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Adsorption Sites and Ligand Effect for CO on an Alloy Surface: A Direct View

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CO adsorption on a PtCo(111) surface was studied by scanning tunneling microscopy. Comparison of images with chemical contrast of Pt and Co and images showing the CO molecules indicates that CO resides exclusively on top of Pt sites and never on Co. CO bonding is highly sensitive to the chemical environment. The probability to find CO on a Pt atom increases drastically with the number of its Co nearest neighbors. *Ab initio* calculations show that this ligand effect is due to different positions of the center of the Pt *d* band.

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It is a well known fact and the basis of many of today's technological applications that the catalytic properties of alloys are often superior to those of pure metals. To explain this phenomenon, two effects have been suggested, ligand effects and ensemble effects [1]. The term *ensemble effect* refers to the fact that adsorption and bonding of a molecule requires a specific number of unoccupied adjacent sites of a particular atom type, i.e., a certain configuration of the atoms it directly binds to. The *ligand effect* represents the modification of the adsorptive properties of a given site via electronic effects by the neighbors (ligands) of an atom that a given adsorbate binds to. Whereas the ensemble effect refers to the availability of adsorption sites compatible with the adsorption geometry and shape of the molecule, the ligand effect is more related to the notion of chemical bonding. Although it is well known that ligands play an important role in the chemistry of molecules, on alloy surfaces up to now only rather indirect evidence of a ligand effect was given, e.g., in the studies of CO adsorption on AgTi₂ [2] and Cu₃Pt(111) [3] by temperature programmed desorption (TPD) and ultraviolet photoemission spectroscopy. Demonstrating the existence of a ligand effect requires one to clearly identify not only the adsorption site but also the chemical environment of this site.

The possibility of obtaining scanning tunneling microscopy (STM) images with chemical contrast on alloy surfaces opens the possibility to determine the alloy constituent on which the molecules adsorb. Chemical contrast has been exploited previously, but correlations between STM images from alloys and the actual adsorption sites were derived indirectly, for instance, by high resolution electron energy loss spectroscopy [4] or TPD [5,6]. A more direct way to determine adsorption sites was demonstrated on the AgPd(111) surface, where oxygen adatoms were found to be stable only when bound to Pd atoms [7]. To our knowledge, a direct determination of adsorption sites on an alloy by STM has never been reported yet.

In this Letter we report on an STM study of CO adsorption on a PtCo(111) surface. Taking images with chemical contrast of the alloy constituents and images of the same surface area showing the CO molecules allows us to determine the adsorption sites of CO and to directly demonstrate the ligand effect for CO adsorption on this surface.

All work was done in a two-chamber ultrahigh vacuum system (base pressure below 10^{-10} mbar). A PtCo alloy of several monolayers thickness was prepared by deposition of 4 monolayers (ML) Co films on a clean Pt(111) surface and subsequent annealing at 425 °C for 5 min. STM constant current topographs were obtained at room temperature with a customized Omicron micro-STM with negative sample bias, using electrochemically etched W tips.

As shown in previous work, our surface preparation results in an almost 10 ML thick alloy with a composition close to Pt₅₀Co₅₀ [8]. In the surface layer, STM shows two distinct species, $\approx 20\%$ dark and 80% bright atoms (Figs. 1a and 2a), which can be attributed to Co and Pt, respectively [9]. This is in reasonable agreement with the interpolation of LEED results [10,11] for Pt_xCo_{1-x}(111) ($x = 25, 80\%$) leading us to expect Pt concentrations $c_1 = 85\%$ and $c_2 = 14\%$ in layers 1 and 2, respectively. The total energies found in our *ab initio* calculations (described below) also confirm a strong segregation of Pt within the alloy layer. As the alloy film assumes its own lattice constant [8], misfit dislocations between the alloy and substrate occur and lead to long-range height variations in the STM images. Additional short-range variations are probably due to local variations of the Pt concentration in the uppermost monolayers. All these height variations are helpful for finding the correct registry of subsequent STM images.

The clean alloy (Fig. 1a) was exposed to CO. CO is visible at comparatively high tunneling resistance R_t (≈ -0.3 V/0.5 nA). The CO molecules appear as protrusions of 0.3–0.5 Å apparent height. The number of CO molecules visible in the STM images increases with CO

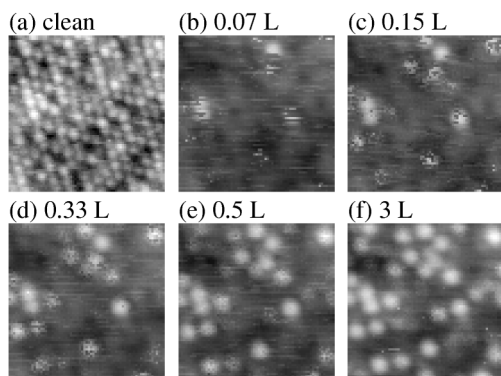


FIG. 1. Subsequent STM images of the same area of a PtCo surface showing (a) the clean surface ($V = -0.5$ mV; $I = 0.5$ nA) and (b)–(f) various stages of CO adsorption ($V = -0.3$ V; $I = 0.5$ nA). As only slight high-pass filtering has been applied to the images, some of the height modulations aiding in correct alignment of the images remain visible. Stronger high-pass filtering would make the chemical contrast of frame (a) more obvious.

dose until saturation coverage is reached at approximately 1.5 L ($1 \text{ L} = 10^{-6}$ Torr s); no changes were observed at higher CO doses up to 18 L (Figs. 1b–1f). Some CO molecules have a striped or mottled appearance, which we attribute to the occasional occupation of an adsorption site, with residence times comparable to the time between measuring successive lines or pixels (80 ms or 0.1 ms, respectively). Especially at higher CO coverages, we also observe some sites which appear like CO with lower corrugation; these are probably sites part-time occupied on a shorter time scale. In Fig. 1 one can also observe that sites which are part-time occupied at low CO dose become fully occupied later. The behavior observed means that CO mobility is large enough to guarantee that the sites are occupied in the sequence of increasing adsorption energy, those with strongest CO bonding first [12]. The CO coverage of the surface estimated from the STM images at low CO dose (<0.1 L) corresponds to

approximately 80% of the gas dose applied. This implies that most or all CO molecules are visible by STM and the initial sticking coefficient is between ≈ 0.8 and 1. The saturation coverage visible by STM is approximately 0.1 ML, in agreement to the coverage determined by x-ray photoemission spectroscopy (0.07 ± 0.05 ML), but far below the room-temperature saturation coverage of Pt(111), which is 0.5 ML. At saturation, on the alloy surface some areas about 5 atomic spacings in diameter still appear uncovered (Fig. 2b), but we cannot exclude a low concentration of rapidly diffusing CO there.

Direct determination of the adsorption sites could be achieved by (i) imaging an area with chemical contrast and subsequent imaging of the same region during CO adsorption or (ii) varying the imaging conditions after CO adsorption. Atomic resolution and chemical contrast of the substrate atoms is observed at low R_t (-0.5 mV/ 0.5 – 3 nA), without and with adsorbed CO. We believe that the tip pushes the CO molecules aside when scanning at the short tip-sample distances associated with these low R_t values. Images taken at high resistance, before and after scanning at low resistance, are identical, in agreement with a fast diffusion of CO molecules which reoccupy exactly the previous sites.

Comparing an image with chemical contrast and one showing CO, both for the same surface area (Fig. 2c), immediately leads to three observations: (i) the CO molecules reside on top of the metal atoms, (ii) the atoms below CO are exclusively the bright species in the atomically resolved images, i.e., Pt, and (iii) all Pt atoms with CO on top have at least one neighboring cobalt atom in the surface [13]. Focusing on point (iii), i.e., the environment of the Pt sites occupied by CO, we note that the probability to find a CO molecule on a given Pt site increases strongly with the number of its Co neighbors in the surface (Fig. 3). This tendency to occupy Pt sites with more Co neighbors is slightly stronger at low CO dose (low CO coverage) than at saturation coverage. We also found that the CO molecules

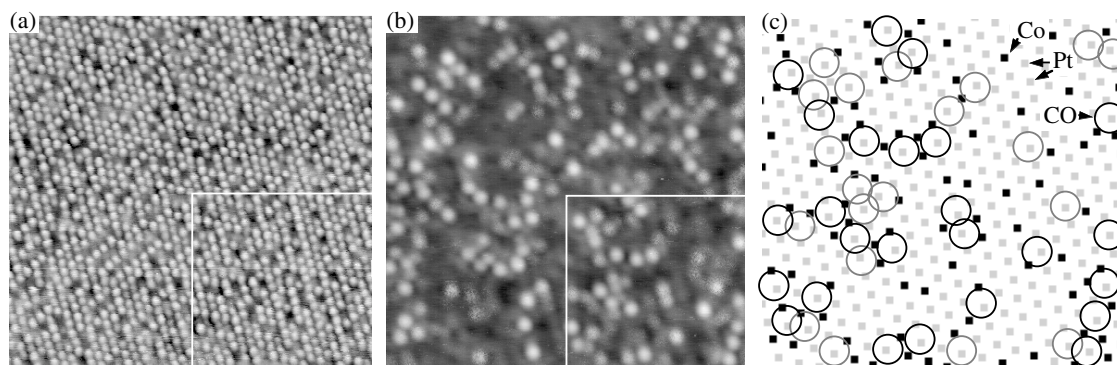


FIG. 2. STM images of a PtCo surface showing (a) atomic resolution and chemical contrast ($V = -0.5$ mV; $I = 1.6$ nA) and (b) the adsorbed CO molecules ($V = -0.31$ V; $I = 0.68$ nA; CO dose 18 L, i.e., saturation) in the same area. In (c), the positions of the metal atoms in the lower right quadrant of (a) are marked as small squares (Co: black; Pt: grey), those of the CO molecules (b) as circles (black for CO appearing with full or almost full brightness, i.e., highest occupation probability; grey for CO appearing weaker or mottled). Strong high-pass filtering has been used to suppress long-range height modulations, making the atomic corrugation and chemical contrast of frame (a) more apparent.

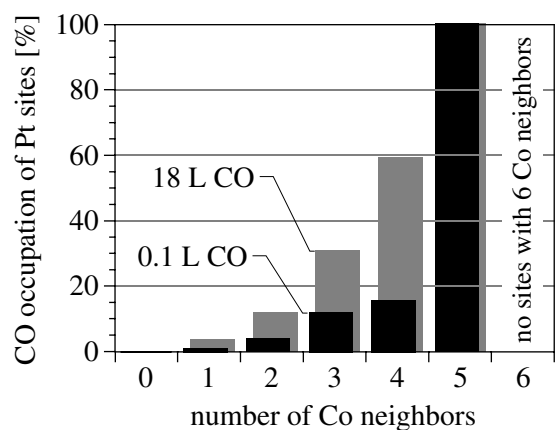


FIG. 3. Probability to find a CO molecule adsorbed on a Pt atom as a function of the number of its cobalt neighbors in the surface, for a low gas dose (0.1 L) and saturation (18 L).

on Pt atoms with only one or two Co neighbors are more likely to appear weak or mottled due to a low occupation probability of these sites as compared to those at sites with more Co neighbors. We further note (iv) that the Pt atoms appearing highest (brightest) are occupied first, i.e., bind CO very strongly, even if they have only one or two Co neighbors (Fig. 1).

Point (i), the CO molecules being on top of the metal atoms, is in agreement with previous experimental studies of CO on the close-packed surfaces of Co [14] and Pt [15] (on Pt for low coverage only). Also (ii) the preference of CO for adsorption on Pt agrees with previous experiments, as the adsorption energies previously determined for low doses of CO on Pt(111) [16] are somewhat higher than those on the close-packed Co surface [17]. The difference in adsorption energies E_{ad} obviously does not change its sign in the alloy. Stronger CO adsorption on Pt than on Co may seem counterintuitive as it does not follow the trend of decreasing reactivity with increasing filling of the d shell. It is known, however, that magnetism of the 3D elements can weaken adsorption significantly and thus counteract this trend [18].

What remains to be explained is (iii) the increase of probability (and, hence, strength) of CO bonding on Pt with an increasing number of Co neighbors. The influence of the neighbors on the adsorption properties of a Pt atom is a clear case of a *ligand effect*. The differences between the adsorption energies E_{ad} on the different Pt atoms cannot be determined from Fig. 3 alone, as E_{ad} will not only depend on the in-plane nearest neighbors, but also on the neighbors of a Pt atom in the second layer and possibly on next-nearest neighbors. Based on the STM images, we estimate that the probability to find a rapidly diffusing CO molecule on Pt atoms differs by more than a factor of 10 between these sites where CO is visible and where it is not, indicating differences of E_{ad} larger than 60 meV. The actual differences of E_{ad} must be higher, however, as we sometimes find two CO molecules adsorbed on two neighboring Pt atoms, in spite of the strong CO-CO repulsion

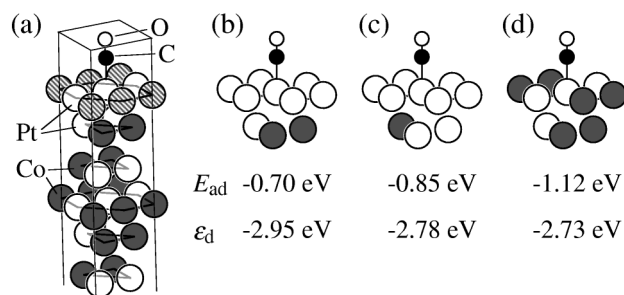


FIG. 4. (a) Simulation cell used and (b)–(d) CO adsorption energies and the d band center ϵ_d for different configurations. The hatched atoms in panel (a) are either Pt or Co.

(≈ 0.24 eV according to Ref. [19]). In such a case, it seems that the CO molecules are slightly shifted or tilted from one another (see, e.g., pair of CO near the center of Fig. 2c).

To rationalize the observed ligand effect, we performed first principles density functional theory calculations using the Vienna *ab initio* simulation package [20] with the projector augmented wave [21] method as implemented by Kresse and Joubert [22]. The surface alloy was modeled using a hexagonal six layer thick slab containing 24 atoms (compare Fig. 4a) with an in-plane nearest-neighbor distance of $d = 2.70$ Å. To model the variation of the local Pt concentration in the first layer, the number of Pt atoms in the top layer was varied between 2 and 4, whereas the concentration in the other three layers was kept to 50% Pt and 50% Co. The slab with two Pt and two Co atoms in the top layer describes the (111) surface of a cubic $L1_0$ ordered PtCo phase with a lattice constant of 3.82 Å, which is the theoretical equilibrium lattice constant of PtCo in this structure. In all calculations, we allowed full relaxation of the three topmost layers. To confirm that segregation of Pt atoms to the surface is favorable, we compare the surface energy of both models. Assuming that the chemical potentials of Pt and Co are given by $\mu(\text{Pt}) = E_{fcc}(\text{Pt})$ and $\mu(\text{Co}) = 2E_{L1_0}(\text{PtCo}) - E_{fcc}(\text{Pt})$, comparison of the two configurations studied yields a reduction of surface energy by 550 meV per segregated Pt atom.

For CO we restrict the present study to on-top adsorption on different Pt sites, since current density functionals fail to predict the correct adsorption site for CO on Pt(111) [23,24]. In agreement with experiment, the calculations predict a higher CO adsorption energy E_{ad} [12] on Pt atoms surrounded by Co in the first layer (Fig. 4d), a result which is independent of the generalized gradient approximation potential used (PW91 [25] or RPBE [26]). Since the RPBE CO adsorption energies are more realistic, only they are reported here [26]. The calculations also confirm that the environment in the second layer affects the adsorption energy, though in a manner opposite to the first layer (more Co in the second layer weakens the Pt-CO bond). To elucidate the changes in the adsorption energy E_{ad} , we have investigated the position of the d band center [27] for each adsorption site. Indeed, we find a strong correlation between this value and the adsorption energies, as

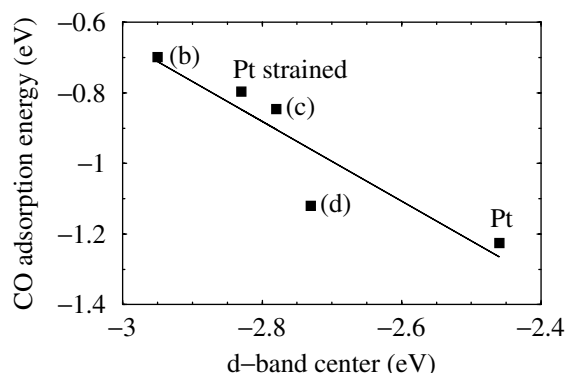


FIG. 5. CO adsorption energy versus d band center (with respect to the Fermi energy) for surface Pt in different configurations, including (b)–(d) of Fig. 4.

shown in Fig. 5. For comparison, we also include the CO adsorption energy on a clean unstrained Pt(111) surface ($d = 2.83$ Å), and on a Pt substrate constrained in-plane to the lattice constant of the PtCo alloy ($d = 2.70$ Å). Although the unstrained Pt substrate yields the largest adsorption energy, a reduction of the in-plane nearest-neighbor distance to $d = 2.70$ Å reduces the adsorption energy to similar values as for the models shown in Figs. 4(b) and 4(c). Hence, the short in-plane Pt-Pt nearest-neighbor distance is responsible for the low CO adsorption energy on Pt sites surrounded by Pt atoms only. Co nearest neighbors in the surface plane release some of the surface strain, shift the d band center towards the Fermi energy and, hence, increase the CO adsorption energy. In the subsurface layer the effect of Pt and Co is reversed (Figs. 4b and 4c) since surface Pt atoms with two Pt neighbors in the subsurface layer relax outwards such that the $\text{Pt}_{\text{surf}}\text{-Pt}_{\text{subsurf}}$ distance becomes even larger (2.87 Å) than in fcc Pt (2.83 Å). This shifts the center of the d band of surface Pt atoms towards the Fermi level and enhances the reactivity. It also nicely fits our experimental observation (iv) of particularly strong CO bonding on the Pt sites appearing highest in the STM image of the clean alloy. Further results show that the binding of CO on Co sites in the alloy is ≈ 0.18 eV weaker than on pure cobalt. Our findings also explain the low saturation coverage of CO on the alloy at room temperature as compared to the pure metals. In this respect our results for the PtCo alloy are similar to $\text{Pt}_{50}\text{Ni}_{50}(111)$, where weak CO bonding was also attributed to compression of Pt in the first layer [28].

We conclude that our results illustrate the power of STM with chemical contrast in determining the local circumstances of bonding at surfaces, in our case illustrating the influence of Co ligands on the adsorption strength of Pt. As *ab initio* calculations show, our results are in line with the model of modification of CO bonding by a shift of the Pt d band. We also note that the ligand effect observed would lead to very misleading results in an attempt to determine the surface composition of the alloy by CO titration, in spite of the presence of CO in on-top sites and on one species (Pt) only.

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