Incorporation of Oxygen-18 into Carbon Monoxide Chemisorbed on Nickel *via* Exchange Reactions with $H_2{}^{18}O$

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Summary It has been possible to observe the oxygen exchange reaction between $H_2{}^{18}O$ and carbon monoxide chemisorbed on silica supported nickel using i.r. spectroscopy.

Oxygen exchange reactions involving $^{13}C^{16}O$ and $^{12}C^{18}O$ have been reported for iron[1] and nickel[2] catalysts. Because these authors used a mass spectrometer to follow the course of the reaction, they were unable to determine whether all or just part of the surface species were participating in the exchange.

More recently, Darensbourg and Drew[3] reported the incorporation of oxygen-18 into some pentacarbonyl compounds *via* exchange reactions with $H_2{}^{18}O$. In discussing this work, Darensbourg[4] indicated that not all carbonyls they investigated would undergo this exchange. Since carbon monoxide is considered to chemisorb in a variety of different surface structures,[5] it was thought that perhaps some of these surface entities could undergo a similar exchange using $H_2{}^{18}O$. We are reporting preliminary results of these studies using i.r. spectra to follow the oxygen exchange of CO chemisorbed on silica supported nickel.

The preparation of the samples and cell design have been described elsewhere.[6] The catalyst samples contained 10 wt% nickel supported on Cab–O–Sil Silica (M–5). All experiments were performed at room temperature. The $H_2{}^{18}O$[7] was placed in a special bulb on the vacuum system and subjected to several freeze–thaw cycles to remove dissolved gases.

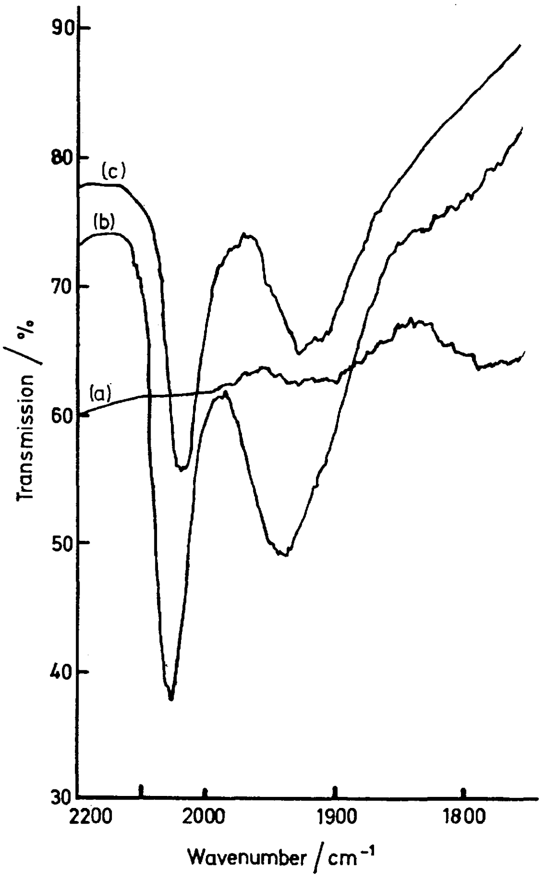

Figure 1. Effect of $H_2{}^{16}O$ on chemisorbed CO: a, background; b, chemisorbed CO; and c, effect of added water at 10 Torr for 60 h at room temperature.

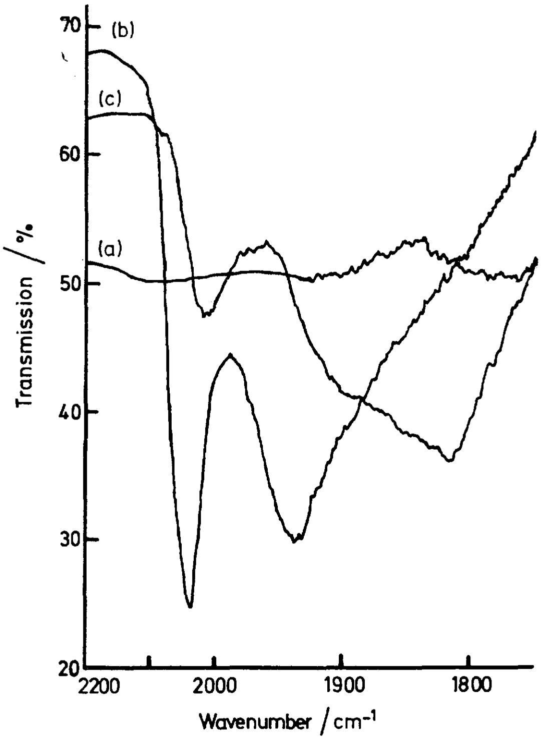

Figure 2. Effect of $H_2{}^{18}O$ on chemisorbed CO: a, background; b, chemisorbed CO; and c, effect of added $H_2{}^{18}O$ at 10 Torr for 48 h at room temperature.

The results of these experiments can be seen in Figures 1 and 2. The addition of 10 Torr of normal water ($H_2{}^{16}O$) results in some displacement of the chemisorbed CO. This displacement is immediate, with no further changes evident up to 60 h. Figure 2 shows the results of the addition of the $H_2{}^{18}O$. In Figure 2, spectra a and b represent the background and chemisorbed CO, respectively. Spectrum c illustrates what is observed after a 48 h exposure to 10 Torr of the $H_2{}^{18}O$. Another series of experiments were conducted to establish the dependence of the 1820 cm^{-1} band on the pressure of the $H_2{}^{18}O$ in the cell. Spectra were recorded after each addition of the $H_2{}^{18}O$. and every

12 h thereafter up to 48 h. Spectra were recorded with $H_2{}^{18}O$ pressures in the cell corresponding to 0·1, 1, 5, and 10 Torr. The spectra indicate that the 1820 cm^{-1} band does not appear until the pressure is 1 Torr and the intensity of the band no longer changes for pressures >5 Torr. In both cases the intensity of the high-wavenumber band (2040 cm^{-1}) decreases and shifts to 2010 cm^{-1}. This has been observed in a number of cases.[5,8] A similar result is observed for the low-wavenumber band when using normal water. The ratio of the absorbance for the two bands (before and after addition of the water as shown in the Figures) indicates that the high-wavenumber band in each case experiences about the same change in intensity. However this is not so for the other peak. Here a significant difference is observed as the formation of a new band at 1820 cm^{-1} when using $H_2{}^{18}O$. This band grows in intensity and after *ca.* 48 h no further change is noted.

Recent theoretical calculations[9] predict a wide variety of surface structures involving different numbers of nickel atoms for both linear and bridge-bonded species. From the spectra it is concluded that only a fraction of the bridge-bonded carbon monoxide undergoes exchange and remains on the surface.

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