Contribution from the Research Laboratories,
Eastman Kodak Company, Rochester, New York 14650

Study of Chlorine Chemisorption on Platinum Clusters

R. C. BAETZOLD

Received July 6, 1981

Photoemission spectra obtained with 21.2-eV He I radiation are reported for clean Pt clusters and those with chemisorbed Cl_2. The peak of the Pt d emission shifts toward the Fermi energy with increasing cluster size. The difference spectra due to Cl_2 show effects dependent upon Pt cluster size up to 25 atoms. Finally, the difference spectra due to Cl_2 chemisorbed to Pt are compared with those of other metals including Ni, Pd, Ag, and Cu, all of which are different.

Introduction

Chemisorption on metal clusters is expected to prove to be a valuable tool for understanding the interrelations of chemical and electronic properties. Since these relationships must ultimately determine catalytic properties of the metal clusters, we need such information to develop a detailed theory of catalysis. Such a theory requires a linkage of electronic properties determined from theory or experiment with the chemical properties of the cluster.

Our prior studies have focused on halogen chemisorption on Cu and Ag clusters.[1] We have shown that the electron-donating ability of the cluster increases with increasing size, in accord with molecular orbital calculations of the ionization potential.[2] In addition, the trends in the strength of interaction of adsorbate with metal cluster, as determined by changes in adsorbate-induced energy levels, were computed correctly within the framework of molecular orbital considerations, increasing our confidence in these computational methods.

The present work extends our prior studies to Pt clusters. This system is interesting because of the long-standing catalytic significance of Pt in many reactions. There is a high density of states at the Fermi energy (E_F) which distinguishes this metal from Ag and Cu. In these studies we wish to determine the extent to which results found for the group 1B metals apply. We will examine Cl_2 adsorbate on these clusters. Cl is expected to be electron withdrawing.

Grunze[3] studied the chemisorption of CO on Pd clusters with the aid of UPS (ultraviolet photoemission spectroscopy). He found that the adsorbate-induced energy levels shift closer to the Fermi energy with increasing Pd cluster size. In addition, an attenuation of d-band emission of Pd was observed. This effect, in conjunction with the greater density of d states near E_F in larger clusters, was interpreted to mean that the upper d levels in Pd stabilize the ligand–metal bond strength. Since these levels are predominantly metal–metal antibonding, their depopulation by the ligand would be expected to stabilize the system. Grunze attempted to interpret his experiments based upon a positive surface charge on the metal. He argued that the 5σ orbital of CO donates electrons to Pd more easily, owing to the positive charge on the cluster.

The interaction of adsorbates with metal clusters has been profitably studied with other techniques such as infrared spectroscopy. Moskovits[4] has reviewed much of this work, which indicates changing patterns of reactivity with size. For example, N_2 combines with Fe_2 and Fe_3, but not with Fe or large clusters, to form adsorbed dinitrogen species at low temperature in an argon matrix.[5] As another example, the IR vibrational frequencies of CO adsorbed to Cu_N or Pd_N show widely varying size dependence. For Cu_4 the frequency is the same as that for CO chemisorbed to bulk Cu, but a large size-dependent effect is reported for Pd clusters. Thus, it is interesting to probe the possibility of considerably different size-dependent effects for groups 8 and 1B metals as we have in this work. Of course, photographic effects of Pd and Ag as a function of cluster size have been conclusively demonstrated[6,7] in both systems.

Bare clusters are not a central part of our study, although they must be characterized here for the requisite comparisons. XPS and UPS have been used to characterize the core shifts and valence-band changes which accompany changes in the size of Cu, Ag, Pd, and Pt clusters.[8-10] These studies have consistently noted significant changes in these properties up to a cluster size of 150 atoms.

Experimental Section

The metal clusters were prepared by evaporation onto amorphous carbon films that had been prepared by evaporation to a thickness of 500 Å on mica in another vacuum system. These carbon films showed only oxygen impurity, as detected by Auger electron spectroscopy (AES). This impurity was removed by Xe ion sputtering, and the films remained clean for several days within the ultrahigh-vacuum chamber. Base pressures of 10^{-9} torr were attained before evaporation of the high-purity Pt wires attached to a resistively heated W wire. The rate of metal deposition was typically 0.5 Å/s. The system pressure rose to 10^{-8} torr during evaporation. A quartz-crystal monitor was used to detect the onset of and control evaporation. The amount of metal deposited on C was measured by using AES in which the Pt/C signal ratio was calibrated to neutron activation analysis data. We estimate the accuracy of this calibration to be >10%. The Pt (64 eV) to C (271 eV) signal ratio was proportional to coverage up to 1.1×10^{15} atoms/cm^2 with a slope of 8.8×10^{-16} cm^2/atom. The conditions of the Auger spectroscopy analysis were 2-kV primary beam energy, 2-eV modulation voltage, and 10-μA current with analysis at normal incidence.

Photoemission measurements were made after the samples were prepared. The 21.2-eV photons from the He discharge lamp strike the sample 72° off-normal with the cylindrical analyzer axis and sample normal aligned. Several scans were signal averaged for up to 30 min to reduce noise-to-signal ratios. These spectra were then subtracted to give the difference spectra shown in Figures 1 and 2. These spectra were run with an instrumental resolution of 0.4 eV. After studies of the clean Pt clusters were completed, high-purity Cl_2 gas was admitted from a cylinder through a leak valve to an exposure level of 50 L (langmuirs; 1 langmuir unit = 10^{-6} torr s). During this gaseous exposure all electron-gas filaments were turned off with the ion pump valved off from the sample chamber. All experiments were performed at room temperature, where Cl_2 did not stick to the carbon support.

The nucleation characteristics of Pt evaporated onto amorphous C have been determined by Hamilton and co-workers.[11] These studies

---

(1) Baetzold, R. C.; Gerenser, L. J. *Chem. Phys. Lett.* **1980**, *73*, 67. Baetzold, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6116.

(2) Baetzold, R. C. *J. Chem. Phys.* **1971**, *55*, 4363.

(3) Grunze, M. *Chem. Phys. Lett.* **1978**, *58*, 409.

(4) Moskovits, M. *Acc. Chem. Res.* **1979**, *12*, 229.

(5) Barrett, P. H.; Montano, P. A. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 378.

(6) Hamilton, J. F.; Logel, P. C. *J. Catal.* **1973**, *29*, 253.

(7) Hamilton, J. F.; Logel, P. C. *Photogr. Sci. Eng.* **1974**, *18*, 507.

(8) Mason, M. G.; Gerenser, L. J.; Lee, S.-T. *Phys. Rev. Lett.* **1977**, *39*, 288.

(9) Unwin, R.; Bradshaw, A. M. *Chem. Phys. Lett.* **1978**, *58*, 58.

(10) Egelhoff, W. F. Jr.; Tibbetts, G. G. *Phys. Rev. B* **1979**, *19*, 5028.

0020-1669/82/1321-2189$01.25/0

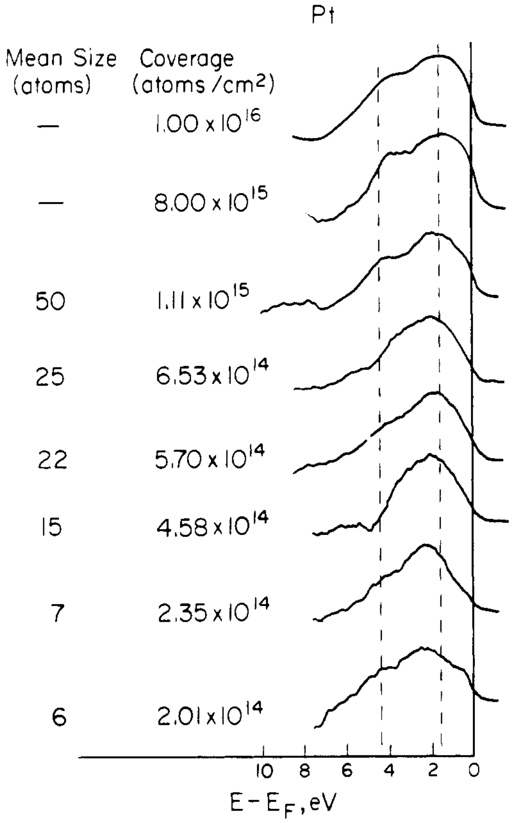

Figure 1. Plot of He I UPS difference spectrum of Pt evaporated onto carbon for various coverages which correspond to a particular mean cluster size. The binding energy (E) is measured relative to the Fermi energy $E_F = 0$.

involved direct observation of the large evaporated particles by electron microscopy. The numbers of invisible smaller particles were counted by a zinc amplification method. By these measurements a detailed size-frequency distribution of the metal particles as a function of coverage was developed. The electron micrographs showed the particles were flattened hemispheres. This shape enables one to assign a number of atoms to a particular cluster radius.

Results

A. Clean Clusters. Figure 1 shows the UPS difference spectra of Pt deposited on carbon at different evaporated coverages. At the heavy coverage the spectra show two basic peaks, but this is less well resolved for smaller sizes. A mean cluster size associated with each coverage in this and the following figures was determined from the nucleation experiment data of Hamilton and co-workers.[11] The changes in spectral shape shown in Figure 1 are similar to those reported in the XPS studies of Mason et al.[8] The d threshold at E_F sharpens, and the dominant peak in the d emission shifts 0.9 eV toward E_F in these examples. This shift corresponds to a change in mean cluster size from six to several hundred atoms. Mean sizes at heavy coverage are difficult to assign from electron microscopic work because particles overlap.[11] At the highest coverage, we measured for the d band a full-width at half-maximum (fwhm) of 4.6 eV for Pt.

B. Chemisorption of Cl on Clusters. The chemisorption of Cl_2 on the Pt clusters is characterized by an increased emission near the bottom of the d states. There is one peak on the small clusters at 5.0 eV (Figure 2). As the cluster size increases the adsorbate-induced emission broadens considerably, with a dominant peak appearing near 5.5. This increased emission extends well into the d region (compare Figure 1). A small attenuation in the d emission is apparent at the Fermi energy. The complex changes which occur in the adsorbate-induced spectra shown in Figure 2 preclude the assignment of a simple mechanism for the size-dependent effects.

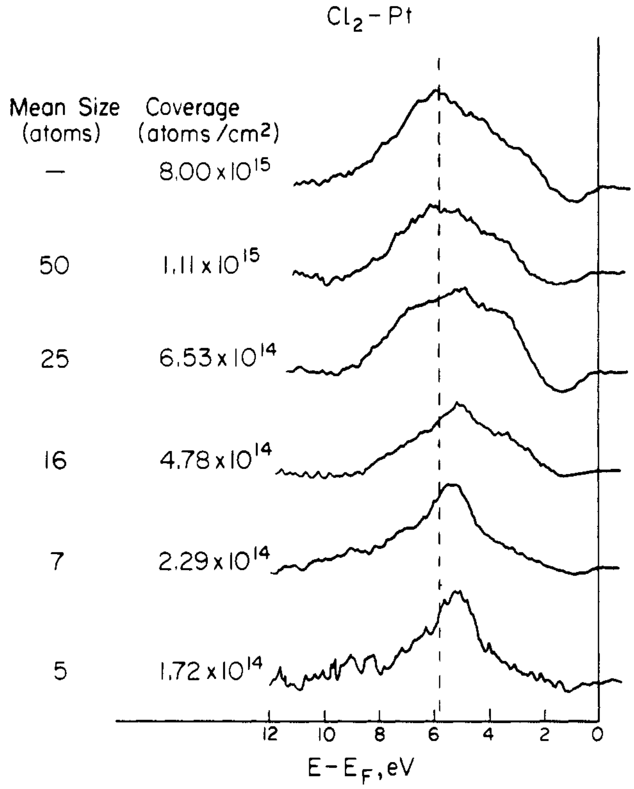

Figure 2. He I difference spectrum of Cl_2 chemisorbed to Pt clusters at indicated coverages and mean size.

Discussion

The broadening of the d emission with increasing cluster size (Figure 1) has been reported in XPS studies on Pt and Pd[8,10] as well as in UPS studies on Pt.[9] It was also observed in earlier UPS work that the Pd d peak position shifts toward the Fermi energy as cluster size increases. The effect is interpreted as a broadening of cluster DOS and has been understood in terms of covalent orbital mixing effects. Undoubtedly, the interactions of metal orbitals with carbon orbitals of the support lead to a broadening, which has its predominant effect for small clusters. Also, final-state effects are an additional broadening mechanism which would be more dominant for small clusters.

The shift of the d peak toward E_F may be due to extraatomic relaxation effects or initial-state effects. Relaxation would be increased by the presence of additional metal atoms in the cluster and lead to the type of shift observed. Alternatively, a difference in electrochemical potential between the carbon support and a small cluster could lead to a small positive potential on the cluster, which would cause cluster levels to shift to greater binding energy. As cluster size increases, this partial positive potential would decrease, giving levels closer to E_F. At present, these two effects cannot be separated.

Let us consider the changes in UPS spectra as arising from initial-state effects. A broadening of the adsorbate-induced difference spectra due to Cl_2 chemisorbed on Pt takes place up to the coverage 6.53×10^{14} atoms/cm^2, which corresponds to a 25-atom cluster. The broadening is consistent with an increase in mixing of halogen p orbitals and metal d orbitals throughout the d-band region. Apparently the interaction between Pt d orbitals and halogen p orbitals is strongest near the bottom of the d band since only minor attenuation occurs near the top. The orbitals near the bottom are primarily

---

[11] Hamilton, J. F.; Logel, P. C. *Thin Solid Films* **1973**, *16*, 41; **1974**, *23*, 89. Hamilton, J. F.; Preuss, D. R.; Apai, G. R. *Surf. Sci.* **1981**, *106*, 146.

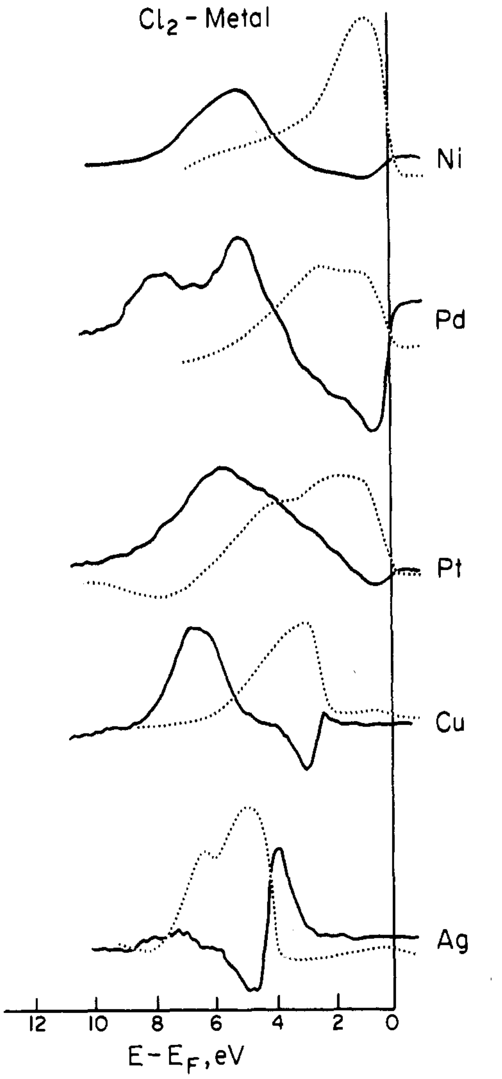

Figure 3. He I difference spectra for heavy coverages of metals bare (- - -) and with Cl_2 chemisorbed (—).

metal–metal bonding, and their mixing with p orbitals of Cl leads to the electron donation to Cl.

The observation that a cluster of 25 Pt atoms is needed to yield a chlorine adsorbate UPS spectrum similar to that on thick films gives information on the range of the chemisorptive interaction. Clearly this interaction involves many metal atoms since a large cluster is required to give a "bulklike" spectrum. Yet it should be remembered that the cluster is attached to a carbon support which can provide a reservoir of electrons for possible donation to Cl. A free Pt cluster may require larger size to provide the same donating effect, particularly if the adsorbate is strongly electron withdrawing.

The broadened Cl adsorbate spectrum on larger particles may be assigned to p–d orbital mixing, leading to σ- and π-type bonding between Cl and metal. This is because the surface (here the surface normal is in the z direction) will split the degenerate chlorine p orbitals into p_z and p_x, p_y sets. The σ bonding is through p_z and would be expected at higher binding energy than the π bonding due to p_x and p_y adsorbate orbitals. These modes of bonding are certainly present on all surfaces, and it is only a question of the strength of interaction which leads to the actual extent of broadening. For the small clusters of Pt the adsorbate-induced peak is narrower. This is consistent with a weaker interaction on the small clusters, where the σ and π components are not separated enough to be resolved.

We have compared the difference spectra for Cl_2 chemisorption on thick Pt films with the spectra determined for other metals. Figure 3 shows the difference spectra due to a thick metal deposit on carbon (i.e., $>1 \times 10^{16}$ atoms/cm^2) and the difference spectra resulting from chemisorbing Cl_2 at saturation coverage. The adsorbate spectrum is broadest on Pt, but this differs significantly from the spectra on Pd and Ni. On Pd there is more attenuation near E_F than for Pt, whereas on Ni the attenuation is nearly constant across the d band. If this attenuation corresponds to a depopulation of orbitals, we would expect stronger Pd–Cl than Pt–Cl bonds. This is because the molecular orbitals near E_F are antibonding and their depopulation should lead to greater Cl–metal bond strength. This deduction is in accord with measurements[12] of the activation energy for Cl_2 desorption from Pd (60.5 kcal/mol), which is greater than the value for Pt (47.5 kcal/mol). Copper has its dominant metal–halogen bonding peak below the d band, in contrast to silver where the predominant adsorbate peak lies above the d band. On both Cu and Ag we observe significant attenuation in the d region of the spectrum.

Conclusions

1. The difference spectrum of Cl chemisorbed to Pt clusters depends upon the Pt cluster size. It becomes bulklike at 25 atoms, indicating a significant range for this chemisorptive interaction.
2. The intensity of d emission at the Fermi energy is considerably reduced for small Pt clusters compared to the bulk. The width of the d emission is also reduced for small clusters.

Acknowledgment. I am grateful to Don Preuss for the carbon support films used in this work.

Registry No. Pt, 7440-06-4; Cl_2, 7782-50-5; Pd, 7440-05-3; Ni, 7440-02-0; Ag, 7440-22-4; Cu, 7440-50-8.

---

[12] Erley, W. *Surf. Sci.* **1980**, *94*, 281.