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# The Chemisorption of Carbon Monoxide on Chromium, Platinum, and Nickel

RALPH A. GARDNER

*From The Standard Oil Company (Ohio), Research Department, Cleveland, Ohio*

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The species resulting from the chemisorption of carbon monoxide on adsorbents containing chromium, platinum, or nickel are classified as intermedions and carbonyls. These designations are based on an equation which relates the vibration frequencies of carbon monoxide species and their number of valence electrons. Intermedions are those species with vibration frequencies which correspond to nonintegral numbers of electrons with different integers but the same fraction. This fraction, a property of the metal, is called the polarization fraction.

The mathematical method described in a previous publication (*1*) is the basis of the assignment of infrared bands obtained in spectroscopic studies of the chemisorption of carbon monoxide on adsorbents containing chromium, platinum, or nickel. The following equation, derived from vibration frequencies of gaseous species, is used to calculate the number of valence electrons corresponding to the vibration frequencies of the chemisorbed species, viz.,

$$[2269.96 - \nu(\mathrm{CO})][12.1182 - E(\mathrm{CO})] = 268.309\ \mathrm{cm}^{-1} \quad (1)$$

where $\nu(\mathrm{CO})$ is the vibration frequency of the infrared band and $E(\mathrm{CO})$ is the number of valence or outershell electrons. The chemisorbed CO species whose vibration frequencies correspond, according to Eq. (1), to numbers of electrons with different integers but the same fraction are "intermedions." The infrared bands which do not satisfy this requirement are considered to result from "carbonyl-type" species. The fractional part of the number of electrons assigned to intermedions on adsorbents containing a certain metal component is thought to be a constant, characteristic of the metal. This constant is named the "polarization fraction."

Intermedions may also be distinguished from carbonyls by evacuation of the sample. Intermedions are weakly bonded in equilibrium with the gas phase and therefore readily removed by evacuation. Carbonyl species are frequently the more strongly bonded adsorbents. It is on the basis of this difference that the band at 2063 $\mathrm{cm}^{-1}$ in Table 1 is tentatively assigned to an intermedion on the adsorbent containing platinum. Our experimental data along with those reported by other investigators are presented in Table 1 in terms of the two groups of adsorbates–intermedions and carbonyls.

## EXPERIMENTAL METHODS

The experimental methods used in this study are similar to those described by Eischens, Pliskin, and Francis (*2*). Detailed descriptions of our infrared *in situ* cell and the modified Model 112 Perkin-Elmer spectrometer are presented in a previous publication (*3*). The following describes the preparation of adsorbents used in this study and those data from other investigators.

(a) The chromium oxide gel was prepared from 1.5 gm of $NaC_2H_3O_2$, 30 ml of $M/3$ $CrCl_3 \cdot H_2O$ solution and 4 ml of conc. $NH_4OH$. The aqua-gel was exchanged 20 times with absolute ethanol. It was heated to 620°F at 1100 psig to remove the ethanol above its critical temperature and pressure.

### TABLE 1
### VIBRATION FREQUENCIES AND NUMBERS OF VALENCE ELECTRONS (CALCULATED FROM EQ. 1)

| Absorbent[a] | | Intermedions | | Carbonyls | |
|---|---|---|---|---|---|
| | | Infrared bands ($cm^{-1}$) | Number of electrons | Infrared bands | Number of electrons |
| Chromium oxide gel | (a) | 2203 (g) | 8.11 | — | — |
| | | 2181 (g) | 9.10 | — | — |
| Chromium oxide | (b) | 2134 | 10.14 | 2129 | 10.21 |
| | | | | 2056 | 10.86 |
| Platinum-metal | (c) | 2063 | 10.82 | 2065 to 2080 | 10.81 to 10.71 |
| Nickel metal | (d) | 2058.0 (g) | 10.85 | — | — |
| Nickel metal | (e) | 2058.3 (g) | 10.85 | 1965 | 11.24 |
| Nickel metal film | (f) | 2060 | 10.84 | — | — |
| Nickel metal film | (h) | 2058.0 | 10.85 | 2030 | 11.00 |
| Nickel oxide | (j) | 1230 | 11.86 | — | — |

[a] Letters refer to description in Experimental Methods section.

(b) The chromium oxide sample was prepared from a 1:10 slurry of chromium metal as the nitrate to Cab-O-Sil and sprayed on a $CaF_2$ plate. The nitrate was decomposed at 550°F with evacuation for 16 hr.

(c) The platinum metal sample was prepared at 1:10 platinum metal as the platinous chloride to Cab-O-Sil. The sample was reduced with hydrogen for 16 hr at 770°F.

(d) The nickel metal sample was prepared at 1:10 metal as nickel nitrate to Cab-O-Sil. The nitrate was decomposed with evacuation and the sample reduced with $H_2$ at 730°F for 15 hr.

(e) Data reported by Courtois and Teichner (*4*) for CO on a sample of supported metallic nickel.

(f) Data reported in an earlier publication (*3*) for CO on a vacuum-evaporated metallic nickel film.

(g) Vibration frequencies labeled (g) were determined with a grating spectrometer, the others with a $CaF_2$ prism spectrometer.

(h) Data reported by Pickering and Eckstrom (*5*) for CO on vacuum-evaporated nickel mirrors.

(j) Data reported by O'Neill and Yates (*6*) for CO on supported nickel oxides.

## DISCUSSION

The infrared band at 2181 $cm^{-1}$ developed upon the incremental addition of CO to the chromium oxide gel adsorbent. When oxygen was added to the cell to a total pressure of 1/2 atm, the band at 2181 $cm^{-1}$ disappeared and a new band formed at 2203 $cm^{-1}$. Since these frequencies correspond according to Eq. (1) to carbon monoxide species having 9.10 and 8.11 valence electrons, a value of 0.10 is considered to be the polarization fraction of chromium. These assignments are further supported by the data of Amberg and Little (*7*), reporting a band at 2200 ± 5 $cm^{-1}$ to be formed immediately upon the admission of CO at 20°C to a supported chromia adsorbent. Evacuation at 20°C immediately removed this band.

The infrared band which appeared immediately upon the admission of CO to adsorbents containing metallic platinum was at 2063 $cm^{-1}$. This band, readily removed by evacuation, corresponds to a CO species with 10.82 valence electrons. Therefore, 0.82 has been tentatively assigned as the polarization fraction of platinum. Further additions of CO skewed the envelope of the band toward the 2070 $cm^{-1}$ region.

Several investigators have made infrared studies of the chemisorption of CO on supported nickel metal adsorbents and vacuum-evaporated nickel films. In addition to agreement in the assignment of the frequency of the spectral band at 2058 $cm^{-1}$, all investigators have noted the mobile equilibrium between this chemisorbed species and gaseous CO. The vibration frequency of 2058.0

corresponds to the $(CO)^{10.85}$ intermedion. O'Neill and Yates (*6*) in their study of CO on supported nickel oxide, reported an unassigned band at 1230 $cm^{-1}$. According to Eq. (1) this vibration frequency corresponds to a $(CO)^{11.86}$ intermedion. If this is a CO intermedion, it has the lowest vibration frequency of any yet detected. The assignment of 0.85 as the polarization fraction of nickel is further supported by data reported by O'Neill and Yates (*6*) and by Eischens and Pliskin (*8*). These investigators observed an infrared band in the vicinity of 2190 $cm^{-1}$ in the presence of $O_2$, CO, and an adsorbent containing nickel. According to Eq. (1), the CO intermedion with 8.85 valence electrons has a vibration frequency of 2188 $cm^{-1}$.

The assignments of 0.10, 0.82, and 0.85 as polarization fractions of Cr, Pt, and Ni will be further examined with respect to the catalytic activity of these metals and their compounds.

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