the dominant O 1*s* peak for the as-deposited La-on-Pt(111) sample (see top and middle curves of Fig. 5). The lower-binding-energy peak is stronger for increasing La coverages where the second desorption structure (near 800 K) is more intense. This shows that the low-binding-energy component near 530 eV in Fig. 5 is related to the complex in which the remaining CO (or C and O) is bound.

The La 3*d* XPS is shown in Fig. 6 for as-deposited (top curve) and annealed (bottom curve) 1-ML La on Pt(111). The shoulder at the low-binding-energy side of the main peak is the $3d^9 4f^1$ shakedown satellite. This is a final-state effect that results from filling a 4f state which is pulled down just below the Fermi level in the presence of the La 3*d* core hole. The intensity of the shakedown satellite depends on the hybridization strength between conduction electrons of *d* symmetry and the 4*f* orbital in the final state of the photoemission process, and thus provides a measure of the density of states near the Fermi level.[14,15] The increase in intensity of the satellite for the annealed sample reflects the increased hybridization between La and Pt states as a result of the formation of the surface alloy.

B. CO adsorption on the surface alloy

The observation was made that the La-Pt(111) surface alloy was relatively inert, and that it showed lower reactivity than the clean Pt(111) surface as to adsorption of oxygen and carbon monoxide. The CO desorption spectra from the La-Pt(111) and Pt(111) surfaces are shown in Figs. 7(a) and 7(b), respectively. The coverage of CO is measured in substrate units, and is in both cases referenced to the saturation value on Pt(111), which is taken to correspond to a coverage of $\theta = 0.6$ (see, e.g., Ref. 13). In comparing Figs. 7(a) and 7(b), two striking differences are noticed: First, desorption starts at a temperature of approximately 170 K on La-Pt(111), whereas on Pt(111) no desorption is observed below 300 K. The entire desorption region is shifted by more than 100° toward lower temperatures in the former case. Second, there is considerably more structure in the TPD spectra from the surface alloy. Three peaks are resolved for initial coverages above $\theta \approx 0.46$, two peaks for coverages between $\theta \approx 0.39$ and $\theta \approx 0.46$, and one peak is observed for lower initial coverages. For Pt(111) a single peak is observed for all initial coverages. Unfortunately, we did not obtain useful LEED images for the adsorption system, so correlation of desorption data with adsorbate structures was not possible. Our desorption data on La-Pt(111) are in contrast to findings on the Ce-Pt(111) surface alloy by Baddeley *et al.*[9], who observed similar CO desorption structures and temperatures for pure Pt(111) and the surface alloy.

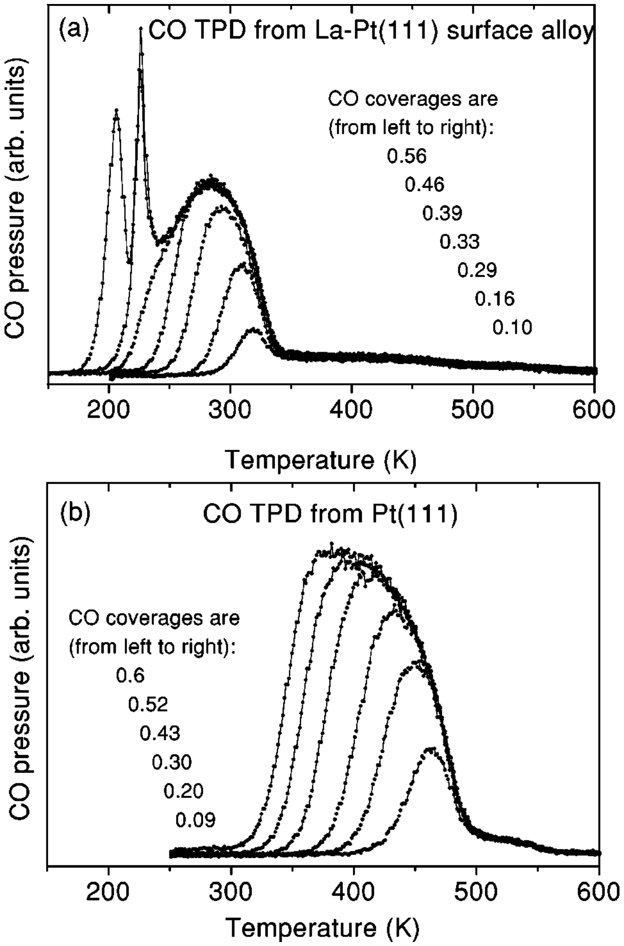

FIG. 7. (a) TPD spectra of CO from the La-Pt(111) surface alloy. The initial CO coverages range from 0.10 to 0.56 (substrate units). (b) TPD spectra of CO from Pt(111). The initial coverages range from 0.09 to 0.6 (substrate units).

The lowered desorption temperature for the surface alloy as compared to pure Pt indicates a significantly weakened CO-substrate bond, reminiscent of that seen for the (111) surface of the Cu_3Pt alloy.[16] We analyze the data in Fig. 7(a) by making Arrhenius plots of the leading edge of each desorption curve, and thus extracting the apparent desorption energy $E_d(\theta)$ and prefactor $\nu(\theta)$ corresponding to each initial coverage θ. This analysis requires E_d and ν to be constant over the fitting region. It is therefore crucial that this region is chosen so narrow that the coverage only decreases by a few percent of the initial coverage.[17] The resulting coverage dependences of E_d and ν are shown in Figs. 8(a) and 8(b), respectively. Extrapolating E_d to zero coverage, we find a CO-substrate bond energy of 0.9 ± 0.1 eV. As a test, we also made similar measurements for clean Pt(111), and found $E_d(\theta = 0) = 1.4 \pm 0.1$ eV, which is in good agreement

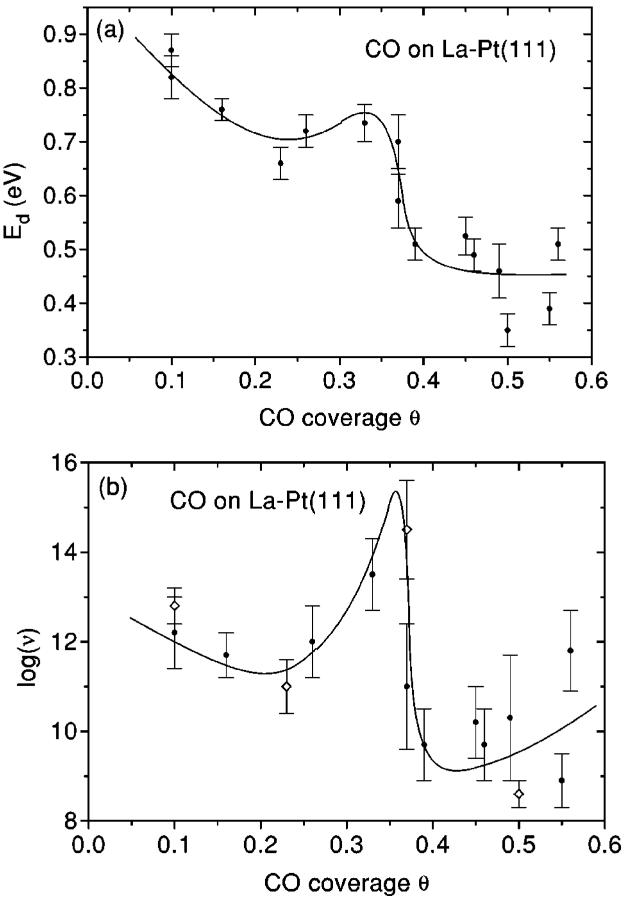

FIG. 8. (a) Desorption energies and (b) pre-exponential factors for CO desorption from the La-Pt(111) surface alloy as deduced from the data in Fig. 7(a), as described in the text. The solid lines are merely drawn as guides to the eye.

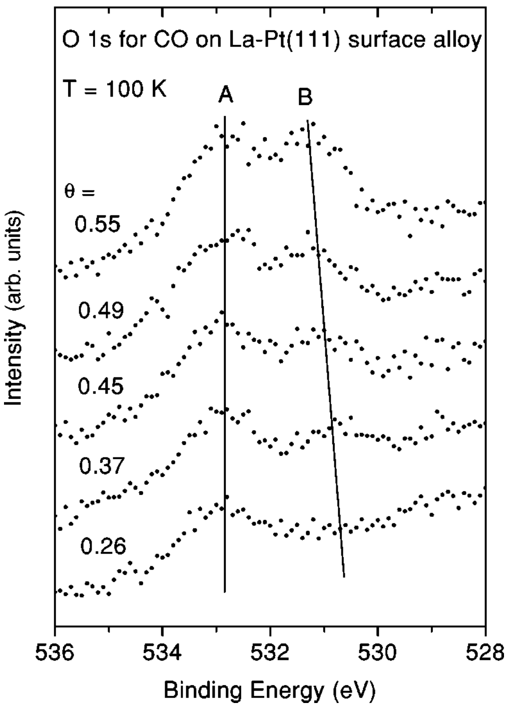

FIG. 9. Oxygen 1*s* XPS for several CO coverages (as indicated) on the La-Pt(111) surface alloy. Peaks labeled *A* and *B* correspond to different adsorption sites, possibly ‘‘on-top’’ and ‘‘bridge’’ sites, respectively.

with literature values.[12,13,18,19] A CO bond energy below 1 eV is not, to our knowledge, observed for any clean transition metal, but is expected for noble metals[20–22] and *sp* metals like, e.g., aluminum.[23] CO bonded to Pt in contact with such metals may also ‘‘feel’’ a low bond energy.[16,24,25] It is, however, more surprising that a lowered bond energy should result from alloying with a highly reactive metal such as lanthanum.

A significant change in the *d*-electron structure upon alloying is evident from the valence-band spectra in Fig. 1 as well as the shakedown intensity in Fig. 6. An increased density of states near the Fermi level (see Fig. 1) does not suggest an increased filling of the *d* band as a result of hybridization between Pt and La states, which might have been expected for a less reactive system. In a recent work on Pt(111), it was concluded that an occupied surface resonance state exists.[26] This resonance state was argued to have the signature of an *sp*-derived Schockley surface state, with a charge density that reaches far out from the surface. If such a surface resonance is removed or strongly perturbed by a surface alloying reaction, it may influence the adsorption properties to some extent,[27] but should not dramatically alter the CO adsorption due to the small charge density carried by such states. A more likely explanation of the rather large reduction in reactivity on the La-Pt(111) surface alloy may be related to the existence of strong resonant interactions of the Pt *d* band with the CO 5σ orbital that give rise to a pronounced 5σ donor contribution to the CO-Pt bond.[28] As the La-Pt(111) surface alloy is formed, the *d* band moves to lower binding energies and the Pt *d*–CO 5σ interaction is no longer resonant, and the CO-Pt bond is significantly suppressed.

A recent model by Hammer, Morikawa, and Nørskov[29] concluded that there should be an increase in the CO desorption energy as the *d*-band center shifts to a lower binding energy. Our observation of a shift in the Pt 5*d* density of states (and thus the *d*-band center) towards the Fermi level, and a decreased desorption energy for CO on the La-Pt(111) surface alloy, seems to oppose this model. However, this model should not apply if the CO adsorb on a La site and not on a Pt site. We still believe that CO adsorbs predominantly on Pt sites, since a higher reactivity than observed from the TPD measurements would be expected on La-dominated sites.

In Fig. 9 we show oxygen 1*s* core-level spectra for various CO coverages on the La-Pt(111) surface alloy. Two distinct peaks labeled *A* and *B* are observed which most likely correspond to two different adsorption geometries. These features coincide in binding energy with previously observed peaks from the CO on Pt(111) system, and which correspond to adsorption in ‘‘on-top’’ (higher binding energy) and ‘‘bridge’’ sites (lower binding energy).[30] Since the topography of the surface alloy remains undetermined, definite assignments of peaks *A* and *B* cannot be done. However, a likely assignment is that peak *A* correspond to on-top sites and peak *B* correspond to bridge sites on the La-Pt alloy.

Structure in a thermal-desorption spectrum may be caused by desorption from different sites on the surface as well as adsorbate-adsorbate interactions. The increased structure in the desorption spectra from La-Pt(111), as compared to the pure Pt(111) substrate, indicates that adsorbate-adsorbate interactions become more important when the binding to the substrate is weakened. In comparing Figs. 9 and 7(a), we notice that the peak labeled B in Fig. 9 appears at similar coverage as the second sharp feature (at higher temperature) in the CO desorption spectra. When this adsorption site starts to become occupied, the distance between adsorbates is suddenly reduced, and consequently the adsorbate interactions become more important. In addition, site-dependent CO-substrate interactions complicate the description of the desorption.

The pre-exponential factor ν shown in Fig. 8(b) has a low-coverage value of $10^{12\pm1}\ \mathrm{s}^{-1}$ which stays approximately constant until $\theta = 0.25$. It then rises by roughly two orders of magnitude up to just over $\theta = 0.35$, where it drops abruptly to $10^{10\pm1}\ \mathrm{s}^{-1}$. A slight rise followed by an abrupt fall is also seen in the same coverage region for the desorption energy E_d in Fig. 8(a). The drop in E_d is of the order of 0.3 eV. A situation where the coverage dependence of the prefactor and the desorption energy mimic each other, is frequently referred to as a compensation effect. It has been shown[17] that using too wide a fitting region when extracting E_d and ν from the Arrhenius plots may force ν to mimic the detailed behavior of E_d, resulting in an artificial compensation effect. In our case we see that ν does not show, for instance, the initial fall seen for E_d. We therefore believe that what we observe is a true compensation effect. The rise followed by an abrupt fall in E_d and ν, has also been found theoretically, in Monte Carlo simulations[31,32] and by using the transfer-matrix method.[33,34] These authors explained the abrupt fall in E_d in terms of a structural phase transition in the CO overlayer. Assuming repulsive nearest-neighbor interactions, the desorption energy of a CO molecule will fall as nearest-neighbor sites start to become occupied. This happens above a critical coverage. Our results for CO on the clean Pt(111) surface show such a drop for a coverage slightly above $\theta = 0.5$. A drop at exactly $\theta = 0.5$ for CO on Pt(111) has been seen previously.[12,18] At $\theta = 0.5$, for low temperatures, CO on Pt(111) is ordered in a $c(4\times2)$ structure containing no CO molecules adsorbed on nearest-neighbor Pt atoms. Increasing the coverage above $\theta = 0.5$, the overlayer melts and then recrystallizes in a series of dense, ordered structures containing an increasing number of nearest-neighbor CO.[35,36] Any structural phase transition in the overlayer will change the desorption energy. Thus if thermal desorption occurs below the melting temperature for a given structure, an abrupt drop in desorption energy should be observable by TPD at the corresponding critical coverage. In fact, it has been shown that the sharp changes in $E_d(\theta)$ around critical coverages are visible even above the structure's melting temperature, but that the sharpness is gradually washed out as the temperature is further increased.[33,34]

The size of a drop in $E_d(\theta)$ is decided by the strength of the interactions among the admolecules: $E_d = E_b - N_{nn}E_{nn} - N_{nnn}E_{nnn} - \dots$, where $E_b = E_d(\theta = 0)$ is the CO-substrate bond energy, N_{nn} is the number of nearest neighbors, E_{nn} is the nearest-neighbor interaction energy, and N_{nnn} and E_{nnn} are, respectively, the number and interaction energy of next-nearest neighbors. Taking as an example the CO-CO interaction potential for CO/Pt(111), the interaction energies corresponding to the shortest CO-CO distances in the $(\sqrt{3}\times\sqrt{3})R30°$ and $c(4\times2)$ structures would be in the order of 0.01 and 0.05 eV, respectively, while the interaction energy for CO adsorbed on nearest-neighbor Pt sites is in the order of 0.3 eV.[36,37] This shows that the onset of CO adsorption on nearest-neighbor sites should produce by far the largest drop in E_d. At this CO-CO distance the Pauli repulsion, which should be virtually substrate independent, dominates over the interaction via the substrate.[36] We argue that changes in CO-CO interactions by phase transitions should also result in large variations in desorption parameters for CO adsorbed on other substrates, especially if the CO-substrate interaction is weak, as in the case of CO on the La-Pt(111) surface alloy

As argued above, we believe that the large drops in $E_d(\theta)$ observed for Pt(111) and the La-Pt(111) surface alloy correspond to the onset of nearest-neighbor adsorption. Taking the most likely termination of the La-Pt(111) surface alloy to be a Kagomé net of Pt atoms,[9–11] a triangular mesh with a 2×2 structure of vacancies, it is clear that the critical coverage where nearest-neighbor sites become filled is lower than 0.5. In the case of CO on the La-Pt(111) surface alloy, the critical coverage is observed at $\theta \approx 0.35$. Incidentally, this corresponds fairly well to the filling of a $(\sqrt{3}\times\sqrt{3})R30°$ structure at $\theta = \frac{1}{3}$, but this overlayer structure is incommensurate with a Kagomé net (or the other possible termination suggested in Ref. 9). From Fig. 9 we know that no bridge sites are occupied before $\frac{1}{4}$-ML coverage. This is possible on a Kagomé net, but the overlayer must then restructure, also filling bridge sites above this coverage in order to avoid nearest-neighbor adsorption. It is also possible to construct simple overlayer structures without nearest neighbors at $\theta = \frac{1}{3}$ on a Kagomé net; however without a certain knowledge of substrate structure or any direct structural information on the overlayer, we do not wish to speculate on this.

IV. CONCLUSIONS

We have observed formation of an ordered La-Pt(111) surface alloy when a La-on-Pt overlayer system was annealed to 900 K. The surface alloy was found to be relatively inert as to adsorption of oxygen and carbon monoxide. The structure of the alloy remains undetermined. The work function of the La-Pt alloy is measured to be in the order of 1 eV smaller than that of pure Pt(111). An analysis of thermal desorption spectra of CO from Pt and La-Pt show that the desorption energy is considerably lower in the case of the surface alloy. The dependence of desorption parameters with CO coverage shows that the desorption depends strongly on lateral interactions in the adsorbed layer. Further experiments to determine the structure of the La-Pt(111) surface alloy are required to gain a comprehensive understanding of this system.

ACKNOWLEDGMENT

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