An Inelastic Electron-Tunneling Spectroscopic Study of the Interaction of $[RhCl(CO)_2]_2$ with an Aluminum Oxide Surface

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Abstract: The interaction of the chlorodicarbonylrhodium dimer, $[RhCl(CO)_2]_2$, with aluminum oxide as a function of surface temperature was studied by means of inelastic electron-tunneling spectroscopy. The complex was found to adsorb dissociatively via an interaction with surface hydroxyl groups, losing chlorine through HCl liberation and bonding to the surface via Rh–O bonds. At room temperature, one monolayer, or less, of the dimer adsorbs strongly. Below room temperature, multilayers of $[RhCl(CO_2)]_2$ condense physically. Evaporation of the Pb counterelectrode on this physically adsorbed complex promotes further chemisorption. Thus, the Pb plays an active role in this interaction. Higher dispersion of the rhodium was attained than when rhodium is evaporated onto the surface in its zerovalent state.

Introduction

Although the importance of supported metal catalysts for industrial applications is unquestionable, a full understanding of how these catalysts function on a molecular level is still lacking. A rather new technique that has been applied recently to this problem is inelastic electron-tunneling spectroscopy (IETS).[1-6] Like infrared (IR) spectroscopy, IETS provides vibrational information concerning the support-supported metal-adsorbate system. However, IETS has several advantages over IR spectroscopy. (1) The IETS sample is planar and of small surface area (approximately 1 mm^2), so uniformity over the surface is more probable. (2) Vibrational frequencies as low as 240 cm^{-1} can be probed without serious interference from the support, allowing low-frequency vibrations such as metal–ligand stretching and bending modes to be observed. (3) The entire sample fabrication may be carried out within a vacuum system, so the history of the surface may be controlled rather carefully.

A technique for making supported metal catalysts which has gained much attention recently is the anchoring of transition-metal carbonyl complexes or organometallic complexes to solid supports.[7-15] These supported complexes may then either be calcined to yield bare metallic catalysts (e.g., ref 10–12) or left with some fraction of the original number of their ligands attached (e.g., ref 14). This procedure has certain advantages over the more standard method of forming the metal catalyst by reduction of a metal salt which has been impregnated into the support material. In many cases, higher dispersion is attained,[10,11] as well as increases in reactivity[13] and modifications in the selectivity of the catalyst.[12,14] Recently, IETS investigations in this area have been carried out in our laboratory with the study of the polymerization catalyst $Zr(BH_4)_4$ on Al_2O_3.[6] However, there has been only one previously successful tunneling investigation of a transition-metal carbonyl complex adsorbed onto an oxide support.[16]

In this paper, we present an IETS investigation of the interaction of the chlorodicarbonylrhodium dimer with alumina. This compound was selected for a number of reasons. First, supported rhodium metal has been studied extensively both by IR[17-21] as well as by IET spectroscopy,[1-4] so a direct comparison with our findings could profitably be made. Second, this complex sublimes readily in vacuum without decomposing and has been observed to adsorb from solution on γ-alumina.[21] Finally, it is more likely to form a very highly dispersed catalyst than larger rhodium-carbonyl complexes which have three or more metal atoms bound together within the molecular complex. This is of interest since significant increases in the activity of some reactions have been related to high dispersion of the metal catalyst.[13,22]

The next section of this paper will describe the experimental procedures followed in the preparation of the tunnel junctions. The third section will present the results obtained and discuss their interpretation. Our conclusions are summarized in the final section.

Experimental Procedures

The fabrication of the tunnel junctions was carried out in an oil diffusion pumped vacuum system with a base pressure below 5×10^{-7} torr. Three samples, each containing three independent tunnel junctions, were made simultaneously. The sample substrates (cleaned glass microscope slides) were mounted on individual copper sample holders. To each of the three sample holders was silver soldered an independent cooling line through which liquid nitrogen could be flowed. With this arrangement, the samples could be cooled to below 170 K under vacuum. By varying the flow rate of the liquid nitrogen through these lines, we could cool each of the three samples individually to a different temperature. These temperatures were monitored by means of iron–constantan thermocouples which were indium soldered to the sample substrates.

The rhodium chlorodicarbonyl dimer ($[RhCl(CO)_2]_2$, 95% purity) was obtained from Alfa Division of Ventron. This complex is a red crystalline solid at room temperature and sublimes readily at 353–363 K. This complex is described as air sensitive and will decompose above 398 K.[23]

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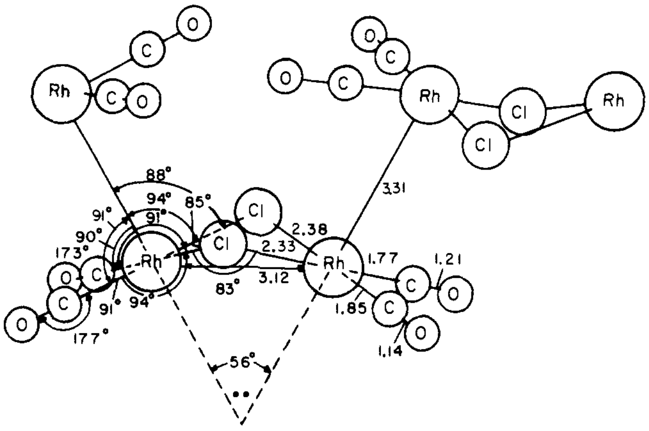

Figure 1. The structure of the $[RhCl(CO)_2]_2$ dimer as determined from X-ray crystallography.[24]

The structure of the dimer, as determined by Dahl et al.[24] from X-ray diffraction, is shown in Figure 1.

For each experiment, approximately 25 mg of $[RhCl(CO)_2]_2$ was placed in a glass ampule mounted within the vacuum system. This ampule was sealed by means of a ground-glass ball-and-socket joint. This arrangement was effective both in inhibiting the undesirable loss of the $[RhCl(CO)_2]_2$ via room-temperature sublimation, as well as in protecting the complex from the oxygen plasma present in the vacuum system during the oxidation of the evaporated aluminum film. Moreover, this type of ampule is much more convenient to use than breakable presealed ampules which can be used only once. This ampule is mounted on an arm which in turn is attached to a high vacuum rotary and linear feedthrough. The stopper of the ampule is mounted on a stationary support. With this arrangment, the ampule could be opened and moved into position approximately 30 cm below the samples during the exposures. Line-of-sight between the positioned ampule and the samples could be blocked with a rotatable shutter. Attached to the base of the ampule are a tungsten heating wire and an iron-constantan thermocouple, which permits heating of the ampule to the correct temperature to sublime the complex without risk of overheating and possibly decomposing the complex.

One problem which was encountered while working with this complex was that during sublimation the pressure within the vacuum system did not rise significantly and no change in the frequency of the quartz crystal microbalance (which was held at room temperature) could be detected. Thus, no direct measure of the exposure of the sample to the complex could be determined. However, the parameters during exposure (sublimation temperature and exposure time) were held constant ensuring that the exposures from experiment to experiment are comparable.

The "standard" procedure used to produce tunneling junctions of optimum quality is very similar to the procedure developed for other adsorbate systems. First, an aluminum strip, approximately 2 mm in width by 20 mm in length by 800 Å in thickness, is evaporated onto a clean glass microscope slide. This aluminum is then exposed to an oxygen plasma discharge in 0.12–0.16 torr of high-purity oxygen. The pressure of the oxygen is adjusted to stabilize the discharge at 20 mA and 1135 V. Oxidation times, which varied from 13 to 20 min depending upon the subsequent adsorbate exposure conditions, were chosen so that the resistance of the completed junction fell in the range 20–200 Ω. This corresponds to an oxide layer 20–30 Å in thickness on the aluminum. The system was then evacuated, and a flow of liquid nitrogen was initiated through the cooling lines of the sample holder. When the samples had cooled to the desired temperature, the ampule containing the $[RhCl(CO)_2]_2$ was moved into position 30 cm below the samples, and the ampule was heated. At this point, line-of-sight between the ampule and the samples was blocked by the shutter. The ampule was heated for 1–2 min to allow evaporation of high vapor pressure contaminants in the complex before the shutter was opened and the samples were exposed. Exposures were all for 20 min with the ampule held at 353–368 K. At the completion of the exposure, the ampule was cooled and reclosed, and the Pb top electrode was evaporated immediately with the samples cold. The completed junctions were then allowed to warm to room temperature under vacuum before being removed and mounted on the measurement supports. This warming was necessary to prevent condensation of atmospheric water onto the samples, since liquid water oxidizes the thin Pb films thus destroying the junctions. The resistances of the junctions were measured and those with resistances between 20 and 200 Ω were stored under liquid nitrogen until the tunneling measurements could be made (as described below).

Several variations on this basic preparation procedure were attempted, the rationale for which will be explained in the next section. For some samples, surface hydroxyls on the oxide were exchanged with D_2O before cooling and exposing to the $[RhCl(CO)_2]_2$. Samples were prepared also by exposing the oxide to the complex at low temperature and then warming to room temperature, either in vacuum or in a background of CO, before the Pb overlayer was evaporated. Other samples were exposed to the complex at low temperature followed by exposure to a hot tungsten filament (to test for radiative heating) before warming to room temperature and evaporating the Pb. Finally, samples were cooled, exposed to the $[RhCl(CO)_2]_2$, and then exposed to low coverages of Pb (50, 10, or 3 Å) before warming to room temperature and completing the Pb evaporation. The final Pb electrodes were 2500–3000 Å in thickness.

The IET spectra were measured with the samples immersed in liquid helium at 4.2 K. The desired acquisition of the data (d^2V/dI^2 as a function of V) was obtained by a modulation and harmonic detection scheme,[25] using a modulation frequency of about 50 kHz.[26] The electronics were controlled, and spectra were recorded in digital form, by a PDP-11/10 laboratory minicomputer as described elsewhere.[27] The modulation voltages used in the measurement were between 1.0 and 2.0 meV rms, depending on the resolution desired and the signal-to-noise characteristics of the junctions.

Results and Discussion

In our inelastic electron-tunneling spectroscopic study of the interaction of $[RhCl(CO)_2]_2$ with aluminum oxide, we found that the intensity of the spectral features associated with the complex depended strongly on the procedure followed in junction preparation, even for constant exposures. The peak positions did not vary, however, and they correspond well with the peak positions seen in IETS investigations of CO adsorbed on evaporated rhodium islands.[1-3] In our study, no spectral features were seen that could be ascribed either to Rh–Cl, to Al–Cl or to O–Cl vibrations. This leads us to conclude that the $[RhCl(CO)_2]_2$ decomposes to form $Rh_n(CO)_m$ species bound to the alumina surface.

For reference, curve a of Figures 2 and 3 illustrates the IET spectrum of a sample not exposed to the $[RhCl(CO)_2]_2$. The peaks seen are characteristic of a "clean" tunnel junction. The small peak near 280 cm^{-1} is a phonon mode of the Al metal electrode. The large peak at 945 cm^{-1} and the weak feature at 1880 cm^{-1} are due respectively to the Al–O stretching vibration of the bulk oxide and to the first overtone of that oxide mode. The low-energy shoulder on the 945-cm^{-1} peak and the peak at 3630 cm^{-1} are due to bending and stretching vibrations, respectively, of surface OH groups. Finally, the small peak at 1089 cm^{-1} and the structure around 2900 cm^{-1} are due to CH vibrations of a small amount of hydrocarbon contamination.

For those junctions prepared by using the "standard" procedure, i.e., cooling the oxidized aluminum strip, exposing to the complex, and evaporating the Pb while cold, the intensity of the IET spectrum depends on the temperature to which the sample was cooled during preparation, as illustrated in Figure 2. For those samples prepared at room temperature, the tunneling spectra show only two features that can be ascribed to the $[RhCl(CO)_2]_2$ interaction with the oxide: a small but sharp peak at 427 cm^{-1} and a broad weak feature at 1968 cm^{-1}. As the fabrication temperature is decreased, the peak at low frequency splits into two peaks at 406 and 443 cm^{-1}. The 406-cm^{-1} peak is very sharp and is always the more intense of the two. Also, this lower frequency peak appears to increase in intensity with coverage more rapidly than the 443-cm^{-1} peak. A third low-frequency mode is seen at 561 cm^{-1}. At higher frequencies, the 1968-cm^{-1} peak increased in intensity and, in some cases, a very broad weak mode can be

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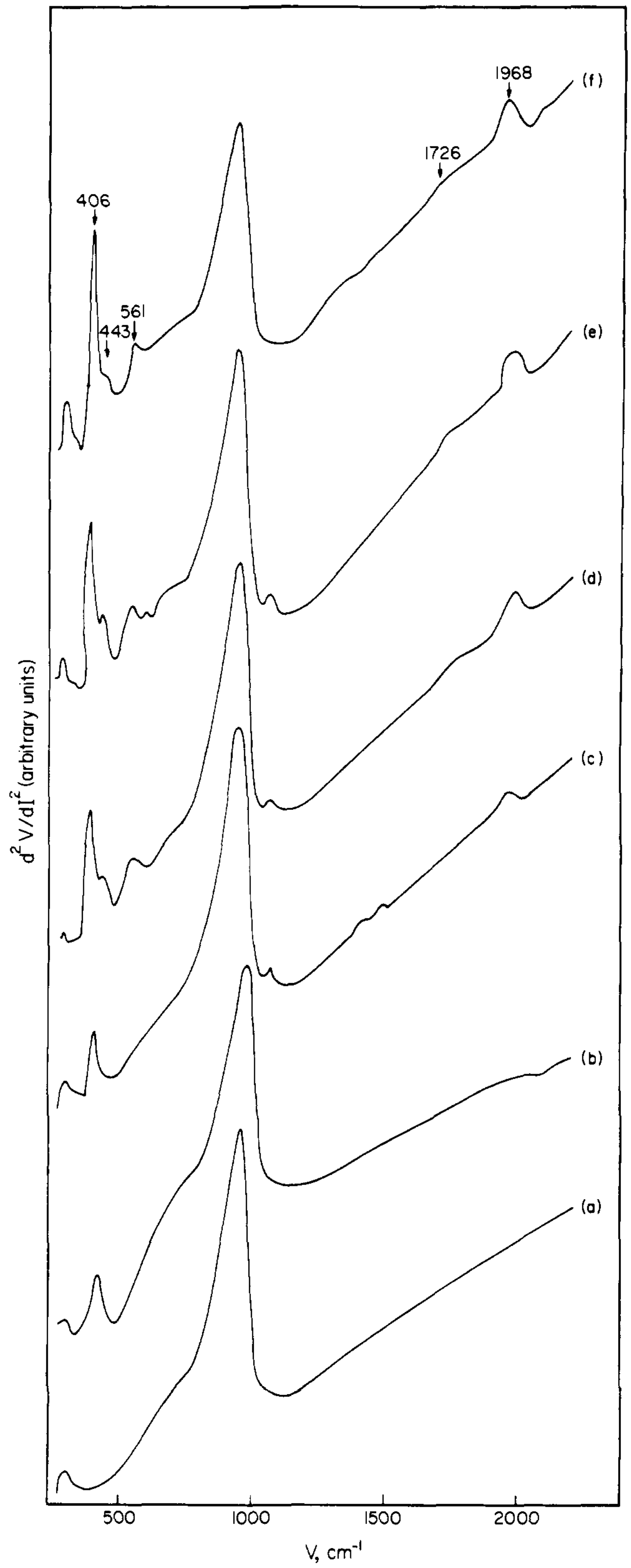

Figure 2. IET spectra of alumina cooled to various temperatures and exposed to [RhCl(CO)$_2$]$_2$ from the gas phase. A clean surface spectrum is shown in a and the other spectra represent the surface exposed to the complex at (b) room temperature (295 K), (c) 240 K, (d) 210 K, (e) 190 K, and (f) 180 K. The lead was evaporated on the cold surface.

distinguished at approximately 1726 cm^{-1}.

The frequencies of these five features, listed in Table I, agree very favorably with the five peaks reported in the IETS studies by Kroeker et al.[2] and Klein et al.[3] for carbon monoxide adsorbed on rhodium which was deposited by evaporation onto the aluminum oxide surface. Also, no features are present in the spectra which can be ascribed to a rhodium-chlorine vibration which would be expected in the range 260–280 cm^{-1} for bridging Cl[28] or between 285 and 358 cm^{-1} for terminal Cl.[28] These results lead us to conclude that, upon adsorption on the alumina, the [RhCl(CO)$_2$]$_2$ partially decomposes, losing the chlorine and leaving rhodium-carbonyl species bound to the surface. This is consistent with the results obtained by Smith et al.[21] for [RhCl(CO)$_2$]$_2$ adsorption on γ-alumina. There is some question, however, concerning the assignment of the five modes associated with these Rh-CO species. There are three types of RhCO bonding geometries present on dispersed rhodium, as deduced from infrared studies.[20-22] Two of these species are classified as linearly bonded CO, one consisting of two CO molecules bound to an isolated rhodium atom, Rh(CO)$_2$, and the other having a single CO bound to one rhodium, RhCO. The third species is bridge-bonded CO, i.e., a single CO bound to two rhodium atoms, Rh$_2$CO.

Infrared studies of the carbonyl stretching region of Rh-CO systems indicate that the peaks associated with the two linear CO species occur between 2030 and 2100 cm^{-1},[20] whereas the bridged

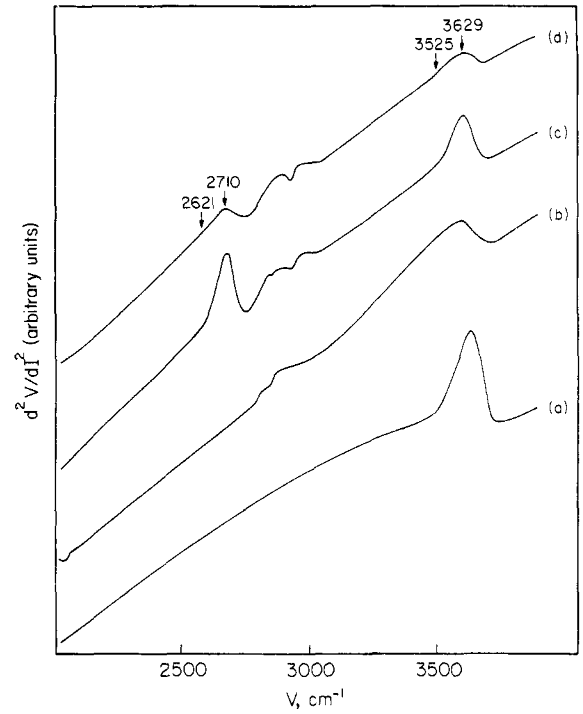

Figure 3. IET spectra showing the OH and OD vibrational region. The spectra are for (a) a clean sample, (b) alumina exposed to [RhCl(CO)$_2$]$_2$ at 210 K (corresponds to spectrum d of Figure 2), (c) clean surface partially deuterated, and (d) deuterated surface exposed to [RhCl(CO)$_2$]$_2$ at 200 K.

Table I. Vibrational Modes Resulting from [RhCl(CO)$_2$]$_2$ Adsorption on Alumina

freq, cm^{-1} [a]	surface species	type of mode
406	Rh(CO)$_2$	M-C-O bending
443	RhCO	M-C-O bending
561	Rh$_2$CO	M-C-O bending or M-CO stretching
1726	Rh$_2$CO	CO stretching
1968	Rh(CO)$_2$ + RhCO	CO stretching
2621	coordinated OD	OD stretching
2710	free OD	OD stretching
3525	coordinated OH	OH stretching
3629	free OH	OH stretching

[a] After subtracting 8.15 cm^{-1} to correct for the effect of the Pb superconducting gap.[35]

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[28] D. M. Adams, "Metal-Ligand and Related Vibrations", Edward Arnold Ltd, London, 1967, pp 65–71.

species should produce a peak between 1860 cm^{-1} [21,22] and 1925 cm^{-1}.[20] In tunnel junctions, the top metal electrode has the effect of downshifting the frequencies of these highly polarizable bonds approximately 120 cm^{-1}.[2] Thus, the linearly bound CO stretching frequency appears at 1968 cm^{-1}, while the bridging CO stretching frequency occurs at 1726 cm^{-1}. The three modes of the two linearly bound CO species lie close together in energy (all three lie within 80 cm^{-1} as shown by IR studies[20-22]). In IETS, the presence of the top Pb electrode will broaden these modes,[2] and since the CO stretching mode depends sensitively on the environment of the metal–carbonyl entity, any variations in binding will tend to broaden the peaks further. Thus, the contributions of the two linearly bound CO species to the CO stretching region cannot be resolved.

There is some dispute as to the assignment of the low-frequency structure. This region of the spectrum is not available to transmission IR studies of dispersed metal systems due to the strong absorption of the radiation by the oxide support. Thus, little work had been concerned with these modes before the advent of IETS (this region can be studied with EELS but only with lower resolution). This low-frequency region includes contributions from Rh–CO stretching and bending modes as well as Rh–C and Rh–O stretching vibrations of possibly dissociated CO. The two IETS studies which have been published concerning the interaction of CO with supported Rh[2,3] disagree as to the assignment of these modes. Kroeker et al.[2] assign their 416-cm^{-1} peak to (primarily) the bending mode of $Rh(CO)_2$, the 469-cm^{-1} peak to (primarily) the bending mode of RhCO, and the 605-cm^{-1} peak to either a bending or a stretching mode of Rh_2CO. On the other hand, Klein et al.[3] assign the same three peaks, respectively, to the Rh–C stretching mode of dissociated CO, the Rh–CO stretching mode or the symmetric Rh_2–CO stretching mode, and the asymmetric Rh_2–CO stretching mode. In our work, the $[RhCl(CO)_2]_2$ molecular complex possesses the $Rh(CO)_2$ structure (as seen in Figure 1), and since adsorption is carried out at room temperature and below, we would expect $Rh(CO)_2$ to be a major surface constituent. Also, we would not expect to observe decomposition of the CO at these low temperatures.[19,29] Thus, the fact that the 406-cm^{-1} peak is by far the dominant feature in our spectra would support the assignment of this peak to the $Rh(CO)_2$ species. Also, in our spectra, the relative intensities of the 443- and 561-cm^{-1} features are not constant and, thus, are probably not associated with the same species on the surface. Therefore, we correlate our 443-cm^{-1} peak with RhCO and the 561-cm^{-1} peak with $Rh_2(CO)$. However, from our data we cannot ascertain whether they are bending or stretching in character.

Due to the selection rules for IETS, as well as the lack in certainty as to the exact vibrations which produce our observed spectra, we cannot make any statement as to the concentration of $Rh(CO)_2$ relative to RhCO and Rh_2CO on our oxide surface. However, by comparing our spectra to those seen for low coverages of evaporated Rh on alumina[1] and assuming that the cross sections for excitation of the respective vibrations are the same in the two studies, we can say qualitatively that there is a higher proportion of $Rh(CO)_2$ in our junctions. Since this species is associated with isolated Rh atoms,[17,19] we conclude that the rhodium deposited on alumina at low temperature through decomposition of $[RhCl(CO)_2]_2$ is more highly dispersed than rhodium deposited by evaporation. This is supported by the very low intensity of the CO stretching mode associated with Rh_2CO, which we would expect to be prominent if a significant fraction of the metal atoms was coalesced into islands or rafts.

In addition to the features which can be ascribed directly to surface rhodium–carbonyl species, we note that the feature associated with free hydroxyl groups on the alumina surface is perturbed strongly by the adsorption of the rhodium complex, as shown in Figure 3. The peak at 3646 cm^{-1} is broadened significantly toward low frequency. It appears that a second OH mode at approximately 3525 cm^{-1} appears in addition to the original peak near 3630 cm^{-1}. If these surface hydroxyls are exchanged partially with deuteroxyl groups (by exposure to D_2O at room temperature before cooling and exposure to the $[RhCl(CO)_2]_2$), the same perturbation of the OD mode is seen. It is impossible to ascertain whether the actual number of hydroxyls is decreased due to the adsorption of the complex. It should be noted, however, that no new peaks were seen in the low frequency region which could be ascribed to Rh–D (seen near 1450–1500 cm^{-1} for complexes with Rh–D bonds.[30]

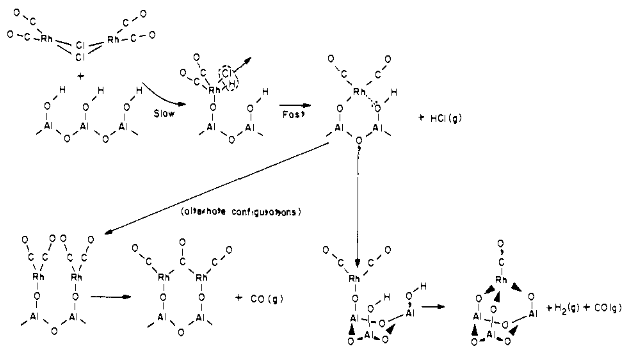

Figure 4. Postulated adsorption mechanism for $[RhCl(CO)_2]_2$ on a hydroxylated alumina surface.

The most plausible mechanism for the adsorption of $[RhCl(CO)_2]_2$ on hydroxylated alumina which is consistent with all our measured spectra is illustrated in Figure 4. The dimer first adsorbs weakly (or physically adsorbs) on the alumina. The temperature dependence of the spectra implies that the number of dimers which adsorb physically and subsequently chemisorb is a strong function of the temperature. The dimer dissociates, and the monomer reacts with a surface hydroxyl. The hydrogen is transferred from the oxygen to the rhodium resulting in the formation of a Rh–O bond. The hydrogen then combines with the chlorine forming HCl which desorbs immediately. This mechanism is consistent also with the bonding seen for organometallic compounds on hydroxylated oxide surfaces.[7-9] The rhodium of this $Rh(CO)_2$ group may now interact with the oxygen of an adjacent hydroxyl forming a coordination bond. This downshifts the OH stretching frequency of that hydroxyl strongly and results in the predominant species on the alumina surface. Some of these $Rh(CO)_2$ groups may interact further with the oxide, desorbing one CO and forming another surface bond, yielding RhCO. Also, if a second Rh atom is on an adjacent site (which is not unlikely since the metal atoms arrive at the surface as a dimer), the two rhodium atoms may interact, allowing a bridge bonding, Rh_2CO, species to form. For this type of chemisorption at room temperature and below, it would seem unlikely that extensive surface migration of the rhodium would occur. Thus we would not expect significant island formation, a fact which is consistent with our data.

This mechanism, however, does not yet explain all the data. New questions were raised by the spectra of junctions formed by variations on the "standard" procedure. If, in the fabrication, the oxidized aluminum is cooled and exposed to the $[RhCl(CO)_2]_2$ but then allowed to warm to room temperature before the Pb is evaporated, the resulting IET spectra show a much weaker $Rh(CO)_n$ structure than would have been obtained if the Pb had been evaporated on the cold sample.

One possible explanation is that the supported rhodium is decarbonylating as the surface is warmed. Desorption of CO from supported rhodium at room temperature was seen in a recent infrared study of Rh dispersed on Al_2O_3.[19] However, this difference in adsorbed CO concentration was seen in going from a background of 50 torr of CO to vacuum; once under vacuum little additional loss was observed without heating.[19] Several experiments were carried out to determine whether this process was occurring with our samples. Warming in a background of CO should inhibit the desorption of CO, so samples were prepared

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(29) J. T. Yates, Jr., E. D. Williams, and W. H. Weinberg, *Surf. Sci.*, **91**, 562 (1980).

(30) Reference 28, p 176.

by adsorbing the $[RhCl(CO)_2]_2$ on a surface at 180 K and then warming to room temperature in 10^{-4} torr of flowing CO before evacuating and evaporating the Pb. The resulting spectra were identical with those of samples warmed under vacuum. Samples were also made by exposing the alumina to the rhodium complex at room temperature and then cooling to 180 K in a background of 10^{-4} torr CO before evaporating the Pb. Others were made by cooling the alumina to 180 K, exposing it to the complex, and then heating the surface resistively[31] to 395 K in 50 μm of CO or to 475 K in 25 μm of CO. The samples were then allowed to cool to 240 K in CO before evacuating and evaporating the Pb. The resulting spectra for all these fabrication procedures were very similar showing only weak features from $Rh(CO)_n$. It should be noted that in the experiments where samples were heated resistively, one set of control samples was left cold. In all cases, the unheated samples had much higher resistances (1 order of magnitude or more) indicative of higher adsorbate concentrations. Also, the physical appearance of the Pb electrodes differed; the Pb on the heated samples was smooth and bright, while on the unheated controls, the Pb was dull and dark. Thus, while desorption of CO from the supported rhodium may contribute to the loss of spectral intensity, it does not appear to be the only cause.

An alternate mechanism could explain our observations, however. As the $[RhCl(CO)_2]_2$ impinges on the cold alumina, the dimers adhere to but do not dissociate on the surface immediately. Rather, a multilayer of physically adsorbed $[RhCl(CO)_2]_2$ forms with only the first monolayer adsorbing as $Rh(CO)_n$. If the surface is allowed to warm, the outer, physically adsorbed layers desorb leaving only a small statistical coverage of rhodium. If, however, the Pb is evaporated on the cold multilayer, sufficient energy is presented to the surface region, either through radiation or heat of condensation, to initiate the scism of the dimers, allowing the adsorption and loss of the Cl through HCl formation.

As a test of the plausability of this mechanism, some rather crude calculations were carried out. From the structure of the complex as determined by X-ray diffraction[24] (cf. Figure 1), it was determined that the dimer would occupy approximately 37 $Å^2$ on the surface. This corresponds to a monolayer consisting of 2.7×10^{14} dimers or 5.4×10^{14} Rh atoms/cm^2. If we assume bulk spacing for Rh at full monolayer coverage, we find that a monolayer of Rh consists of 1.6×10^{15} atoms/cm^2 and a thickness of 2.16 Å. Thus, one monolayer of $[RhCl(CO)_2]_2$ decomposed on the surface yields one-third of a monolayer of Rh metal or a statistical thickness of 0.7 Å of Rh. Thus, we can compare our IET spectra for samples prepared by adsorbing the complex at low temperature and warming (to desorb the physically adsorbed multilayers) before evaporating the Pb to the spectra of samples prepared by Hansma et al.[1] after evaporation of 0.5–1 statistical Å of Rh metal and exposing that to CO. The qualitative agreement is quite good.

We now address the question of what occurs when Pb is evaporated onto the cold surface with the multilayer present. Since there is no evidence that the $[RhCl(CO)_2]_2$ remains intact within the junction, it evidently decomposes during the Pb evaporation. As noted earlier, this complex is heat sensitive and has been found to decompose at 400 K[23] or at kT of only 34 meV. During the Pb evaporation, energy must be dissipated across the adsorbate–alumina interface. Thus, it is quite probable that the multilayer may gain enough energy sufficiently rapidly to decompose before it has a chance to desorb. It is possible to calculate the flux of energy reaching the samples due to radiation from the Pb evaporation source. If we assume that the source is a 1-cm diameter sphere at 770 K with an emissivity of 0.1 (approximate for Pb at 775 K[32]), then the amount of radiant energy incident on the samples 40 cm away is approximately 20 meV/(A^2 s), or approximately 740 meV per dimer per second. Not all of this radiation will be absorbed by the adsorbate. On the time scale of molecular vibrations (10^{-13} s), the dimer will undergo 10^{10} vibrations before even 1 meV of radiant energy is absorbed. Thus, even if the dimer is only weakly coupled to the surface, it should be able to transfer this energy to the alumina at an adequate rate not to heat appreciably more than the oxide itself. Even if all the incident radiant energy were trapped in the first 10 Å of the alumina film, the surface would only be heated by approximately 0.2 K/s at 200 K. Thus, radiant heating is not causing the breakup of the dimers on the surface.

A much more likely cause of the dissociation is the energy released in the condensation of the Pb atoms. The heat of condensation of Pb (in going from a gas to a solid) is 43.64 kcal/mol,[33] or, in other words, each Pb atom striking the surface must release 1.9 eV on the time scale of many molecular vibrations (perhaps 10^{-9} s). Each dimer will encounter an average of 1.8 Pb atoms before the first monolayer of lead is evaporated. Since the adsorbate is thermally unstable and since it is not coupled strongly to the surface, enough of this energy could reasonably be trapped in the $[RhCl(CO)_2]_2$ sufficiently long to result in the dissociation of the dimer, thus allowing the monomers to adsorb on the alumina via the mechanism described above. A similar effect has been observed by Lindau et al.,[34] where the heat of condensation of gold deposited on III–V semiconductors is postulated to initiate the decomposition of the semiconductor surface.

To test these hypotheses, two final experiments were performed. In the first, a set of junctions was prepared by adsorbing the $[RhCl(CO)_2]_2$ on alumina (below 180 K) and exposing this cold surface to a hot tungsten filament (much hotter than the Pb source) for 25 s. The samples were then warmed to room temperature before the Pb was evaporated. The junction resistances were comparable to those of junctions fabricated by the same procedure but without exposure to the hot filament, and the resulting IET spectra showed no significant enhancement of the spectral features due to $Rh(CO)_n$. In the final experiment, several sets of junctions were prepared by the following procedures. The $[RhCl(CO)_2]_2$ was again adsorbed on alumina below 190 K. Following this, varying amounts of Pb were evaporated on the three samples while they were still cold. One was covered with approximately 50 Å of Pb, enough to cover the surface completely. The second was exposed to approximately 10 Å of Pb, on the order of three or four monolayers. The third was exposed only to approximately 3 Å of Pb, approximately one monolayer, which is not enough to bury the surface region physically but which should be enough to cause decomposition of some of the $[RhCl(CO)_2]_2$ layer. The samples were then warmed to room temperature, and the remainder of the Pb overlayer was evaporated. In all instances, the resulting junction resistances of the three samples were comparable to each other and were approximately 2 orders of magnitude greater than for junctions prepared without any Pb evaporation at low temperatures. This is indicative of a higher adsorbate concentration. Unfortunately, the resulting IET spectra were too noisy to give useful spectra.

It has been assumed in the past that the Pb overlayer in IETS tunnel junctions plays no direct role in the interaction of an adsorbed species with the aluminum oxide surface (apart from downshifting the observed frequencies somewhat[35]. This appears to be valid for stable species chemisorbed on the oxide surface. However, we have seen in this study that for weakly bound multilayers of unstable molecules, the energy released in the condensation of the Pb may be sufficient to initiate further chemical reaction. Thus, the lead may play an active role in the chemistry of the interfacial region.

Conclusions

We have studied by means of inelastic electron-tunneling spectroscopy the interaction of the chlorodicarbonylrhodium dimer, $[RhCl(CO)_2]_2$, with aluminum oxide films during the formation

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of Al–Al_2O_3–complex–Pb tunnel junctions. This is only the second published IETS study of a transition metal–carbonyl complex.[16]

The postulated reaction pathway is illustrated in Figure 4. The dimer adsorbs physically on the surface, but it must dissociate before chemisorption can occur. When the dimer dissociates, the monomers react with surface hydroxyl groups resulting in the formation of HCl gas and allowing the rhodium atom to bond to the resulting surface oxygen. The metal atom can interact further with a neighboring hydroxyl, possibly coordinating with the lone pair of electrons on the oxygen. This is the predominant surface species, consisting of an isolated rhodium atom binding two carbonyl ligands, $Rh(CO)_2$. Some of these groups may lose one of their carbonyls, or, if two rhodium atoms are on adjacent sites, a CO may form a bridge bond between the two. These result in RhCO and Rh_2CO species, respectively. The scism of the dimer appears to be the rate-limiting step. Adsorption at low temperatures results in a multilayer of physically adsorbed $[RhCl(CO)_2]_2$. If this surface is allowed to warm to room temperature, the multilayers desorb, leaving only the chemisorbed monolayer. If, however, Pb is evaporated on the cold surface, the energy released by the condensing Pb is sufficient to dissociate the dimers present in the multilayer. These monomers then lose their chlorine and bind to the surface.

Our spectra indicate that, compared with evaporated Rh, a large proportion of the Rh present on the surface is in the form of $Rh(CO)_2$, indicating almost atomic dispersion of the metal.

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An Interstitial Hydrogen Atom in a Hexanuclear Metal Cluster: X-ray and Neutron Diffraction Analysis of $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$

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Abstract: A six-coordinate H atom has been found in the octahedral metal cluster complex $[HCo_6(CO)_{15}]^-$ by single-crystal neutron diffraction analysis at 80 K. Within experimental error, the H atom is situated in the geometric center of the cluster, with an average Co–H distance of 1.82 Å. The mean Co–Co distance of 2.58 Å is longer than those in $[Co_6(CO)_{14}]^{4-}$ (2.50 Å) and $[Co_6(CO)_{15}]^{2-}$ (2.51 Å). $[HCo_6(CO)_{15}]^-$ is prepared via the protonation of $[Co_6(CO)_{15}]^{2-}$. The monoanion shows an unusual ^1H NMR chemical shift at τ −13.2 (acetone-h_6 solution, 173 K), which disappears upon warming to room temperature. Experimental evidence seems to point to the existence of some type of exchange of the proton in solution, as $[HCo_6(CO)_{15}]^-$ shows no ^1H NMR signal in acetone-d_6 and is readily deprotonated by water, methanol, and other proton-accepting solvents. $[(Ph_3P)_2N]^+[HCo_6(CO)_{15}]^-$ crystallizes in space group $P2_1/n$, with $Z = 4$ and unit cell constants at 80 K of $a = 17.922$ (3) Å, $b = 17.524$ (4) Å, $c = 16.329$ (8) Å, $\beta = 92.27$ (2)°, and $V = 5124$ (3) Å^3. The conventional R value is 0.071 for 3574 reflections with $I > 3\sigma(I)$. Neutron diffraction data were collected at the Brookhaven high flux beam reactor. The nonhydrogen portion of the structure was originally solved with X-ray data collected at 177 K.

Introduction

The bonding of hydrogen to transition metals has been shown to take a wide variety of forms by means of single-crystal X-ray[3] and neutron diffraction[4] analyses. Besides the terminal M–H bond such as is commonly found in mononuclear complexes,[5] many different types of hydrogen bridge bonds have been discovered. It is now known that metal–metal bonds can be bridged by one $[HW_2(CO)_9(NO)]$,[6] two $[H_2Os_3(CO)_{10}]$,[7] three $[H_3Ir_2(C_5Me_5)_2]^+$,[8] and even four H atoms $[H_8Re_2(PEt_2Ph)_4]$.[9] (Abbreviations used in this paper are as follows: Me = methyl, Et = ethyl, Ph = phenyl, Cp = cyclopentadienyl.) In some clusters, the hydride ligand has been shown to be bonded to three metal atoms on a triangular face of the cluster, as in $H_3Ni_4Cp_4$[10] and $HFeCo_3(CO)_9(P(OMe)_3)_3$.[11] Interstitial H atoms have been

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