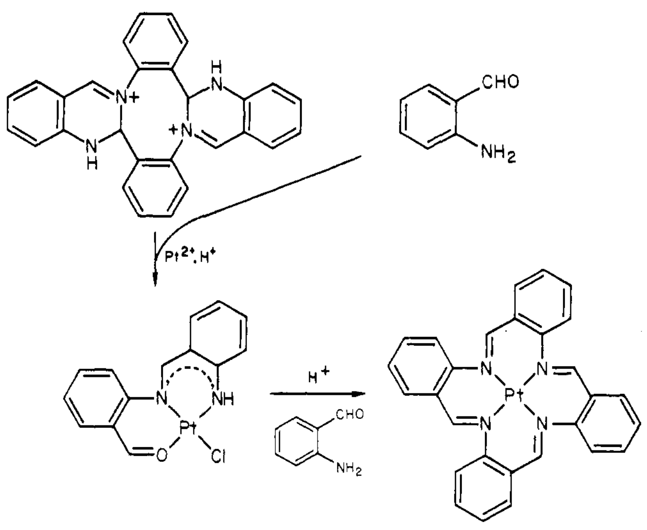
Scheme I



plexes.[32] Such a shift would be anticipated with an increase in electron delocalization which would affect the C=N bond order. The band at 1529 cm^{-1} thus has been assigned on the basis of these observations to the C=N stretching vibration rather than one of the higher energy bands. Of the remaining bands, two possible assignments are available: the N–H deformation vibration, normally occurring between 1650 and 1550 cm^{-1}, and the phenyl ring vibrations, from 1650 to 1450 cm^{-1}. The former are often hidden by the strong phenyl absorptions and are noted to be weak in secondary amines and iminato-like species.[33] As a consequence, the remaining medium to strong bands are most probably related to aromatic absorptions as well as phenyl ring conjugation with C=N and C=O, known to produce enhancement of the ring vibration intensities.[33]

The UV–Vis absorption spectrum of Pt(AAA)Cl consists of a series of intense bands and shoulders throughout both regions. In $CHCl_3$ two bands are observed at 17 300 and 29 900 cm^{-1} with extinction coefficients of 14 200 and 9840, respectively. Shoulders occur at 18 100, 24 300, 26 900, 36 000, and 37 600 cm^{-1}. The origin of these bands is most probably related to metal to ligand charge transfer or to ligand transitions in view of the intensities involved. Similar intense visible bands are observed in complexes of the reduced TAAB ligand as well as in nucleophilic adducts of TAAB where electron delocalization throughout the chelate rings leads to highly chromophoric species.[10,34]

The intermediate nature of Pt(AAA)Cl is confirmed by experiments in which concentrated solutions of the purple crystals in acetonitrile are reacted with *o*-aminobenzaldehyde. Upon acidification the intense bands in the visible region immediately disappear. UV–Vis spectra recorded after heating and stirring of the solution for 1 day are identical with that of $Pt(TAAB)^{2+}$. The total reaction sequence can therefore be described as shown in Scheme I. The mechanistic implications of the presence of the deprotonated *o*-aminobenzylidene moiety, at least in the platinum system, are being investigated.

This is, to our knowledge, the first isolated intermediate in the self-condensation of *o*-aminobenzaldehyde to give transition-metal complexes of the fully cyclized ligand. It forms readily from either *o*-aminobenzaldehyde or the diacid salt in the presence or absence of light or oxygen. The formation of the deprotonated *o*-aminobenzylidene moiety is particularly interesting in view of its rarity. The complex further reacts with a variety of amines, and the products are currently being investigated in order to provide convenient routes to novel polydentate and macrocyclic ligand systems.

Acknowledgments. The authors thank Professor B. K. Lee for use of his diffractometer, for the low-temperature data collection, and for many helpful discussions. K.B.M. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Kansas general research allocation No. 3227-XO-0038 for support of this research.

Supplementary Material Available: A list of observed and calculated structure factors (Table IV) (8 pages). Ordering information is given on any current masthead page.

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An Inelastic Electron-Tunneling Spectroscopic Study of $Ru_3(CO)_{12}$ Adsorbed on an Aluminum Oxide Surface

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Abstract: The adsorption of $Ru_3(CO)_{12}$ on aluminum oxide has been studied by means of inelastic electron-tunneling spectroscopy. The complex was found to retain its molecular structure when adsorbed on a hydroxylated alumina surface at low temperature. Upon heating the surface to 470 K in 0.1 torr of O_2, the $Ru_3(CO)_{12}$ is lost from it through desorption and possible oxidation of the complex.

Introduction

In the area of chemisorption and heterogeneous catalysis, one of the more technologically important fields of study is research aimed at understanding the properties of supported metal catalysts on a molecular level. A rather new technique, ideally suited for the investigation of such systems, is inelastic electron-tunneling spectroscopy (IETS).[1-3] IETS provides vibrational information concerning the support-supported metal–adsorbate system. In this sense, IETS is analogous to IR spectroscopy. Tunneling spectroscopy, however, has several advantages over IR spectroscopy; for example: (1) IETS is sensitive to both infrared (dipolar) and Raman (induced dipolar) active excitations; (2) the IETS sample is a planar surface with an area on the order of 1 mm^2,

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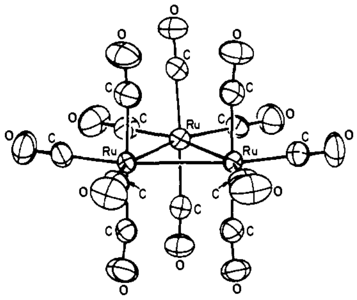

Figure 1. $Ru_3(CO)_{12}$, viewed from a direction 75° from the normal to the Ru_3 plane.[21]

making uniformity over the sample more probable; (3) vibrational modes as low as 240 cm^{-1} are visible, allowing metal-ligand-stretching and -bending modes to be seen; and (4) since the sample preparation is carried out entirely in a well-controlled environment (a high vacuum system), the history of the sample is known.

Recently, IETS has been shown to be useful in several studies of supported metals which have been evaporated onto an alumina surface.[4-7] The standard commercial approach to making supported metal catalysts is to reduce metallic salts which have been impregnated into high surface area oxides. The synthesis of tunnel junctions in this manner, however, has not been reported. A third approach in forming supported metal catalysts, which is receiving much attention, is the attachment of homogeneous catalysts onto solid supports.[8-19] The supported complex may be calcined to bare metal[11,12] or left with some fraction of its original ligands attached.[13,14] This technique provides several advantages over the use of calcined metallic salts, for example: (1) higher dispersion;[11,12] (2) an increase in activity;[15] and (3) a modification in the selectivity for some reactions.[16,17] Investigations in this area utilizing IETS were begun in our laboratory when studies of the polymerization catalyst, $Zr(BH_4)_4$ supported on Al_2O_3, were carried out successfully.[18] Also, the interaction of $[RhCl(CO)_2]_2$ with the hydroxylated alumina surface has been studied by using IETS.[19]

In this paper, we extend our investigations in this area by considering $Ru_3(CO)_{12}$ adsorbed on Al_2O_3. This complex was selected for a number of reasons. First, the vibrational spectra of several small molecules adsorbed on the (001) surface of single crystalline Ru have been measured in our laboratory by using high-resolution electron energy loss spectroscopy (EELS),[20] and a comparison with the vibrations associated with the supported metal and supported complex is of interest. Second, since $Ru_3(CO)_{12}$ is thermally quite stable, the prospects of subliming the molecular complex successfully were good. Third, since the molecule is stable, the possibility of adsorbing the complex on the alumina surface without decomposition was good. This would allow us subsequently to study its decomposition on the surface more easily than if decomposition occurred already at low temperatures. Finally, $Ru_3(CO)_{12}$ has been attached successfully to commercial (high surface area) oxide supports.[12,13,16]

This work examines the adsorption of $Ru_3(CO)_{12}$ onto hydroxylated Al_2O_3 and the interaction of the supported complex with oxygen at elevated temperature. The next section of the paper will discuss the experimental details of the work. Section 3 will present the results and discuss their interpretation, and the final section will delineate the important conclusions.

Experimental Procedures

The sample preparation procedures used in the adsorption of the $Ru_3(CO)_{12}$ complex were very similar to those used in the study of $[RhCl(CO)_2]_2$ and are described in detail elsewhere.[19]

The $Ru_3(CO)_{12}$ was obtained from Strem Chemicals. This complex is an orange crystalline solid described as air stable but does decompose at 423 K. The structure of the complex, as determined by Churchill et al.[21] is illustrated in Figure 1. The complex consists of an equilateral triangle of Ru atoms, each metal atom being bound directly to the other two metal atoms. Attached to each Ru atom are four terminal CO groups, two of which are axial, aligned perpendicular to the Ru triangle, and two of which are radial, lying in the plane of the Ru triangle.

The $Ru_3(CO)_{12}$ was introducted into the vacuum system via a sealed glass ampule with a ground glass ball-and-socket joint, as described elsewhere.[19] In order to effect the exposure of the complex to the alumina surface, we moved the ampule into position approximately 30 cm below the samples, and the ampule was heated to approximately 408 K to sublime the complex.

As with the $[RhCl(CO)_2]_2$, there was no direct method of determining the number of molecules of the complex which actually impinged on the sample surface during exposure. Hence, the parameters associated with the exposure were kept constant from run to run to assure consistency between samples.

It was found that $Ru_3(CO)_{12}$ adsorbs well on a fully hydroxylated alumina surface. Hence, the tunnel junction fabrication procedure was modified slightly from the procedure followed for $[RhCl(CO)_2]_2$. First, an Al film approximately 2 mm in width by 20 mm in length by 800 Å in thickness was evaporated onto a cleaned glass substrate. The Al strip was then oxidized in a plasma discharge initiated in 0.12–0.16 torr of high-purity oxygen. The discharge current was kept at 20 mA at 1135 V for 6–8 min. The oxygen was then evacuated from the system and 0.3–0.6 torr of H_2O vapor admitted, exposing the samples to this vapor for approximately 8–10 min. This was done to ensure that the surface was fully hydroxylated. Deuterium oxide was substituted for water when a partially deuteroxylated surface was desired. The system was then evacuated to below 1×10^{-5} torr. At this point, a flow of liquid nitrogen was initiated through the sample holder cooling lines,[19] and the samples were allowed to reach the desired temperature of exposure as measured by an iron-constantan thermocouple (In soldered to the sample substrate). This temperature was generally in the range 175–195 K. The ampule was then moved into position 30 cm below the samples, and the ampule (and complex) was heated to approximately 408 K. After 1–2 min of heating, the shutter blocking line-of-sight between the ampule and the samples was removed, and the samples were exposed to the complex for 20 min. The ampule heating was then terminated and the ampule resealed.

The preparation procedure followed subsequent to this point was varied. For some samples, the top Pb electrode was evaporated onto the cold samples immediately after the exposure to the $Ru_3(CO)_{12}$.

For the second type of sample, at the conclusion of the $Ru_3(CO)_{12}$ exposure, 0.1 torr of high-purity oxygen was introduced into the system. The samples were then heated resistively (by a technique described elsewhere[22]) to approximately 473 K for 250 s. The samples were then

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allowed to cool in oxygen. The vacuum system was then evacuated and the Pb evaporated.

In the final variation, the sample was heated in oxygen, as described above. However, after evacuation, 0.1 torr of CO was introduced, and the samples were reheated to approximately 473 K for an additional 250 s. The samples were allowed to cool in CO. The system was evacuated once more, and the Pb electrode was deposited.

The flow of liquid nitrogen to the sample holders was terminated during the $Ru_3(CO)_{12}$ exposure stage of the preparation to prevent the freezing of the O-ring sealing the LN_2 feedthrough. Thus, the temperatures reached by the samples after heating in O_2 and in CO were generally on the order of 250 and 275 K, respectively.

After evaporation of the Pb, the samples were allowed to warm to room temperature under vacuum. This warming was necessary to prevent the condensation of water from the air onto the samples. Condensed water quickly oxidizes the thin (3500 Å) lead films, destroying the junctions. The samples were then removed from the system and their resistances measured. Those junctions with resistances between 20 and 200 Ω were stored under liquid nitrogen to avoid the occurrence of slow structural changes and to ensure junction stability until the IETS measurements could be made.

The IET spectra were measured with the samples immersed in liquid He at 4.2 K. The desired derivative (d^2V/dI^2 as a function of V) was obtained by a modulation and harmonic detection scheme,[1] by using a modulation frequency of 50 kHz.[23] The electronics were controlled, and the spectra were recorded in digital form, by a PDP 11/10 laboratory minicomputer.[24] The modulation amplitudes used in the measurement were between 1.0 and 2.0 meV root mean square (as measured at a bias voltage of 250 meV), depending on the resolution desired and the signal-to-noise characteristics of the junction.

Since data were collected in digital form, differences between spectra could be made more obvious by digital subtraction of the individual spectra. This proved to be of some aid in the analysis.

Results and Discussion

An unfortunate property of the tunnel junctions prepared with $Ru_3(CO)_{12}$ as an adsorbate was that the features present in the resulting spectra were quite weak. This may be either a consequence of a low coverage of the complex or a consequence of weak coupling between the tunneling electrons and the vibrational modes of the complex, or a combination of both effects. In a study of the adsorption of $Ru_3(CO)_{12}$ from solution on high surface area γ-alumina and silica, it was found that the extent of adsorption of the Ru complex was quite low.[12] There is some indirect evidence, however, that the coverage on the oxide of the tunnel junction was not extremely low. In order for those junctions exposed to the complex to have a resistance below 200 Ω, the Al strip had to be oxidized for on the order of 400 s. As a comparison, junctions with no adsorbate present require an oxidation time of 800–1000 s to yield acceptable resistances (over 20 Ω). Also, those samples exposed to $[RhCl(CO)_2]_2$ showing intense spectral features still required 700 s to oxidize the Al sufficiently.[19]

It has been shown recently that adsorbates may present an additional effective barrier of significant height and width to the tunneling electrons.[25] It may be that the Ru surface species present a barrier of unusual height or width, resulting simply from the physical size of the complex. With the assumption that it adsorbs molecularly (as will be discussed later), the $Ru_3(CO)_{12}$, from the outside of the van der Waals radii of the oxygen on opposing axial CO groups, is over 9 Å in width[21] which is quite significant compared to the width of the oxide (15–20 Å). The electrons would then show a large preference for tunneling through those regions where no adsorbate is present. This would increase the average distance between the tunneling electrons and adsorbed molecules, reducing the coupling between the electrons and the complex, resulting in a weak spectral intensity. This explanation has been proposed also to explain the nonlinear peak intensity as a function of coverage seen with tritiated benzoic acid.[26] Thus, the weak signals observed are evidently due to a combination of less than monolayer coverage and weak coupling of the tunneling electrons to the vibrational modes.

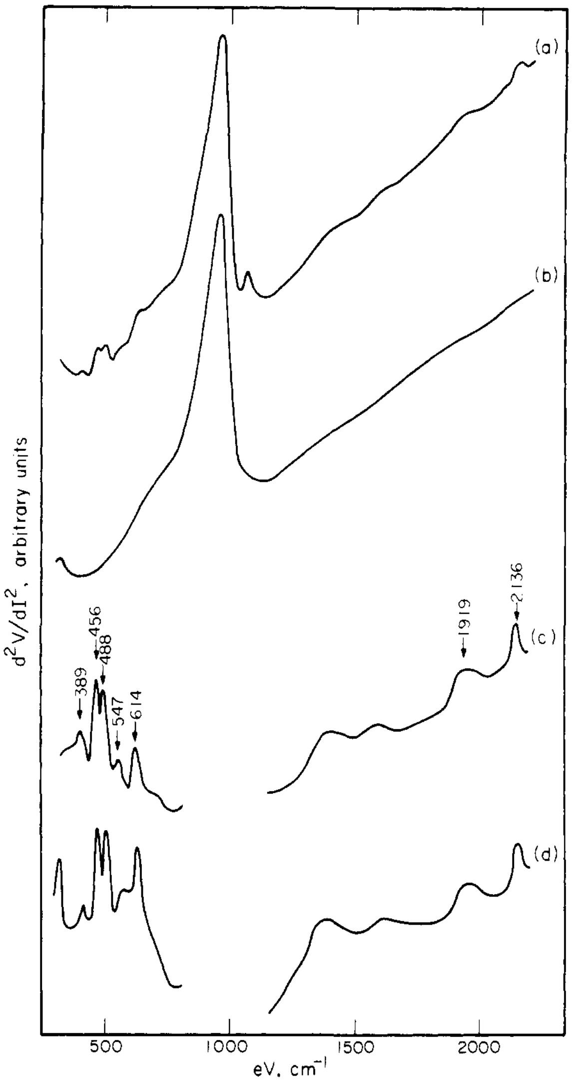

Figure 2. (a) The IET spectrum, from 240 to 2220 cm^{-1}, of $Ru_3(CO)_{12}$ adsorbed on aluminum oxide at approximately 180 K. (b) The IET spectrum of a clean sample, over the same energy range as spectrum a. (c) The spectrum resulting from the digital subtraction of spectrum b from spectrum a, expanded vertically by a factor of 3. (d) The difference spectrum, analogous to spectrum c, for $Ru_3(CO)_{12}$ adsorbed on a deuteroxylated alumina surface.

In order to enhance the visibility of those features due to adsorbed $Ru_3(CO)_{12}$, we employed a digital background subtraction technique in some cases, as illustrated in Figure 2. Figure 2a shows the spectrum in the range 240–2250 cm^{-1} obtained by averaging the IET spectra from four separate junctions, each exposed to the $Ru_3(CO)_{12}$. Figure 2b shows the spectrum of a clean junction in the same frequency range. The intensities of the aluminum oxide vibrational modes at 940 cm^{-1} in the two spectra are matched visually, and the clean spectrum is then subtracted from the spectrum with the adsorbate present. The result is shown in Figure 2c, expanded vertically by a factor of 3. The region between approximately 800–1150 cm^{-1} has been omitted for clarity. Sharp spurious features appear in this region due to a slight mismatch in the shape of the sharp aluminum oxide modes.

The strongest, most reproducible spectra were obtained by heavily hydroxylating (or deuteroxylating) the aluminum oxide surface before cooling and exposing the sample to $Ru_3(CO)_{12}$. This

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Table I. Vibrational Frequencies for $Ru_3(CO)_{12}$ and Corresponding Mode Assignments, as Observed by IET, Raman, and IR Spectroscopies[a]

IETS[b]	Raman[c]	IR[c]	IR[d]	mode assignt for $Ru_3(CO)_{12}$[e]	EELS[f]
2136	2127			A_1' symmetric axial CO stretching vibration	
		2062	2065	A_2'' antisymmetric axial CO stretching vibration	2080
		2053			
		2042			
	2034			E'' axial CO stretching vibrations	
1919	2028	2026	2035	E'	
	2011			A_1' symmetric radial CO stretching vibration	
	2004	2002	2010	E' radial CO stretching vibrations	
	1994			E'	
	1989	1989		A_2' antisymmetric radial CO stretching vibration	
614	607	606		predominantly Ru–C–O deformation in character (no detailed assignment attempted)	
	596	594			
		574			
547	546	546			
	513	512			
488	489				
456	458	466		predominantly Ru–C stretching in character (no detailed assignment attempted)	
	446	448			444
		400			
389	392	389			

[a] The bands observed for CO bound to the (001) surface of Ru via EELS are included on the far right for comparison. [b] Inelastic electron tunneling spectrum of molecular $Ru_3(CO)_{12}$ bound to Al_2O_3 (this study). [c] Raman and IR spectra of solid $Ru_3(CO)_{12}$.[27] [d] IR spectrum of molecular $Ru_3(CO)_{12}$ bound to silica.[13] [e] With D_{3h} symmetry.[27] [f] Electron energy loss spectrum of CO bound to the (001) plane of Ru.[20]

is consistent with the results of Anderson et al.[12] which showed that $Ru_3(CO)_{12}$ did not adsorb on silica or γ-alumina if the oxides were dried at high temperature (630 K) under vacuum.

Several features can be identified clearly in the IET spectra obtained from junctions prepared by adsorbing $Ru_3(CO)_{12}$ on cooled, hydroxylated aluminum oxide, followed by Pb evaporation on the cold sample. Figures 2a,c show the normal and difference spectra, respectively, obtained from such junctions. At low frequency, there is a weak feature at 389 cm^{-1}, next a prominent doublet at 456 and 488 cm^{-1}, followed by two peaks at 547 and 614 cm^{-1}. At the high-frequency end of the spectrum, two features are seen: a broad peak centered at approximately 1919 cm^{-1} and a somewhat sharper peak at 2136 cm^{-1}. The three remaining features, a sharp peak at 1052 cm^{-1} and two broad peaks at 1395 and 1580 cm^{-1}, are due to hydrocarbon contaminants present in the junction. For junctions prepared following the same procedure except that the oxide surface is partially deuteroxylated by exposure to D_2O before cooling and adsorbing the $Ru_3(CO)_{12}$, the resulting low-frequency spectra are identical with those described above, as shown in Figure 2d. The features ascribed to the adsorption of $Ru_3(CO)_{12}$ are listed in Table I.

In the spectral region between 2200 and 4000 cm^{-1} no features are seen that may be attributed to $Ru_3(CO)_{12}$ adsorption. Broad features are located at approximately 3630 and (for deuteroxylated samples) 2710 cm^{-1} which are due to surface OH and OD stretching vibrations, respectively. Peaks are also seen at approximately 2900 and 3030 cm^{-1} which are attributed to CH stretching modes of hydrocarbon contamination.

It has been reported that $Ru_3(CO)_{12}$, when adsorbed on silica[12,13] and γ-alumina[12] at room temperature, retains its molecular structure. Thus, it would be reasonable to expect that $Ru_3(CO)_{12}$ would also adsorb molecularly on the cooled alumina surface of a tunnel junction. This hypothesis is supported by the close agreement between the observed IET spectral features and observed infrared and Raman features found in solid $Ru_3(CO)_{12}$.[27] These IR and Raman peak locations are listed in Table I. Also listed in Table I are the CO stretching frequencies seen in an IR study of $Ru_3(CO)_{12}$ molecularly adsorbed on silica. Mode assignments for the IR and Raman Bands are also listed.

In the CO stretching frequency region, for the optical spectra we see a strong Raman active mode located at 2127 cm^{-1} and, at lower frequency, a number of closely spaced peaks centered at approximately 2020 cm^{-1}. Although this correlates rather well with the IET spectra, there is one significant question. In IETS, the top Pb electrode has the effect of downshifting the frequencies of vibrational modes and broadening the peaks.[28]

This effect is generally significant for chemisorbed CO.[4-6] Why, then, is the 2136-cm^{-1} IETS peak, in fact, shifted *up* in frequency over the corresponding 2127 cm^{-1} Raman mode? This can be explained easily. The small upshift in frequency (9 cm^{-1}) is due simply to a change in the electronic environment of the complex upon adsorption on the alumina surface. Upshifts of similar magnitude are also seen for two of the three IR bands for $Ru_3(CO)_{12}$ adsorbed on silica,[13] as noted in Table I.

If we assume that the $Ru_3(CO)_{12}$ is bound to the oxide surface with the plane of the Ru_3 triangle parallel to the surface, then those axial CO ligands located on the complex adjacent to the oxide will be significantly farther from the Pb interface, approximately 5 Å, than the other CO groups. This will greatly decrease the influence of the Pb on the vibrations associated with these bonds. For an estimate of the frequency shifts expected, the theory outlined by Kirtley and Hansma[28] may be used. They have shown that the frequency shift is given by eq 1, where q_0

$$\Delta\omega = \frac{-{q_1}^2}{32\pi\epsilon_0 m\omega_0 {n_1}^2 d^3}\left\{1 + \frac{3}{2}\left(\frac{m{\omega_0}^2}{2E_D}\right)^{1/2}\frac{q_0 d}{q_1}\left[1 - \left(1 + \frac{a}{2d}\right)^{-2}\right]\right\} \tag{1}$$

and q_1 are the dipole moment and dipole derivative, respectively, of the bond, ω_0 is the unshifted frequency of vibration, m is the reduced mass, d is the distance separating the bond and the Pb image plane, E_D is the dissociation energy of the bond, n_1 is the dielectric constant of the oxide, and ϵ_0 is the permittivity constant. The second term in braces will be much less than one for CO,[5] and so it will be neglected.

The lower frequency CO stretching mode is seen to be shifted by approximately 100 cm^{-1}. If we assume that this shift is due to the close proximity of the Pb to those CO groups located on the side of the complex nearest the Pb, we may use this observed shift to estimate the effect of the Pb on the other vibrations. For CO bound to Rh on alumina, Kroeker et al. estimated d to be approximately 0.8 Å (if ${n_1}^2 = 3$).[5] We would expect d to be the same for the CO ligands nearest the Pb for the $Ru_3(CO)_{12}$ complex. The CO ligands adjacent to the oxide will then be approximately 5.8 Å from the Pb. With the assumption that the

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bonds are otherwise the same, the frequency shift expected for the CO stretching vibrations of those axial ligands on the complex adjacent to the oxide is $100\,(0.8/5.8)^3$ or approximately 0.3 cm^{-1}, and this is not observable in our spectra. Since the 2136 cm^{-1} is associated with the stretching of these axial CO groups, it is not surprising that our spectra do not show an observable downward shift in frequency.

The effect of the Pb on the low-frequency metal-carbon stretching modes may also be estimated. Ibach has found from electron energy loss spectra that the dipole derivatives of the metal-carbon stretching modes of CO groups terminally bound to Ni and Pt are 0.34 and 0.38, respectively, of the dipole derivatives of the corresponding CO stretching mode.[29] Thus, we will assume $q_1(\mathrm{MC}) = 0.4q_1(\mathrm{CO})$. The d associated with the M-C stretching mode will be taken as approximately 2.9 Å. As a worst case estimate, ω_0 will be taken as 389 cm^{-1}. The reduced mass of the Ru-CO mode is approximately 22 amu as compared to 6.9 amu for the CO stretching mode. Thus, the expected mode shift is

$$\Delta\omega(\mathrm{CO})\left(\frac{q_1(\mathrm{MC})}{q_1(\mathrm{CO})}\right)^2\left(\frac{d(\mathrm{CO})}{d(\mathrm{MC})}\right)^3\left(\frac{\omega_0(\mathrm{CO})}{\omega_0(\mathrm{MC})}\right)\left(\frac{m(\mathrm{CO})}{m(\mathrm{MC})}\right) = 100(0.4)^2\left(\frac{0.8}{2.9}\right)^3\left(\frac{2020}{389}\right)\left(\frac{6.9}{22}\right)$$

which is approximately 0.5 cm^{-1}. Since this was calculated for the lowest frequency mode for a Ru-C bond closest to the Pb, the effect on any other Ru-C stretching mode is expected to be even less. If the effect on the MCO bending modes is assumed to be of the same order of magnitude, then the shifts in the frequencies of the low-energy features will not be detectable, in agreement with our observations.

The locations of the IETS features in the low-frequency region of the spectrum agree quite well with features reported in optical spectra,[27] as seen in Table I. Not all of the features are resolved in the tunneling spectra, due to the fact that the resolution in IETS at 4.2 K using a 1 meV modulation voltage is on the order of 15 cm^{-1}. Thus, modes separated by less than that amount will appear as a broadened feature. Exact assignment of these low-frequency modes was not attempted, due to the lack of any isotopic data. However, in general, those bands between 350 and 500 cm^{-1} are ascribed to modes with predominantly metal-carbon stretching character, while those bands between 500 and 650 cm^{-1} are attributed to modes of metal-carbon-oxygen bending character.[27]

Our results can be compared also to the EELS results for CO adsorbed on the close-packed (001) surface of a Ru single crystal.[20] In EELS, only two peaks are observed corresponding to the symmetric CO stretching vibration (the frequency of which varies with coverage from 1984 to 2080 cm^{-1}) and the symmetric Ru-C stretching vibration (445 cm^{-1}) attributed to CO bound linearly on the surface. The frequencies of these modes observed at saturation coverage of CO are listed in Table I. For specular scattering, only vibrations with a dipole derivative normal to the surface can be observed with EELS. Hence, the Ru-CO bending vibrations are not seen. The Ru-C stretching frequency fits quite well into the general assignments made for the low-frequency modes of $Ru_3(CO)_{12}$. In the CO stretching region, due to interadsorbate interactions, the frequency of the symmetric CO stretching mode is seen to increase as the density of CO groups on the surface increases.[20] At saturation on Ru(001), the CO molecules are still separated by 3.33 Å,[20] whereas the axial CO ligands on $Ru_3(CO)_{12}$ are separated by only 2.88 Å. Thus, if this frequency shift with CO coverage continues, we would expect the symmetric stretching frequency for the axial CO groups on $Ru_3(CO)_{12}$ to be higher than the CO stretching frequency for a saturation coverage of carbon monoxide adsorbed on Ru, as observed. Thus, the EELS results for CO bound to the Ru(001) surface are consistent with the IETS results for $Ru_3(CO)_{12}$.

In view of these results, we conclude that when a hydroxylated alumina surface is exposed to $Ru_3(CO)_{12}$ in the vapor phase, this complex will adsorb associatively, retaining its molecular structure.

When the sample with the adsorbed $Ru_3(CO)_{12}$ is heated to approximately 470 K (by heating the Al film resistively) in the presence of 0.1 torr of oxygen (undoubtedly with some H_2O vapor in the background) and recooled prior to evaporation of the Pb, the resulting IET spectrum is altered appreciably. First, all IET spectral features associated with adsorbed molecular $Ru_3(CO)_{12}$ are no longer observed. Second, there is a significant increase in the 1840-cm^{-1} harmonic of the 940-cm^{-1} oxide peak (indicative of an increase in bulk hydroxide in the alumina[30]), as well as an apparent increase in the low-frequency shoulder of the 940-cm^{-1} peak usually attributed to OH bending vibrations. This latter effect is seen also in junctions prepared in the same manner without the presence of adsorbed $Ru_3(CO)_{12}$ and may indicate that when the oxide is heated in the presence of background H_2O vapor with an excess of O_2, additional hydroxyl groups may form on the alumina. These hydroxyls, at elevated temperatures, may then be able to diffuse into the bulk. A similar effect was seen when excess hydroxyl groups were formed by the adsorption of ethanol on alumina at elevated temperatures.[31]

Also, the junction resistances of those samples with adsorbed $Ru_3(CO)_{12}$ heated in oxygen were not appreciably lower than the resistances of those junctions with $Ru_3(CO)_{12}$ present, but unheated. Samples prepared following the same heating procedure, without exposure to the complex, required twice the oxidation time to obtain acceptable resistances. This would imply that some contribution from the Ru is still present after the complex is heated in O_2. Robertson and Webb found that if $Ru_3(CO)_{12}$ adsorbed on silica is exposed to air, even at room temperature, the complex is oxidized losing all its CO ligands leaving a catalytically inactive surface species.[13] This may be occurring to some extent with the IETS samples. However, no reproducible features are seen in the tunneling spectra which may be attributed to Ru-O vibrations. This would imply that the coverage of Ru oxide species, if it is present, is small, or very weakly coupled to the tunneling electrons. Desorption of the $Ru_3(CO)_{12}$ is likely to occur also, as was seen with $[RhCl(CO)_2]_2$,[19] which would account for at least some of the decrease in intensity.

Reheating this type of sample in 0.1 torr of CO to greater than 470 K did not alter the appearance of the resulting IET spectrum. This does not prove that there is no Ru on the surface. However, if there is Ru present, it is not in a form which is easily reduced. One experiment which would clearly show the presence of Ru would be to examine the oxides, as prepared above, with X-ray photoelectron spectroscopy (XPS). This may also yield information on the oxidation state of the metal atoms. Plans are being made to conduct this study.

Conclusions

This paper presents the results of an IETS investigation of the adsorption of $Ru_3(CO)_{12}$ on aluminum oxide.

It was found that $Ru_3(CO)_{12}$ adsorbs, retaining its molecular structure, when exposed to a cold, hydroxylated alumina surface, as evidenced by the agreement between IET spectra and Raman and IR spectra of solid $Ru_3(CO)_{12}$. If this adsorbed $Ru_3(CO)_{12}$ is subsequently heated to 470 K in O_2, the IETS features due to the complex are no longer observed due to probable desorption and possible oxidation of the complex.

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