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Infrared Spectra of CO and O_2 Adsorbed on Tungsten

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While adsorption on tungsten surfaces has received much attention[1] from workers using field emission and field ionization microscopy, LEED and flash desorption techniques there has been no successful room temperature infrared spectroscopic work reported for species chemisorbed on tungsten. Since no single technique gives a definitive view of chemisorption, it is desirable to have information from as many different techniques as possible. The main difficulty to applying the usual infrared methods[2] in surface chemistry to tungsten is its refractory nature which makes obtaining it in a highly dispersed form difficult. In the only reported[3] attempt to work with tungsten, a technique which involves evaporating a thin film of metal onto a salt plate at 170 K and then admitting the adsorbate was tried. This method produced spectra for CO on Ni, Co, Fe, and Ir but not for tungsten. If the tungsten was evaporated in 10^{-2} Torr of CO, a weak band appeared at 1970 cm^{-1} but this disappeared upon warming to room temperature. This raises the question as to whether tungsten is different from the other transition metals for which infrared spectra of adsorbed CO and other gases have been obtained.

The wide spectral range experimental technique, which has been described in detail elsewhere,[4] consists of evaporating tungsten from a filament made by twisting together 4 strands of 0.06″ diameter tungsten wire. The evaporated metal deposits in a purified hydrocarbon oil film on the salt windows of an infrared cell. Spectra are recorded before and after admission of the gas to be studied. The spectra were recorded on a Perkin-Elmer Model 457 spectrometer.

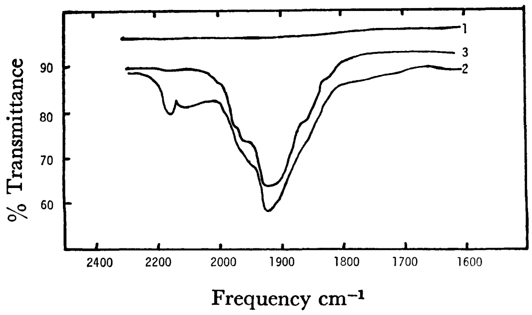

Fig. 1. Infrared spectra of CO adsorbed on tungsten. 1) background; 2) 50 Torr CO for 16 hr at room temperature; 3) evacuated at 10^{-5} Torr for 1.5 hr.

Infrared spectra of CO adsorbed on tungsten are shown in Fig. 1. After exposure to 50 Torr of CO for 16 hr at room temperature the result is curve 2, which has a band maximum at about 1920 cm^{-1} and a major shoulder at 1950 cm^{-1} as well as several lesser shoulders. The bands in the 2100—2200 cm^{-1} region are due to gas phase CO. The intensity of the band in the 1900 cm^{-1} region did not decrease appreciably after evacuation of the cell for 1.5 hr as shown in curve 3.

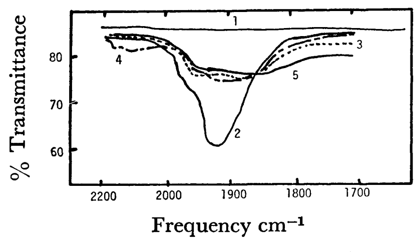

Fig. 2. Effect of heating. 1) background; 2) chemisorbed CO; 3) evacuated at 100°C for 1 hr.; 4) reexposed to 50 Torr CO for 16 hr.; 5) additional evacuation at 150 °C for 45 min.

The effect upon the spectra of mild heating is shown in Fig. 2, where curve 2 is for chemisorbed CO in an evacuated cell at room temperature. Evacuating and heating at 100 °C for 1 hr greatly decrease the band

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intensity in the 1920 cm^{-1} region as shown in curve 3. The permanent nature of the change caused by heating is demonstrated by exposing the cell to 50 Torr of CO for 16 hr and observing that curve 4 shows little change after this treatment. Again the bands in the 2100 cm^{-1} region are due to gas phase CO. Curve 5 shows the sample after further evacuation at 150 °C for 45 min. After noting that the background at lower wave numbers has been shifted it is evident that this last treatment has further reduced the absorption in the 1920 cm^{-1} region while that at 1970 cm^{-1} is much less decreased by the heat treatments.

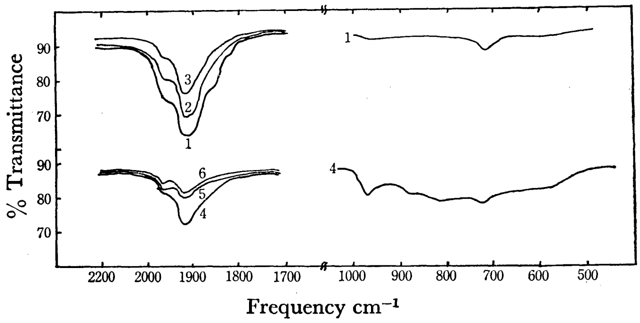

Fig. 3. O_2 addition to chemisorbed CO. 1) chemisorbed CO; 2) exposed to 30 Torr O_2 at room temperature; 3) after 6.5 hr exposure to O_2; 4) after 12 hr with 90 Torr O_2; 5) after 90 Torr O_2 at 100 °C for 30 min.; 6) evacuation at 100 °C for 5 min.

The effect of added O_2 on the chemisorbed CO is shown in Fig. 3, where curve 1 is for chemisorbed CO and the band at 720 cm^{-1} is a background oil band. After exposure to 30 Torr of O_2 at room temperature the chemisorbed CO band intensities decreased as shown in curve 2. Further exposure to O_2 for 6.5 hr gives curve 3 while 90 Torr of O_2 for 12 hr results in curve 4. By this time a broad band from 500 to 1000 cm^{-1} and a sharper band around 965 cm^{-1} have become evident. Heating the cell at 100 °C with 90 Torr of O_2 for 30 min further reduced the intensity around 1920 cm^{-1} while not changing the intensity near 1970 cm^{-1} as indicated by curve 5. Evacuation for 5 min at 100 °C resulted in curve 6.

In order to understand the bands resulting from the O_2 treatment of chemisorbed CO, a freshly evaporated tungsten surface was exposed to 115 Torr of O_2 at room temperature. The spectra obtained after 1.5 and 5 hr, shown in Fig. 4, reveal the formation of a broad absorption from 500 to 1000 cm^{-1} and a peak at 970 cm^{-1}.

In reviewing these results it is evident that tungsten does indeed behave similarly to other transition metals with respect to the infrared spectra of chemisorbed CO. Since so much work has been done by other techniques on tungsten, it is good to have this additional evidence that tungsten is not unrepresentative of transition metals in general. The question may arise as to whether the oil matrix changes the chemical character of the metal surface. At least with respect to CO adsorption the answers seems to be no. Infrared spectra, where obtainable, for CO adsorbed on metals evaporated in high vacuum onto salt plates[3,5–7] or into an argon matrix[8,9] are like those for oil-matrix metals.[10] The spectrum obtained here by CO on tungsten is most like those for Cr, which is directly above it in the periodic table, and V which is above and one group to the left.

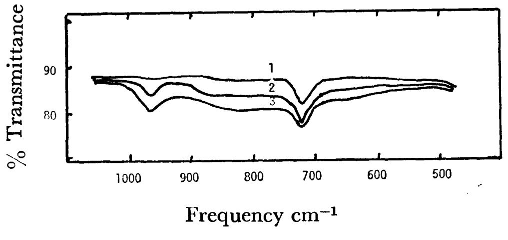

Fig. 4. O_2 adsorption on tungsten. 1) background; 2) 115 Torr O_2 at room temperature for 1.5 hr.; 3) 115 Torr O_2 at room temperature for 5 hr.

The decrease in infrared band intensity upon heating is more likely due to sintering than to simple thermal desorption since it occurs at 100 °C whereas the first major desorption in flash filament work occurs in the 150 to 200 °C range. That sintering can be a major cause of an infrared band intensity decrease is also shown in work with Ni in an argon matrix.[9] Noting the sintering effect and the fact that for spectra of CO on metals evaporated directly onto salt plates the intensities are always very low, it appears that most of the CO causing the large broad band centered around 1920 cm^{-1} is on surface tungsten atoms that have a low coordination number, *i.e.* that are not part of a high atom density surface plane. In view of the metal being evaporated in such a way as to inhibit sintering it is not surprising that there is large number of such sites. The band intensity around 1970 cm^{-1} suffers a less drastic decrease upon heating and oxygen treatment, suggesting that a part of this intensity is due to CO on the high atom density surface planes.

The spectral results of oxygen addition to chemisorbed CO shown in Fig. 3 indicate that the CO is displaced by the oxygen and new bands for surface species are produced in the 500 to 1000 cm^{-1} region. Subsequent adsorption of O_2 on fresh tungsten shows these bands to be entirely due to oxygen on tungsten. Thus tungsten does not behave like Ni where O_2 addition to surface CO produces a surface CO_3 species.[11]

The infrared bands produced by oxygen adsorption are quite similar to bands for tungsten oxides. Weltner and McLeod[12] report that the frequency of the terminal W=O stretch in W_2O_6 and W_3O_8 is at 989 cm^{-1} and

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that WO_3 has a strong band at 1007 cm^{-1}. This leads to our assigning the 970 cm^{-1} band to a terminal W=O structure at the surface. The broad band in the 500—1000 cm^{-1} region is presumed due to the W–O–W structure since many W_nO_m compounds have several weak bands in this region. Thus on tungsten samples suitable for infrared studies the adsorption of O_2 is clearly dissociative. No infrared bands corresponding to O–O stretches were found. The formation of a surface structure in which an oxygen atom has a double bond to a metal atom has been found previously for V[13)] and Cr[14)] but not for transition metals to the right of group VIB such as Mn, Fe, Co, and Ni, which we have investigated.

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