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Infrared Spectra of Carbon Monoxide on Ruthenium Predicted by Intermedion Theory

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The infrared spectra of weakly bonded species from CO in contact with adsorbents containing Cr, Fe, Co and Ni were characterized as "intermedions." The vibrational frequencies of these CO intermedions were related to the electronic energy levels of gaseous ions of these metals. From this relationship and the electronic energy levels of Ru II and Ru III, the vibrational frequencies were calculated for CO intermedions on adsorbents containing ruthenium. The infrared spectra of weakly bonded CO on adsorbents containing Ru showed bands at the calculated frequencies of 2146, 2074, and 2041 cm^{-1}. The vibrational frequencies of species that are strongly bonded to the surface, that is, not readily removed by evacuation at room temperature are reported also.

INTRODUCTION

The data and equations have been presented (*1–3*) to calculate the vibrational frequencies of certain weakly bonded adsorbates resulting from the adsorption of carbon monoxide (CO) on adsorbents containing any of some sixteen different metals. The following report describes an experimental test of the intermedion theory by comparing calculated frequencies with those measured for CO in contact with adsorbents containing ruthenium in the 1+, 2+, and 4+ oxidation states. A brief description of the development of these concepts is presented in an accompanying paper on the infrared spectra of carbon dioxide intermedions (*4*).

EXPERIMENTAL METHOD

The experimental method followed that described by Eischens, Pliskin and Francis (*5*) in their pioneering work on the infrared spectra of adsorbed species. A Perkin-Elmer model 112 single-beam, double-pass infrared spectrometer was modified by the installation of a source unit in a vertical position and the replacement of the prism by a grating ruled at 240 lines/mm. Spectra were obtained between 1900 and 2300 cm^{-1}.

The gas handling system is a Varian Associates metal vacuum system composed of a roughing pump, gas manifold, gauge manifold, hivac manifold, and a Vacion pump. The roughing pump is a liquid nitrogen cooled Vacsorb pump with 5A molecular sieves. The Vacion pumps 8-liters/sec giving a clean vacuum at 10^{-6} to 10^{-8} Torr.

The *in situ* cell is 18 cm in length, wrapped with heating tape and fitted with rock salt windows. The infrared beam is focused at the center of the cell on the sample pellet. The cell can be heated to 500°C and evacuated during preparation of samples.

Samples contained $RuCl_3 \cdot 3H_2O$ with Cab-O-Sil at 3–5% metal. A pellet was prepared by compressing 100 mg of this mixture at 60,000 psig into a thin disc, 1 in. in diameter.

Background spectra of the sample were recorded at room temperature after treatment of the sample described with each figure. Carbon monoxide was introduced to 5 Torr and computed spectra run to subtract the background. All spectra were tested by evacuation of the gas from the cell at room temperature. When bands were removed from the spectra by evacuation, spectra were run with the readmission and reevacuation of CO.

EXPERIMENTAL RESULTS

A pellet containing 0.0072 g of $RuCl_3$ and 0.1128 g of Cab-O-Sil, was heated to 300°C and evacuated to 1.2×10^{-5} Torr. The sample was then cooled to room temperature while evacuating to 1×10^{-6} Torr. Carbon monoxide was added to 5 Torr and the spectrum obtained. Two bands were observed at 2143 and 2086 cm^{-1} as shown in Fig. 1. Evacuation of the sample to 8×10^{-3} Torr did not remove these bands from the spectrum. The sample was then heated to 400°C while evacuating. The infrared bands at 2143 and 2086 cm^{-1} decreased. Since these bands were not removed by evacuation at room temperature, they are assigned to strongly bonded species. The sample was heated in 0.1 Torr of oxygen to 300°C and then evacuated. When cooled to room temperature, the addition of CO produced bands at 2008, 2080, and 2140 cm^{-1}, shown in Fig. 2. Evacuation did not remove these bands.

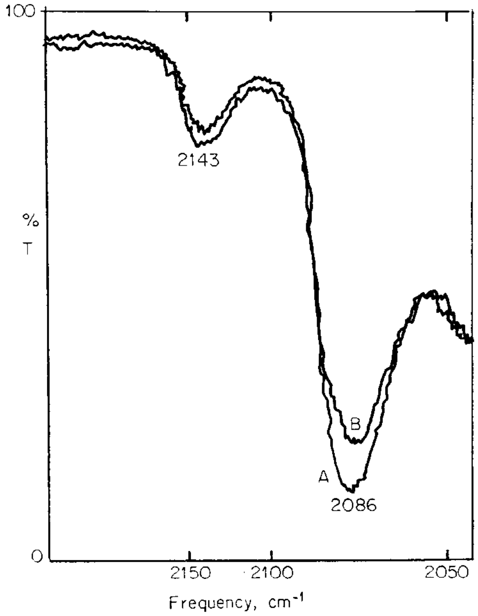

FIG. 1. Infrared spectra of CO adsorbed on $RuCl_3$ after heating sample at 300°C for 4 hr: (A) after addition of CO to 5 Torr; (B) after evacuation.

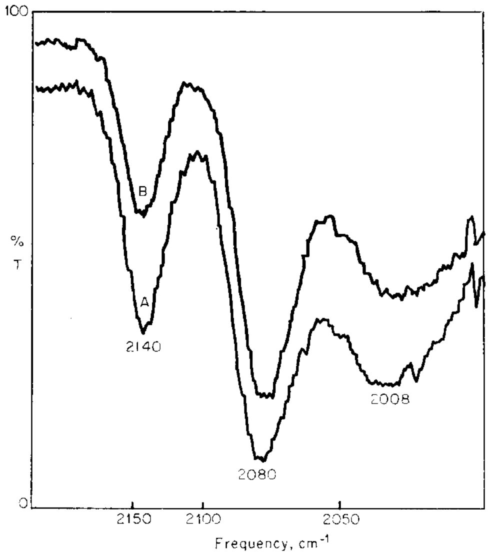

FIG. 2. Infrared spectra of CO adsorbed on $RuCl_3$ after heating sample in oxygen at 0.1 Torr at 300° for 1 hr and then degassed: (A) after addition of CO; (B) after evacuation.

The sample was next reduced with hydrogen at 500°C for 12 hr and evacuated to 10^{-5} Torr. After cooling to room temperature, the sample adsorbed 0.6 Torr of CO. The spectrum contained bands at 2146 and 2040.6 cm^{-1} (Fig. 3). The band at 2146 cm^{-1} was completely removed by evacuation. The band at 2040.6 cm^{-1} was due to a weakly bonded species which absorbed close to a strongly bonded species at 2020 cm^{-1}. The center of the absorption band of the weakly bonded species was obtained by subtracting the absorbance of the band of the strongly bonded species from the larger band envelope which contained both species. The differences in absorbance are plotted in Fig. 3 as the ordinate with wave number as abscissa.

The sample was again oxidized with oxygen at 0.9 Torr at 500°C for 50 hr and evacuated to 6×10^{-6} Torr. After cooling while evacuating to 1×10^{-6} Torr, CO was admitted to a pressure of 5 Torr. The spectrum contained a band at 2074 cm^{-1}, Fig. 4. This band was also removed by evacuation.

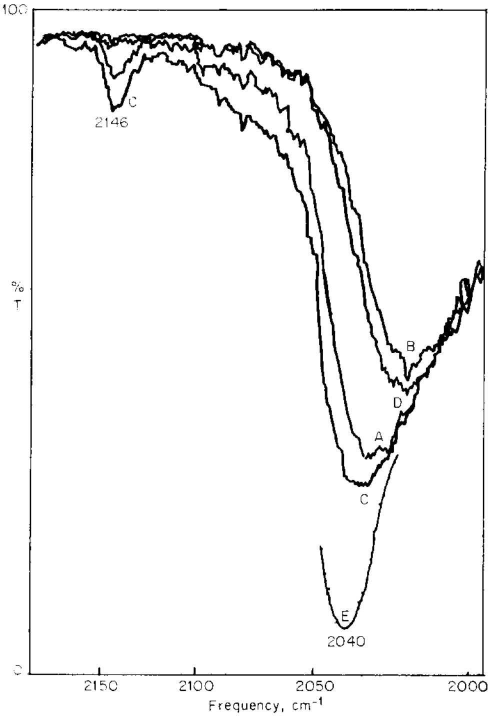

FIG. 3. Infrared spectra of CO adsorbed on $RuCl_3$ after heating sample in 500 μ of hydrogen at 500° for 12 hrs and then degassed: (A) after addition of CO to 0.6 Torr and (B) after evacuation; (C) after addition of CO to 2.0 Torr and (D) after evacuation; (E) the plot of the differences in absorbance between (D) and (C).

DISCUSSION OF EXPERIMENTAL RESULTS

Previous publications (*2*, *3*) present a relationship between the polarization fractions of Cr, Fe, Co and Ni and the electronic energy levels of gaseous ions of these metals. The polarization fraction appears to be related to the presence of low-lying electronic spin-orbit states of gaseous ions of the metal. From this relationship (*2*, *3*), it was possible to calculate polarization fractions for many metals that had not been studied spectroscopically as adsorbents for CO. In addition, the polarization fractions were observed to change for certain oxidation states of the metal. Ruthenium is one of the metals whose polarization fractions were calculated from the energy levels of its ions. The fraction corresponding to the positive ruthenium gaseous ion is 0.942 and the fraction corresponding to the double positive ion is 0.745. According to the relationship proposed between chemical oxidation states and gaseous ionization states (*3*), the polarization fractions of Ru 1+ and 2+ are 0.942 while Ru 3+ and 4+ are 0.745. The integers of the calculated nonintegral numbers of electrons are 9 and 11 for the 1+ and 3+ oxidation states and 8 and 10 for the 2+ and 4+ oxidation states. Thus, with these polarization fractions and the following equation, predictions could be made of the vibrational frequencies of CO intermedions on adsorbents containing Ru. The equation relating vibrational frequencies ν and numbers of valence electrons E for CO is:

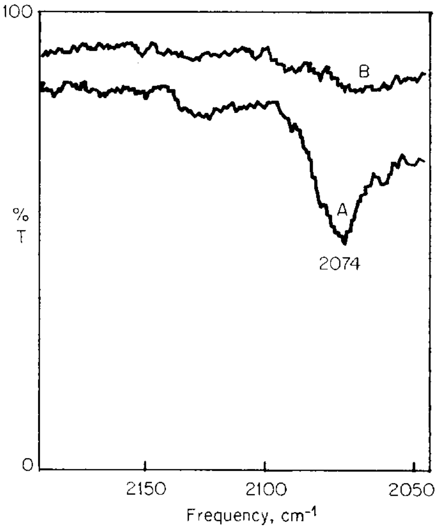

FIG. 4. Infrared spectra of CO adsorbed on $RuCl_3$ after oxidation with oxygen at 0.9 Torr at 500° for 50 hr: (A) after addition of CO to 5 Torr and (B) after evacuation.

$$(\nu\text{CO} - 2269.96)(E_{\text{CO}} - 12.1182) = 268.309. \quad (1)$$

The metal oxidation states, predicted CO frequencies, and measured frequencies are presented in Table 1.

The experimental results indicate that a special preparation of the surface was necessary to generated detectable quantities of intermedions. The adsorbent was reactive after being heated at 300°C, yet only strongly bonded adsorbates were observed

TABLE 1

Metal oxidation states	Calculated frequencies[a]	Experimental frequencies	
		Intermedions	Strongly bonded
Ru 1+	$\nu CO^{9.942} = 2146.67$	2146	2143
	$(\nu CO^{11.942} = 747.21)$		2140
Ru 2+	$\nu CO^{8.942} = 2185.49$		2086
	$\nu CO^{10.942} = 2041.84$	2040	2080
Ru 3+	$\nu CO^{9.745} = 2156.90$		2020
	$(\nu CO^{11.745} = 1551.02)$		2008
Ru 4+	$\nu CO^{8.745} = 2190.42$		
	$\nu CO^{10.745} = 2074.57$	2074	

[a] Frequencies in parentheses were not within the spectral range investigated.

in Fig. 1. Heating at 300°C in oxygen removed these bands. When CO was admitted to the sample at room temperature, strongly bonded species were again formed at slightly different intensities and frequencies in Fig. 2. Only after reduction of the adsorbent with hydrogen were bands assigned to intermedions observed in Fig. 3. As expected, these bands at 2146 and 2040 cm^{-1} correspond to the lower oxidation states of Ru. Upon subsequent reoxidation, the spectrum contained a band at 2047 cm^{-1} corresponding to the $CO^{10.745}$ intermedion on Ru 4+ in Fig. 4. Certain dislocations on certain lattice faces may be required to generate intermedions. The method of sample preparation used in this study may not have generated sufficient surface sites for the formation of detectable concentrations of the $CO^{8.942}$, $CO^{8.745}$, and $CO^{9.745}$ intermedions.

Another study of the infrared spectra of CO on adsorbents containing Ru has been reported by Lynds (*6*). The description of his experimental method suggests that he observed only the spectra of species which were strongly bonded. He reported infrared absorption bands due to chemisorbed CO at 2143 and 2083 cm^{-1}. These bands were removed by prolonged heating and evacuation. These bands correspond with those at 2143 and 2086 cm^{-1} assigned to strongly bonded species in this present study.

In conclusion, it should be noted that although intermedions are described in terms of nonintegral numbers of electrons, it is thought that they are neutral species. The interaction with the surface is thought to be of a dipole induced-dipole type without electron sharing or transfer. The force constant of the bond of the intermedion is apparently perturbed so that it has the vibrational frequency corresponding to the calculated nonintegral number of electrons. This view is supported by (a) the weak bonding of the intermedion to the surface, (b) the description of the vibrational frequencies by an equation derived from data for gaseous species and (c) the discontinuity in the effect of changes of the environment (ligands) at the adsorption site on the intermedions formed.

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