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The Application of High Resolution Electron Energy Loss
Spectroscopy to the Study of Model Supported Metal Catalysts

by

L.H. Dubois, P.K. Hansma and G.A. Somorjai

Prepared for Publication

in the

Applications of Surface Science

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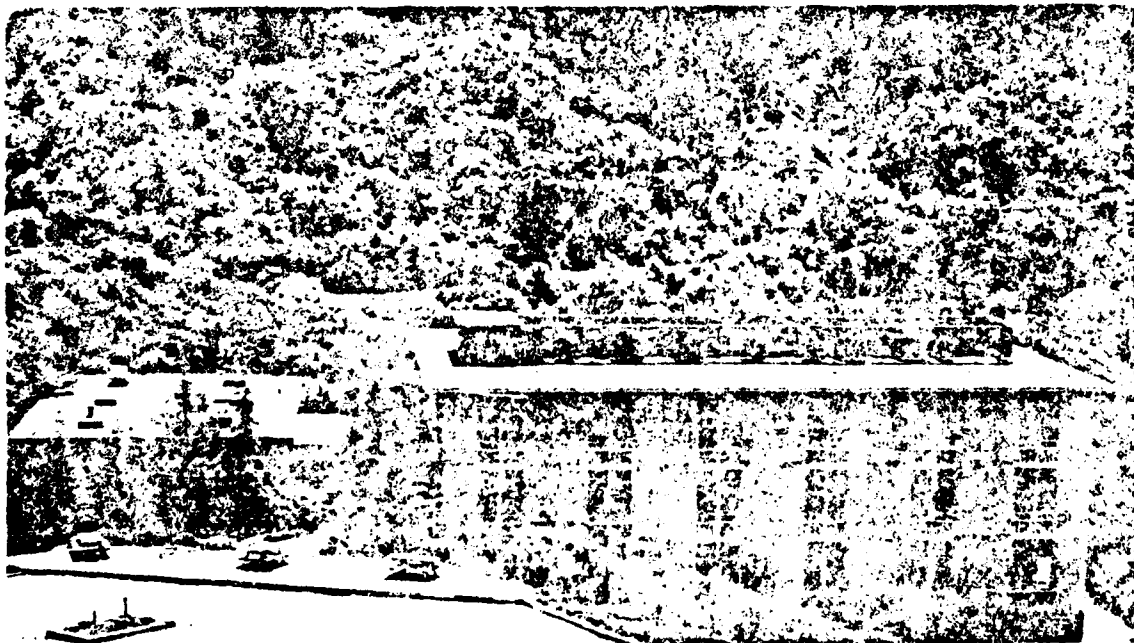
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THE APPLICATION OF HIGH RESOLUTION ELECTRON ENERGY LOSS
SPECTROSCOPY TO THE STUDY OF MODEL SUPPORTED METAL CATALYSTS

L. H. Dubois, P. K. Hansma and G. A. Somorjai

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Model supported metal catalysts were fabricated by evaporating a small quantity of rhodium onto an oxidized aluminum substrate. High resolution electron energy loss spectroscopy (ELS) was successfully used to obtain the vibrational spectra of carbon monoxide chemisorbed on these model catalysts. The ELS spectra are compared with vibrational spectra obtained by infrared spectroscopy and inelastic electron tunneling spectroscopy for CO chemisorbed on similar model catalysts.		

The Application of High Resolution Electron
Energy Loss Spectroscopy to the Study of
Model Supported Metal Catalysts

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Abstract

Model supported metal catalysts were fabricated by evaporating a small quantity of rhodium onto an oxidized aluminum substrate. High resolution electron energy loss spectroscopy (ELS) was successfully used to obtain the vibrational spectra of carbon monoxide chemisorbed on these model catalysts. The ELS spectra are compared with vibrational spectra obtained by infrared spectroscopy and inelastic electron tunneling spectroscopy for CO chemisorbed on similar model catalysts.

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Introduction

The characterization of molecules adsorbed on supported metal catalysts is of key importance for gaining a fundamental understanding of the mechanisms of catalysis. Vibrational spectroscopy has been, and will continue to be, one of the most important tools for this characterization.¹ To date, infrared spectroscopy has been the most widely used technique.^{2,3} Its key advantage is that it can be applied to real catalysts under conditions similar to those used in the chemical technology with very high resolution ($<1\text{ cm}^{-1}$). However, due to light adsorption by the oxide support below $\sim 1200\text{ cm}^{-1}$ low frequency vibrational modes, which are essential in structural determination, are completely masked.⁴⁻⁶ More recently, Raman spectroscopy⁷ and inelastic electron tunneling spectroscopy have been used to obtain the vibrational spectra of molecules adsorbed on model supported catalysts.⁸⁻¹⁰ These spectroscopic techniques can extend the spectral range over which a catalyst can be studied, but both present problems of their own including fluorescence and sample heating in the case of Raman spectroscopy⁷ and uncertainty due to the top metal electrode in the case of tunneling spectroscopy.¹¹ Nevertheless, the problem of characterizing adsorbed molecules on surfaces is sufficiently complex that any vibrational spectroscopy that can yield new information or information from a different perspective will be useful. In this sense these spectroscopies complement one another.

In this paper we report the first application of high resolution electron energy loss spectroscopy (ELS) to the study of molecules adsorbed on model supported metal catalysts. Most ELS experiments to date have employed well-characterized single

crystal substrates under ultrahigh vacuum conditions.¹² High resolution ELS has been successful in these studies due to its broad spectral range (400 - 4000 cm^{-1}) and high surface sensitivity (0.001 monolayer for strong scatterers¹²).

We have now extended our previous ELS experiments on single crystal rhodium surfaces^{13,14} to include studies of the chemisorption of carbon monoxide on model rhodium on alumina catalysts. Good quality vibrational spectra were obtained from CO adsorbed on small rhodium particles vapor deposited on an oxidized aluminum substrate. We employed the same catalyst preparation procedure that proved successful in inelastic electron tunneling investigations.⁹ The ELS results can be favorably compared with the vibrational spectra of adsorbed carbon monoxide obtained by infrared¹⁵⁻¹⁷ and inelastic electron tunneling⁹ spectroscopy on similar rhodium on alumina model catalysts.

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Experimental

Experiments were carried out in an ion pumped stainless steel ultra-high vacuum chamber built in two levels. The upper portion contained the standard single crystal surface analysis equipment (four grid LEED/Auger optics, glancing incidence electron gun and a quadrupole mass spectrometer) and our evaporation sources. The metal deposition was monitored using an oscillating quartz crystal microbalance. After fabrication, the sample was lowered into the high resolution electron energy loss spectrometer by an extended travel precision manipulator. The spectrometer is described elsewhere.¹⁸ In the present series of experiments the electron beam has an energy of approximately 5 eV and the angle of incidence is fixed at 65° to the surface normal. Electrons are only collected in the specular direction. The elastic scattering peak has a full width at half maximum (FWHM) between 80 and 100 cm^{-1} and a maximum intensity of 1×10^4 counts per second.

Figure 1 is a cross sectional view of our model supported metal catalysts. They were formed by:

1. evaporating from 200 to 2000 Å average thickness of Al from an aluminum wire on a stranded tungsten filament onto a clean metal substrate. The metal deposition rate was approximately 10 Å/sec. In our studies a Pt(111) single crystal was used as the metal substrate, although the results should be independent of the substrate material. The evaporated aluminum layer is polycrystalline with grain sizes on the order of microns.⁹
2. oxidizing this aluminum in oxygen or air at exposures ranging from 1000 L (1 L = 1 Langmuir = 10^{-6} torr·sec = 1.33×10^{-4} Pascal·sec) to greater than 10^6 L at temperatures between 300 and 480 K. Aluminum oxidized in this manner has been shown to resemble γ -alumina in

both its physical and catalytic properties.^{19, 20} The polycrystalline oxide layer is typically $10 \text{ \AA}$ thick;^{21, 22} the grain size is not known.

3. evaporating from 1 to $20 \text{ \AA}$ average thickness of Rh from a rhodium wire wrapped around a stranded tungsten filament in 1×10^{-5} torr of CO. The metal deposition rate was approximately $0.25 \text{ \AA/sec}$. Rhodium evaporated in this manner has been shown to agglomerate into small, highly dispersed particles on the alumina support.⁹ Kroeker, et al. using the same type of rhodium sources, source to substrate distances and oxidized aluminum substrates found with transmission electron microscopy that typical Rh particle diameters were $20 - 30 \text{ \AA}$ for a $4 \text{ \AA}$ average thickness.⁹ These particles are similar in both size and distribution to those formed from the reduction of transition metal salts on alumina to prepare commercial catalysts.

Preparing samples by first evaporating rhodium in vacuum and then exposing the dispersed metal particles to carbon monoxide caused a decline in both the scattering intensity and in the resolution of the vibrational spectra. Similar observations have been reported using inelastic electron tunneling spectroscopy;²³ however, the reasons for these findings are not understood at present.

Experimental Results

Figure 2 shows Auger spectra of the oxidized aluminum used as a substrate for our model supported metal catalysts (upper trace), the substrate plus evaporated rhodium particles (middle trace), and a single crystal surface of rhodium (lower trace). Note in the Auger spectrum of the oxidized aluminum substrate that there are only peaks corresponding to the aluminum in an oxidized state and to oxygen.²⁴ This Auger spectrum is independent of oxidation conditions over the range studied. After the evaporation of the rhodium particles in 1×10^{-5} torr of carbon monoxide the characteristic rhodium Auger peaks can be clearly seen.²⁵ All peaks in the spectrum can be accounted for as due to oxidized aluminum, to rhodium metal or to carbon monoxide adsorbed on the metal surface. In particular, there are no observable peaks due to the possible evaporation of tungsten from the filament sources (100 - 200 eV).²⁶ We also studied the evaporation of iron and platinum from tungsten filaments and find no trace of tungsten in the deposited particles.

The lower trace in figure 3 is the high resolution electron energy loss spectrum of the oxidized aluminum substrates. The most prominent feature in this spectrum can be assigned to the aluminum oxide phonons. It is a broad band centered just below 900 cm^{-1} and assymmetric to lower energies. This relatively intense alumina phonon band is similar in both position and shape to the peak found by inelastic electron tunneling spectroscopy.^{5,20} It is independent of the oxidation conditions over the range studied. A relatively broad, weak band between 3500 and 3600 cm^{-1} corresponding to the O-H stretching mode of surface hydroxyl groups is generally seen in both the infrared² and inelastic electron tunneling spectra^{19,20} of γ -alumina. Due to the rather low intensity of this band and to

the decreased sensitivity of our spectrometer at these relatively high energies, this mode is not well resolved here.

The middle and upper traces of figure 3 show the vibrational spectra of CO chemisorbed on the highly dispersed rhodium particles supported on the oxidized aluminum. These spectra have a smaller expansion scale than the alumina spectrum ($\times 10$ as compared to $\times 30$) and this represents a relatively large ratio of inelastic electron scattering to elastic electron scattering. Furthermore, the rhodium is covering a significant portion of the exposed alumina surface. By a $4 \text{ \AA}$ average thickness of evaporated rhodium (middle trace) the intensity of the aluminum oxide phonon band has significantly decreased. By a $20 \text{ \AA}$ average thickness of rhodium (upper trace) this mode has completely disappeared. The prominent low frequency band centered above 400 cm^{-1} is typical of Rh-CO stretching and bending modes^{9,13,27,28} while the two losses near 2000 cm^{-1} are characteristic of $\text{C} \equiv \text{O}$ stretching vibrations.^{9,13,15-17,27,28} In the next section we will discuss the interpretation of these spectra by comparison with infrared¹⁵⁻¹⁷ and inelastic electron tunneling⁹ results on similar model systems.

As can be seen from figure 3, the results are not particularly sensitive to rhodium coverage over this range ($1 - 20 \text{ \AA}$ average thickness); neither are they sensitive to additional CO exposure. Spectra run with CO partial pressures as high as 1×10^{-5} torr show no substantial differences. However, the relative intensities of the two high frequency $\text{C} \equiv \text{O}$ stretching modes can be significantly altered by heating the sample above 530 K in vacuum. After exposing this surface to $>1000 \text{ L}$ of CO only a single carbon-oxygen stretching vibration is observed at 2010 cm^{-1} . This is clearly

shown in figure 4. Spectra run with 1×10^{-5} torr of CO in the background also show no significant intensity in the 1870 cm^{-1} mode (fig. 4, upper trace).

Discussion

Figures 3 and 4 clearly show that we are now able to obtain high resolution electron energy loss spectra from carbon monoxide adsorbed on model rhodium on alumina catalysts. One might anticipate charging of the aluminum oxide and diffuse scattering due to the rough surface. We find that charging does not present a problem because the oxidized aluminum layer is thin enough ($10 - 15 \text{ \AA}$) to allow relatively low impedance electron tunneling. In particular, under similar oxidation conditions we expect an Al-Al₂O₃-Pb tunnel junction to have a barrier impedance of much less than 100 ohms for a 1 cm^2 sample.⁹ The incident beam current in our spectrometer is less than 10^{-9} amps;¹⁸ thus the potential across the oxide is expected to be less than 10^{-7} volts. We could not calculate in advance the effect of the diffuse surface scattering, although the aluminum grains are in the micron size range and the rhodium particles are $20 - 30 \text{ \AA}$ in diameter. Experimentally we find that though both the elastic and inelastic peaks are broader in their angular distribution when compared to scattering from a clean Rh(111) surface,¹³ the intensity loss is not severe enough to prevent the measurements. We find that the elastic peak intensity (I_0) is down by roughly an order of magnitude; the inelastic peak intensity (I_s) is down by less than an order of magnitude. The reasons for the relatively large ratio of inelastic electron scattering to elastic electron scattering are not completely understood at present. However, Ibach²⁹ has shown that due to the finite collection angle of the spectrometer this intensity ratio (I_1/I_0) can be a function of surface disorder. In particular, I_1/I_0 increases with increasing surface disorder and therefore care must be taken in the analysis of peak intensities.

Finally, we see no evidence for significant peak broadening and loss of resolution due to local charging. However, with this sample configuration both the elastic and inelastic scattering peaks are approximately 10 cm^{-1} broader (FWHM) when compared to scattering from either a CO covered Rh(111)¹³ or Rh(331)¹⁴ single crystal surface.

Figure 5 compares the electron energy loss spectra of the current work to previously obtained inelastic electron tunneling⁹ and infrared spectra¹⁶ of CO on rhodium supported on alumina. Some of the advantages and disadvantages of the various techniques are clear in this figure. Infrared spectroscopy has the best resolution but the spectrum does not extend to the low frequency region. Tunneling spectroscopy has reasonable resolution in the low frequency region, but there are questions about the effects of the top metal electrode that are not fully answered in the existing literature. In particular, how much should the low frequency modes be perturbed by the presence of the top metal electrode? Although there are estimates based on the observed mode shifts in other systems,¹¹ there have been no direct measurements on this type of system.

Previous researchers have identified three different types of carbon monoxide molecules adsorbed on alumina supported rhodium catalysts (see figure 5).^{13, 26} These include a bridge bonded species, $\text{Rh}_2 = \text{CO}$ ($\nu_{\text{C=O}} \approx 1870 \text{ cm}^{-1}$), a terminally bonded species, Rh-CO ($\nu_{\text{C=O}} \approx 2020 \text{ to } 2070 \text{ cm}^{-1}$, depending on coverage) and a gem dicarbonyl species, Rh-(CO)_2 ($\nu_{\text{C=O}} \text{ symmetric} \approx 2031 \text{ cm}^{-1}$, $\nu_{\text{C=O}} \text{ asymmetric} \approx 2101 \text{ cm}^{-1}$). Similarly, we can assign the 1870 cm^{-1} loss in the ELS spectrum of Fig. 5 to a bridge bonded carbonyl. The 2020 cm^{-1} mode most likely belongs to a linearly bonded CO species. The infrared spectrum taken at low CO exposures near the top of figure 5 is similar to the high resolution ELS spectra that we observe. Linearly bonded carbon monoxide molecules dominate the $\text{C}\equiv\text{O}$ stretching region, but some gem dicarbonyl species are also present. The presence of Rh-(CO)_2 species cannot be ruled out on our model supported catalysts since the observed loss at $\sim 2020 \text{ cm}^{-1}$ is quite broad ($\sim 100 \text{ cm}^{-1}$ full width at half maximum). Furthermore, such species are seen with

inelastic electron tunneling⁹ on model rhodium on alumina catalysts prepared in similar manner (figure 5, bottom). The infrared spectrum labeled "saturation coverage" was taken under 50 torr of CO¹⁶ and at these pressures one would expect the gem dicarbonyl surface species to be abundant.

A comparison between the inelastic electron tunneling and electron energy loss spectra in figure 4 indicate that the ELS results seem to represent an envelope of the tunneling results in the low frequency region ($400 - 1000 \text{ cm}^{-1}$). The low frequency modes observed with high resolution electron energy loss spectroscopy for the chemisorption of carbon monoxide on single crystal metal surfaces have been traditionally assigned as metal-CO stretching vibrations on the basis of the normal dipole selection rule.²⁹ This selection rule, which appears to be valid for infrared spectroscopy as well as for high resolution ELS, suggests that only vibrations with a component of the oscillating dipole moment normal to the surface can be excited. Thus if the carbon monoxide is oriented perpendicular to the surface, the incident electrons will only couple to the metal-CO and carbon-oxygen stretching modes. Isotopic substitution studies,⁹ however, have shown that the two most intense low frequency modes in the tunneling spectrum of model rhodium on alumina catalysts (413 and 465 cm^{-1}) are bending modes. Thus one wonders if the low frequency vibrations observed in this spectrum with high resolution ELS are bending or stretching modes. More studies are clearly needed to resolve this question.

The only way we found to significantly alter the intensity ratio of the two $\text{C}\equiv\text{O}$ stretching modes was to heat the rhodium sample above 530 K in vacuum and then to re-expose the surface to carbon monoxide (fig. 4). The vibrational spectra indicate that

there is negligible CO remaining on the surface above 500 K. Carbon monoxide is thought to decompose on both stepped single crystal³⁰ and polycrystalline³¹ rhodium samples at this temperature. Residual carbon and/or oxygen from dissociated CO may be blocking some of the surface sites and inhibiting further CO adsorption. Consistent with this is a decrease in the total integrated intensity of all of the observed ELS peaks. Even with 1×10^{-5} torr of CO above the catalyst sample, no significant intensity is seen in the 1870 cm^{-1} mode (fig. 4, upper trace).

Summary

1. High resolution electron energy loss spectroscopy can be used to study the vibrational spectra of molecules adsorbed on model supported metal catalysts. This technique works well in spite of the surface disorder and roughness. The elastic intensity is lowered by about one order of magnitude from its intensity on single crystal substrates; the inelastic peak intensity is decreased by less than an order of magnitude. The angular distribution of all peaks is broader.
2. ELS spectra of oxidized aluminum (a model system for γ -alumina) are similar to those found by inelastic electron tunneling. They show a relatively intense alumina phonon band that is broad, asymmetric to lower energies and centered around 860 cm^{-1} .
3. High resolution electron energy loss spectroscopy, inelastic electron tunneling spectroscopy and infrared spectroscopy are complementary techniques for studying the vibrational spectra of molecules adsorbed on model supported metal catalysts. The low frequency ^{spectrum} ELS ($400 - 1000\text{ cm}^{-1}$) is an envelope of the tunneling spectrum; the high frequency electron energy loss spectrum ($1000 - 2500\text{ cm}^{-1}$) is an envelope of the infrared spectrum.

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Figure Captions

1. Cross-sectional view of the model supported metal catalyst.

If a small quantity of rhodium is evaporated onto oxidized aluminum it agglomerates into small particles. For an average thickness of $4 \text{ \AA}$ the rhodium particles are 20 to $30 \text{ \AA}$ in diameter.⁹ The oxidized aluminum substrate is 10 to $15 \text{ \AA}$ thick and is similar to γ -alumina.^{19,20}

2. The top trace shows the Auger electron spectrum of the oxidized aluminum support material. Only aluminum in an oxidized state and oxygen peaks are present.²⁴ The middle trace shows the spectrum after $4 \text{ \AA}$ average thickness of rhodium has been evaporated in the presence of 1×10^{-5} torr of carbon monoxide. Both the oxygen and aluminum peaks from the support material are attenuated and there are new peaks due to rhodium and carbon. The bottom trace shows the Auger electron spectrum from a clean single crystal surface of rhodium.

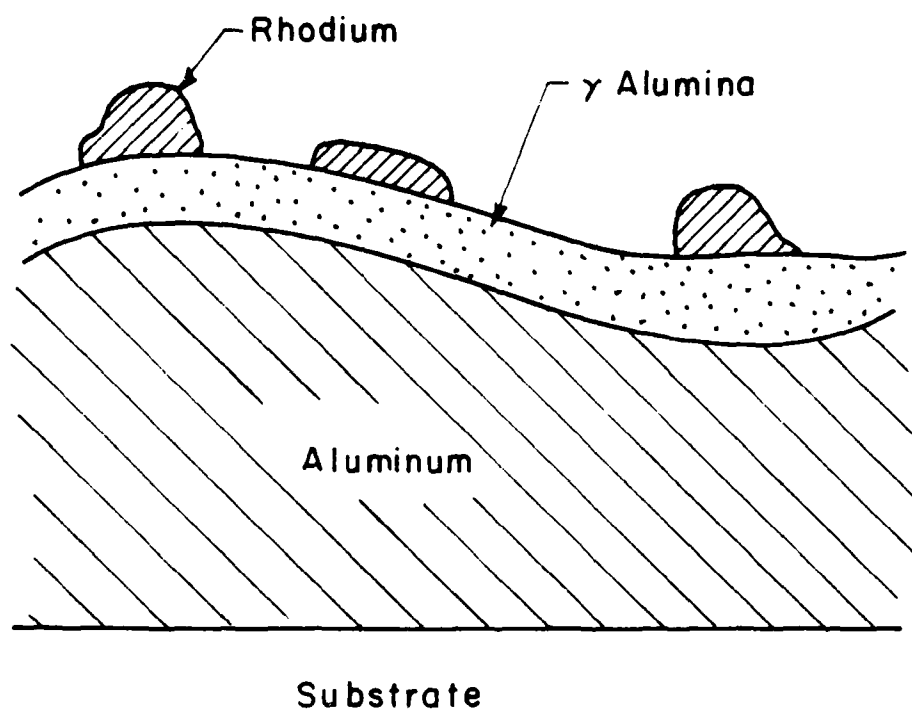
3. The high resolution ELS spectrum for the aluminum oxide support is shown in the lowest trace. The broad band, asymmetric to lower wavenumbers and centered around 860 cm^{-1} is the aluminum oxide phonon band.^{9,20} The upper two traces show the ELS spectra for two different amounts of rhodium evaporated onto the alumina support in 1×10^{-5} torr of CO ($4 \text{ \AA}$ and $20 \text{ \AA}$ average Rh thicknesses). The assignment of the observed losses is discussed in the next section.

4. Vibrational spectra of CO chemisorbed on a $4 \text{ \AA}$ average thickness of rhodium as a function of temperature. The lower trace was run after formation of the model catalyst. The middle trace was taken

after flashing the sample to 530 K in vacuum and then adding 1000 L of CO at 300 K. The upper trace was run in 1×10^{-5} torr of CO also at 300 K.

5. Vibrational spectra taken by three different techniques for carbon monoxide adsorbed on rhodium particles supported on alumina. The infrared spectra (upper traces) are from the work of Yates, et al.¹⁶ The high resolution of ir spectroscopy is evident. The inelastic electron tunneling spectrum (lower trace), taken from the work of Kroeker, et al.,⁹ shows the downshift in the CO stretching vibrations that are characteristic of tunneling spectroscopy and the relatively strong low frequency modes. The electron energy loss spectrum of the present work (middle trace) approximates an envelope of the low frequency ($400 - 1000 \text{ cm}^{-1}$) tunneling spectrum and of the high frequency ($1000 - 2500 \text{ cm}^{-1}$) infrared spectra.

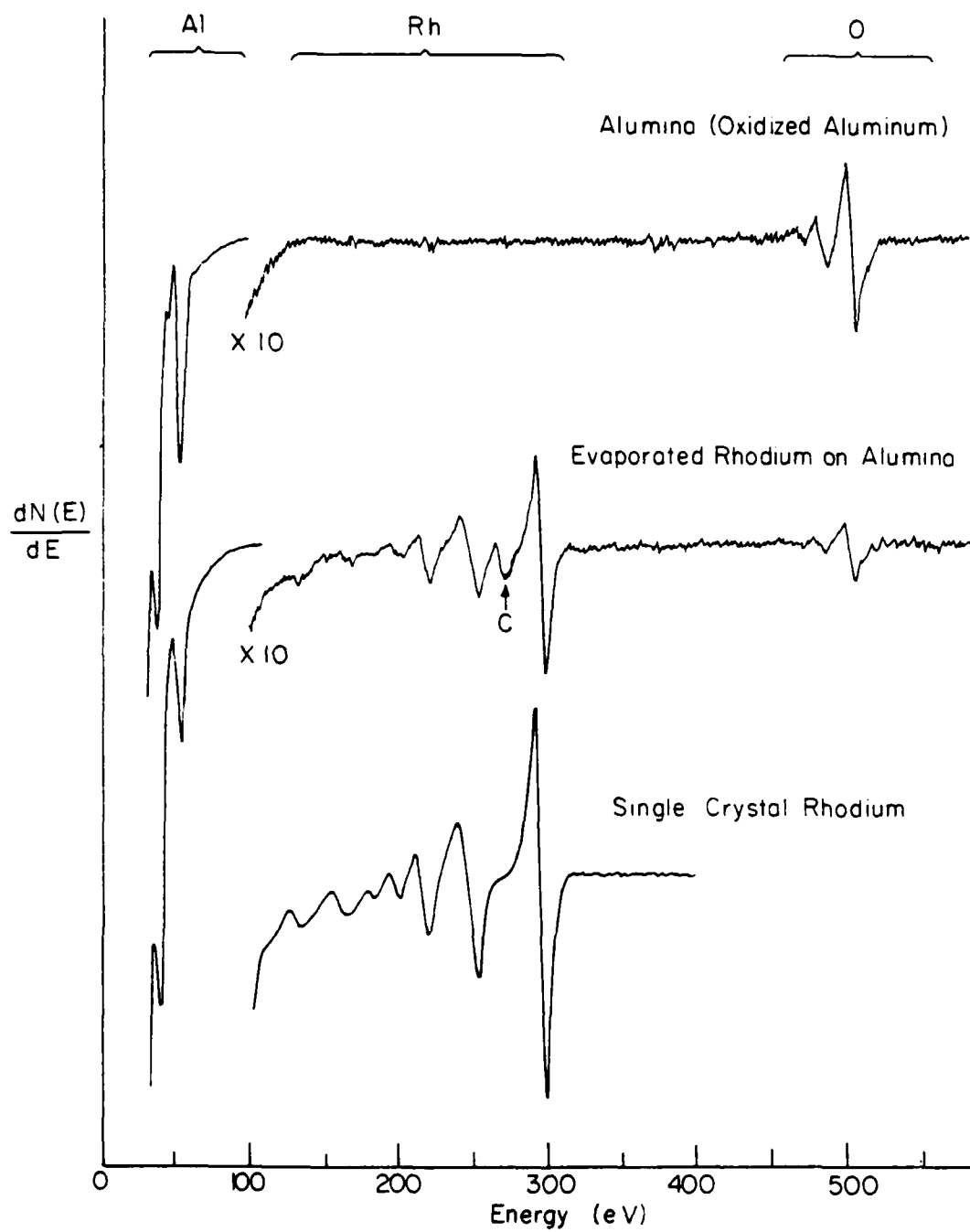
Model Supported Rhodium Catalyst



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Fig.1

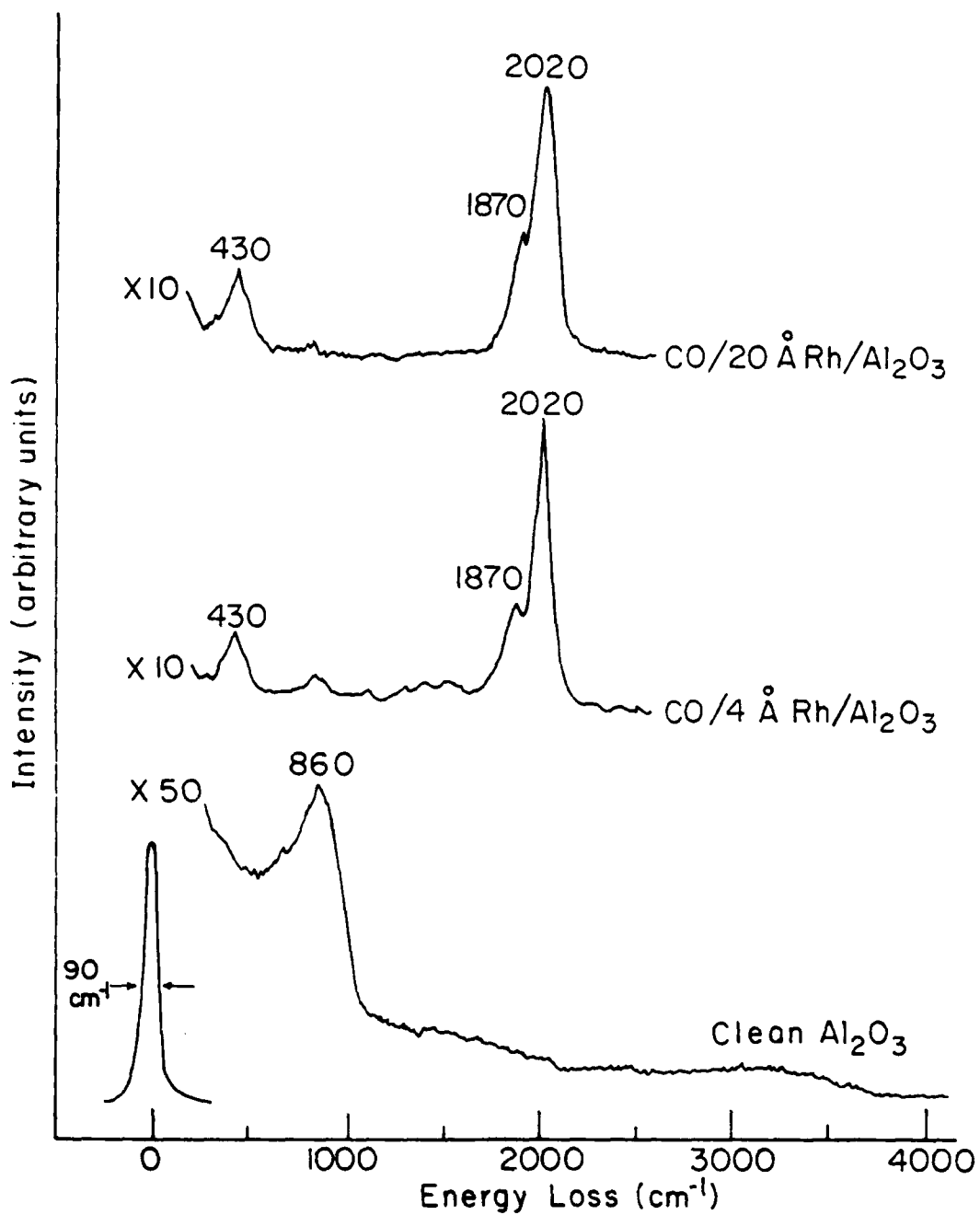
Auger Electron Spectra of Model Catalysts



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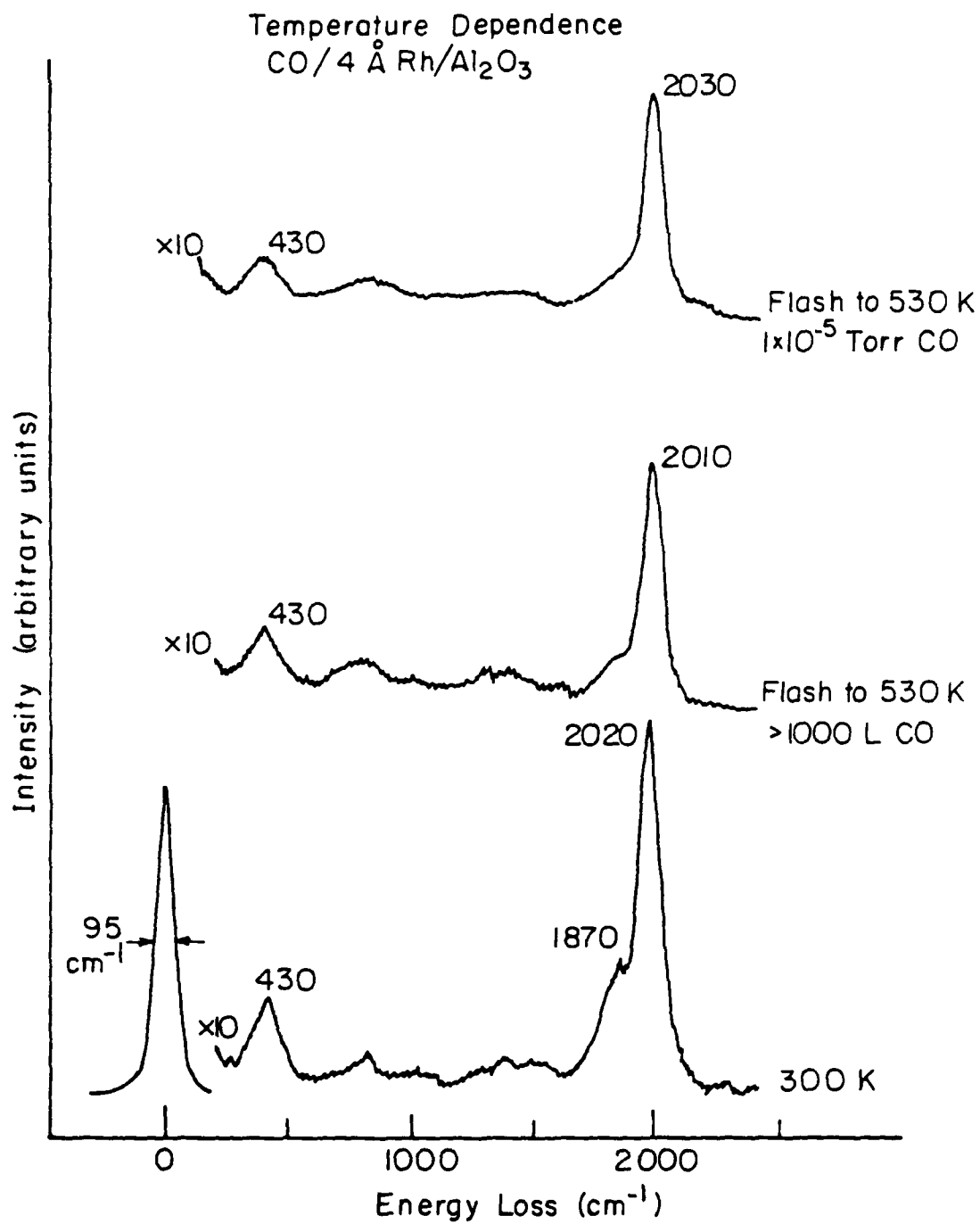
Fig.2

Vibrational Spectra of Model Catalysts



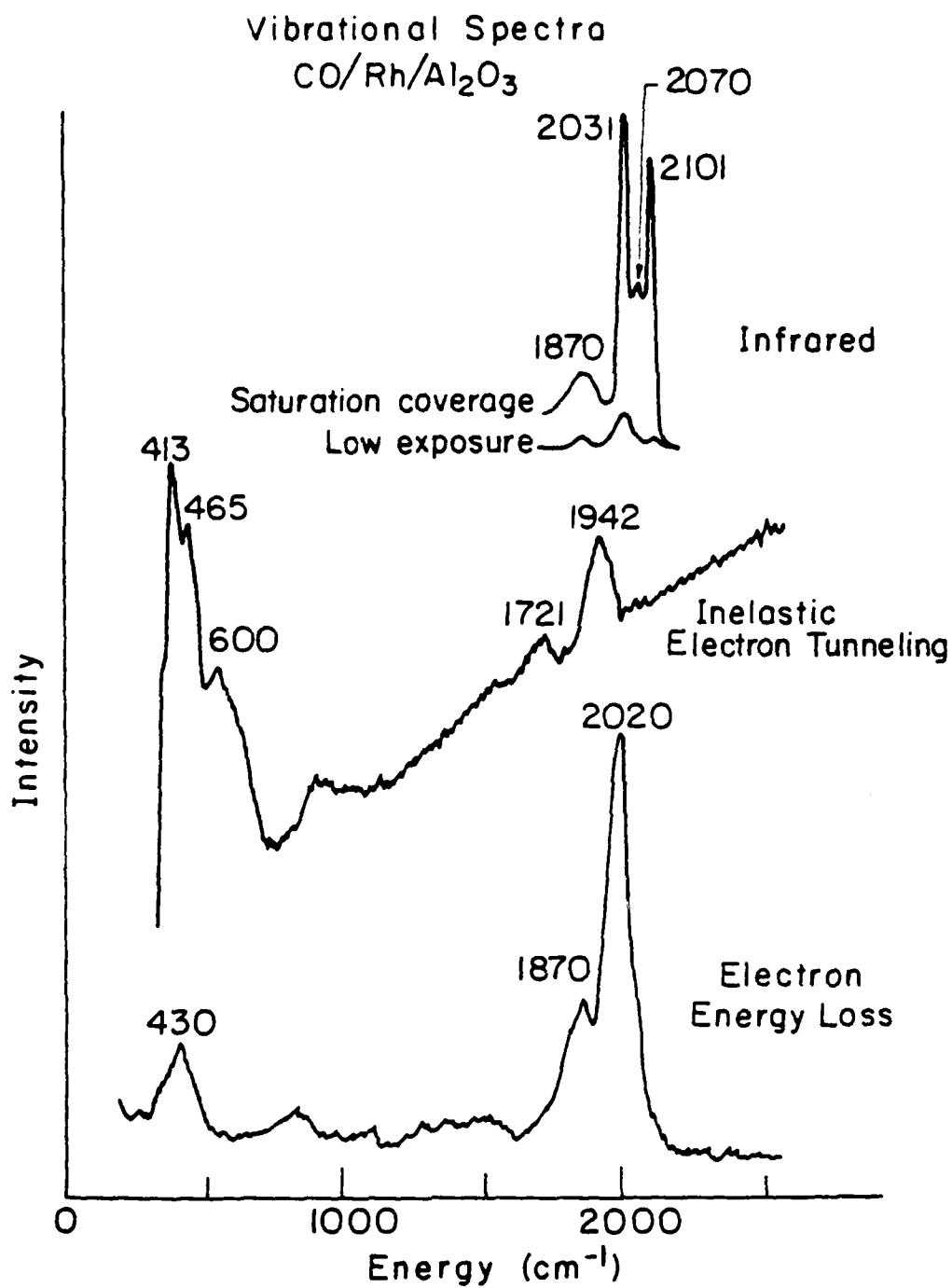
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Fig.3



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Fig.4



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Fig.5

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