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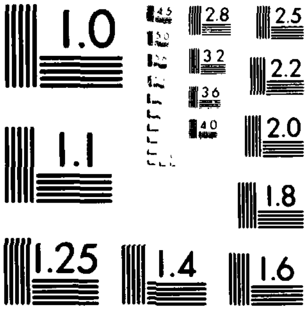

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Vibrational Spectroscopic Studies of Chemisorbed Species on Metal Surfaces

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National Bureau of Standards
Washington, DC 20234

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Abstract

The use of transmission infrared spectroscopy to investigate the chemisorption of CO and an electronic analog to CO is described.

1. Introduction

The study of the chemisorption of molecules on transition metals represents a particularly fertile area of research at the present time. Surface measurement techniques currently at our disposal range from those useful for studying adsorbed layers on single crystal surfaces to techniques which may be readily applied to highly dispersed-supported metal surfaces. It is the latter class of surfaces which more closely resemble heterogeneous catalysts; in fact, the ability to disperse precious metals has been of major importance in enhancing their usefulness as catalysts. In this paper we summarize infrared studies of CO chemisorption on Al_2O_3-supported Rh surfaces, compared to the Rh(111) surface. In addition, we show that electronic analogs to CO exhibit interesting chemisorptive properties.

2. Experimental

Transmission infrared spectroscopy measurements are made through dispersed Rh surfaces supported on γ-Al_2O_3. This high area supported Rh is made by H_2 reduction at 150°C of dispersed Rh^{III} ions on the Al_2O_3. The final preparations contain about 2-3% of Rh by weight, and exhibit a total surface area of about 55 m^2/g (BET, N_2) {1}. The infrared spectrum of chemisorbed species on these surfaces may be measured following the adsorption of known quantities of gas.

3. Results and Discussion

The infrared spectrum following the chemisorption of CO by Rh is shown in Fig. 1. Four spectral features in the carbonyl stretching region are clearly seen. A broad band at 1855 cm^{-1} develops and shifts to 1870 cm^{-1} as CO coverage increases. A second band at ~2056 cm^{-1} shifts upward to 2070 cm^{-1} as coverage increases. These two bands are assigned as bridged and linear (terminal bonded) CO species chemisorbed on Rh sites present in crystalline aggregates of Rh. Recent measurements using electron energy loss vibrational spectroscopy on Rh(111) have shown that at full CO coverage, two carbonyl vibrational frequencies exist at 1870 cm^{-1} and at 2070 cm^{-1} {2} confirming the above assignment. LEED and thermal desorption studies of CO chemisorption on Rh(111) also suggest that two kinds of CO bonding (linear and bridged) exist together at full coverages {3}. The most prominent spectral feature in Fig. 1 is a pair of sharp bands which develop together at 2101 cm^{-1} and 2031 cm^{-1}, without shift of wave number over their entire intensity range. These two features are assigned as the symmetric and asymmetric stretching modes for the species $Rh(CO)_2$.

The lack of wavenumber shift is indicative that the Rh(CO)$_2$ species exist as isolated entities on the surface, i.e., that we are dealing with chemisorbed species on isolated Rh atomic sites. The spectra of Fig. 1 are entirely consistent with previous work {4-7}; the assignments were first made by Yang and Garland {4}.

Additional observations supporting this vibrational assignment have recently been made by our group and others:

a) By changing the loading of the Rh on the Al$_2$O$_3$ from 0.2% to 10%, it has been shown that the spectral features at full CO coverage systematically change. Higher Rh loadings lead to enhancement of intensity near 2070 cm^{-1} and near 1870 cm^{-1} and to reduced intensity for the doublet. The 0.2% Rh surfaces exhibit *only* the Rh(CO)$_2$ doublet, and these surfaces chemisorb 1.9 CO/Rh.

b) ^{13}CO substitution into the Rh(CO)$_2$ species has been shown to exhibit the expected IR spectrum for the species Rh(^{12}CO)$_2$, Rh(^{12}CO)(^{13}CO) and Rh(^{13}CO)$_2$ {1}.

c) Oxygen chemisorption on the Rh surfaces has been shown to destroy the infrared features due to CO chemisorption on Rh crystallites, leading to a spectrum containing only the Rh(CO)$_2$ doublet {8}. It is well-known that oxygen chemisorption on Rh(111) is accompanied by penetration of oxygen into the crystal {9}. For small crystallites, this could be completely disruptive, leading to crystallite destruction.

d) Knozinger et. al {10} have recently prepared Rh(CO)$_2$ species anchored on organic linkages at the surface of high area SiO$_2$. The infrared spectrum for Rh(CO)$_2$ exhibits a sharp doublet at 2085 cm^{-1} and 2003 cm^{-1}. ^{13}CO substitution into the Rh(CO)$_2$ leads to the proper number of spectral features as indicated in (b) above. Decarbonylation of the Rh(CO)$_2$ results in Rh(CO) with a single band at 1943 cm^{-1}. Reversible reformation of Rh(CO)$_2$ may be achieved by exposure of Rh(CO) to CO.

e) ^{13}C-NMR studies of CO on Rh/Al$_2$O$_3$ have detected two ^{13}C-spin lattice relaxation times differing by a factor of $\sim$50 at 300K. These two relaxation times have been attributed to the presence of crystalline and isolated Rh sites {11,12} binding CO in different environments.

Thus, the combined evidence from a number of experiments strongly suggest that for Rh supported on Al$_2$O$_3$, atomic Rh sites capable of chemisorbing 2 CO/Rh coexist with Rh crystallite sites which adsorb both bridged and linear CO species in a fashion similar to that observed on Rh(111) single crystal surfaces.

The similarity of the inorganic chemistry of the CO ligand and the isocyanide ligand is well known {13}. In transition metal carbonyl chemistry, CO ligands and isocyanide ligands are often interchangable moieties. The frontier orbitals of the CO molecule and the isocyanide group are strikingly similar as shown in Fig. 2. CO bonds to transition metals (in carbonyls and in chemisorption) by electron donation from the filled 5σ orbital, followed by back donation into the unfilled antibonding 2π orbital. In CH$_3$NC, more extensive σ_{CN} electron donation would be expected (due to the lower ionization potential) while back donation into the π^*_{CN} would be less likely, compared to CO.

We have begun the investigation of CH_3NC chemisorption by Rh/Al_2O_3 to determine whether analogies exist with CO chemisorption. Infrared spectra for CH_3NC adsorption on 2.8% Rh/Al_2O_3 are shown in Fig. 3. A strong N≡C stretching mode is observed at 2200 cm^{-1}. (For $CH_3NC(\ell)$, the N≡C mode is at 2161 cm^{-1} (13).) In addition, C-H stretching modes are observed at 3003(S), 2946(S), 2918, 2883, 2861, and 2813 cm^{-1}. Bands at 1448(S), 1415(S), and 1391 cm^{-1} are assigned as CH_3 bending modes. Comparable CH_3 modes for $CH_3NC(\ell)$ are at 3002 cm^{-1}, 2951 cm^{-1} and 1456 cm^{-1} and at 1414 cm^{-1}. Subsequent exposure of the CH_3NC-covered surface to CO (50 Torr) is shown in spectrum (d) of Fig. 3. A single new feature, of low intensity, at 2020 cm^{-1} is observed. The absence of strong features normally seen for CO adsorption on Rh indicates that CH_3NC has almost completely blocked specific Rh-CO binding sites. The observation of a single N≡C stretching frequency for chemisorbed CH_3NC indicates that only <u>one</u> CH_3NC ligand adsorbs on Rh sites capable of adsorbing 2 CO ligands. This cannot be understood on the basis of steric effects, and may be due to the greater electron donating ability of CH_3NC compared to CO.

We have used the strong chemisorption of CH_3NC to systematically displace CO from Rh. In Fig. 4, ^{13}CO was chemisorbed initially to full coverage. Addition of CH_3NC is accompanied by loss of intensity of the $Rh(CO)_2$ doublet. In the limit, two ^{13}CO features remain at 1910 cm^{-1} and 1750 cm^{-1}. These features are definitely due to adsorbed CO strongly perturbed by coadsorbed CH_3NC, as their exchange with $^{12}CO(g)$ is observable by infrared spectroscopy. The features are believed to be due to linear and bridged CO species on crystalline Rh sites which have interacted with CH_3NC. This interaction is probably a consequence of σ_{CN} electron donation to the crystallites leading to enchanced back donation into chemisorbed CO and hence to the $\sim$100 cm^{-1} reduction in wavenumber for the two kinds of chemisorbed CO on the crystalline sites.

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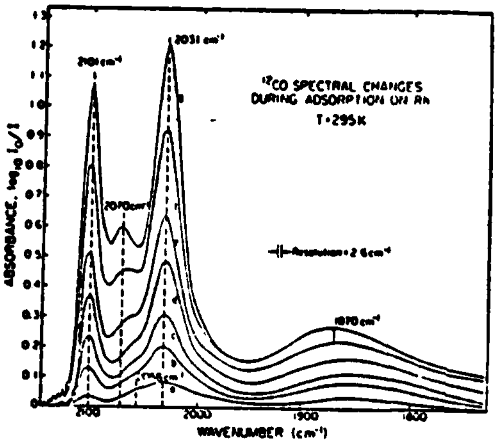


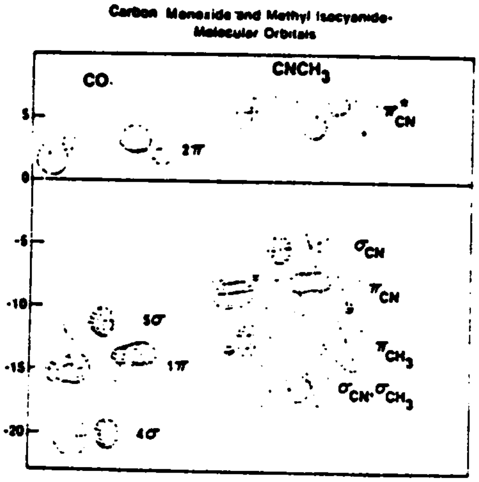
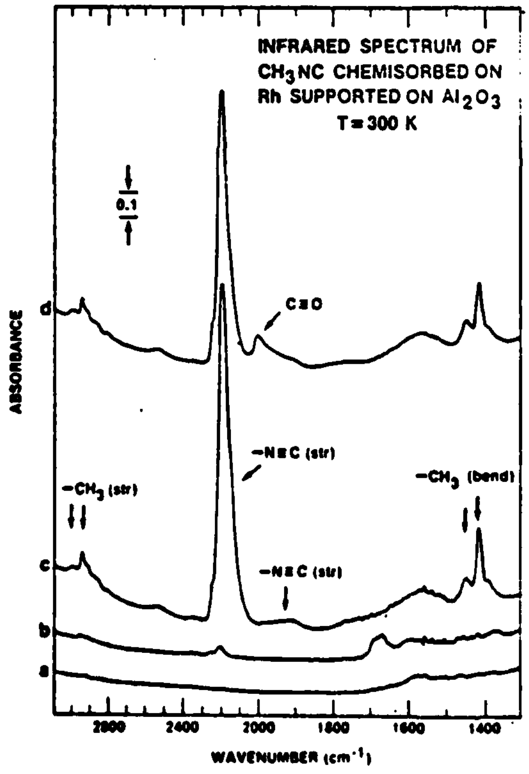


Fig. 1. Infrared spectra for ^{12}CO adsorbed on Rh(2.2%)/Al_2O_3. The CO pressure corresponding to these spectra ranges from 4×10^{-3} Torr-50 Torr.

Fig. 2. CO and CH_3NC Molecular Orbitals



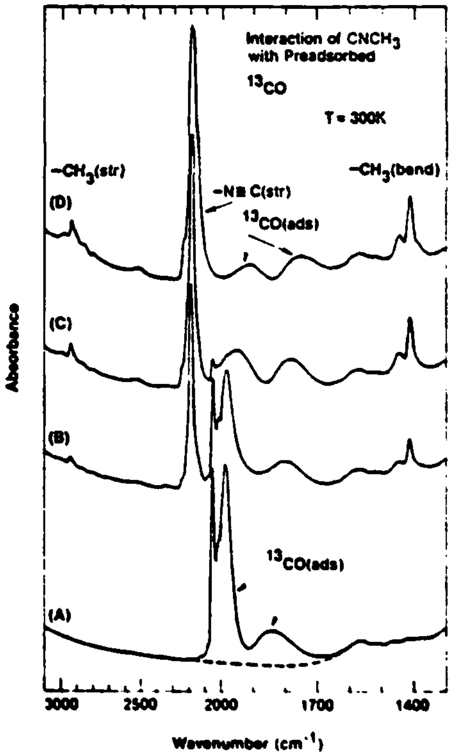


Fig. 3. Infrared Spectrum of CH_3NC Chemisorbed on Rh(2.8%)/Al_2O_3.

Fig. 4. Interaction of CH_3NC with Preadsorbed CO on Rh(2.8%)/Al_2O_3.