

The Dissociative Adsorption of CO on Nickel and Nickel-Copper Alloys

Adsorption of CO has been the subject of many studies using infrared spectroscopy, and the work has often been reviewed (1). However, most of the investigations were limited to temperatures around room temperature and to low pressures of CO. At higher pressures of CO and higher temperatures the surface processes may be, in principle, different. Besides adsorption we have to consider also the formation of carbonyls, dissociation of CO, formation of surface and bulk carbides and similar processes. The surface which has been attacked by the formation of carbonyls may behave differently in subsequent low temperature CO adsorption, etc. A recent review of the mechanism of the Fischer-Tropsch reaction (2) stressed the importance of the formation of carbonyls for this reaction and the work performed in our laboratory [thermal desorption (3), methanation (4)] has revealed the importance of dissociative CO adsorption. An attempt has now been made to gain more information on these processes by ir measurements. The experimental technique was the same as in the previous papers from this laboratory (5). Also Ni and Ni-Cu alloys were prepared as in Ref. (5). Aerosil was impregnated by a solution of nitrates, the powder was dried and then reduced in a flow of hydrogen at 450°C, for at least 16 hr. Under these conditions one-phase alloys are formed which have a surface composition very near to that of the Cu-rich phase which would be stable under conditions where two-phases are present at equilibrium (under 170°C) (9, 10).

Formation of Ni carbonyls at room temperature (in the beam) can be easily detected. The infrared spectra of CO adsorbed on Ni at $p_{\text{CO}} < 1$ Torr and at the temperature of the beam reveal the typical two-peak structure (1) (1925 and 2055 cm^{-1} bands) and an increase of the CO pressure to 5–10 Torr leads to a substantial increase of infrared absorption in the 2055 cm^{-1} region. Under these conditions the gas phase shows the presence of volatile $\text{Ni}(\text{CO})_4$, the spectrum of which is identical with the published spectra of this compound (6).

When the temperature of the adsorbent had been kept in vacuum at 600 K for several hours, no infrared absorption was observed any more when the sample was cooled to room temperature. From thermal desorption (3), volumetric measurements (3) and methanation studies (4), we know that after such a treatment carbon is deposited on the surface of Ni. When adsorption (room temperature) and desorption (up to 600 K) of CO is repeated on the same sample, the amount of deposited C increases gradually. The infrared spectra reveal the following picture. On the surface where some "C" has been deposited the 1925 cm^{-1} "M" band corresponding to the adsorption mode of CO with stronger back-donation (multiply bound CO, multisite adsorption) decreases while the 2055 cm^{-1} "L" band (low-coordinated CO) is slightly shifted to lower frequencies and increases in its intensity (Fig. 1). Only when the surface is covered by "C" to a still higher extent does the high frequency band decrease in intensity (Fig. 2). Therefore, it can be con-

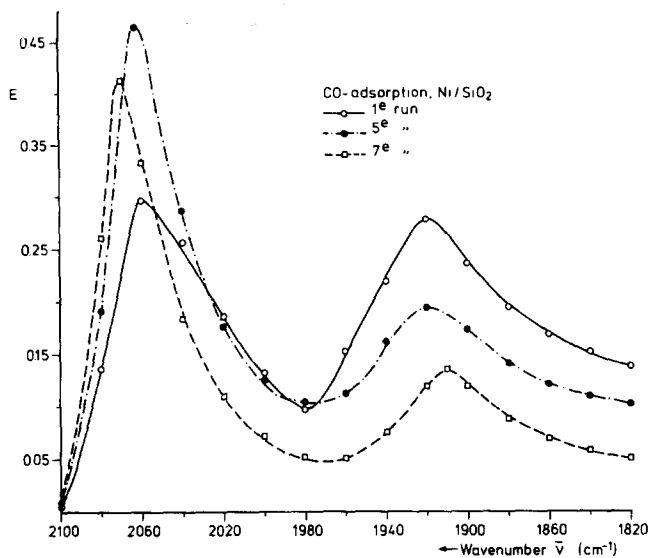


FIG. 1. Infrared spectra upon CO adsorption on the fresh Ni adsorbent and after five and seven adsorption-desorption (600 K) runs.

cluded that "C" is deposited at places where CO can be adsorbed in its multiply bound form and dissociated into "C" and "O." However, deposition of "C" causes an *increase* in the intensity of the L-band (see Fig. 2). This can have several reasons. Deposited "C" might eliminate one of the

infrared inactive (or less active) forms like CO horizontally lying on the surface (with both C and O bound to the surface), but allow CO adsorption to take place in the low-coordinated form ("linear" form, 2055 cm^{-1} band) on the same surface. Another possibility would be that elimination of a valley for the CO adsorption (M-band) still allows adsorption on the tops of the atoms surrounding the valley. However, in this way also the next valley cannot be occupied by CO and the region with adsorption on the tops of atoms (L-band) expands and prevails on the whole plane of the microcrystal where C has been deposited. This would also lead to results such as those in Fig. 2.

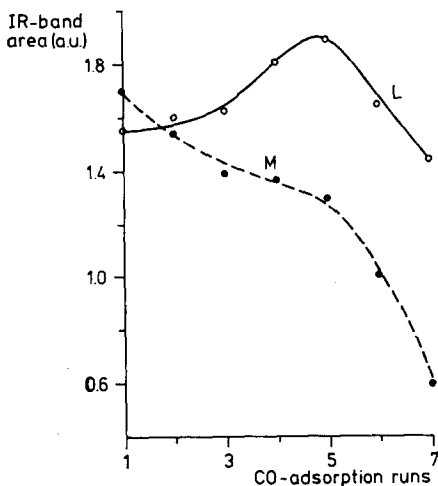


FIG. 2. Intensity of high-frequency (L, low coordinated CO) and low-frequency (M, multiply coordinated CO) bands (surface area in arbitrary units) upon subsequently repeated adsorption-desorption runs on the Ni-adsorbent.

The surface of Ni particles of the size used here is probably mainly composed of (111) and (100) planes (7). The experiments performed by Gwathmey and Cunningham (8) have shown that of these planes the (111) is much more active in CO decomposition than the (100) plane. Therefore, the place where CO is adsorbed in its multiply bound form with stronger back-donation can be, for example, visualized as

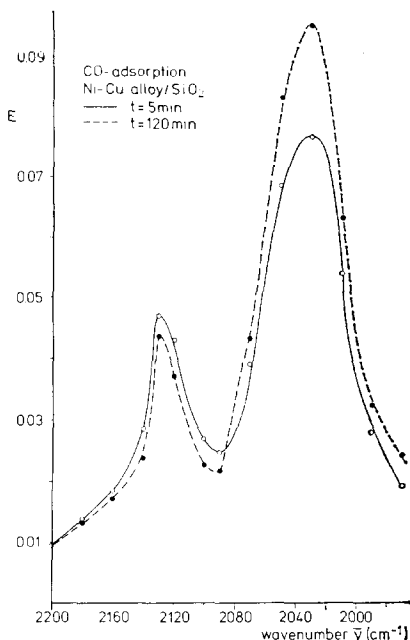


FIG. 3. Infrared spectra upon CO adsorption on the Ni-Cu 50/50 alloy. $p_{\text{CO}} = 6.2$ Torr; (—) after 5 min; (---) after 120 min.

the surface hole on the (111) plane among three Ni atoms. According to Gwathmey and Cunningham's observations for Co (8), such a surface hole is only active in CO decomposition when it has a certain structure (and evidently, composition) of the second and third layer under the surface.

The study on methanation (4) revealed that addition of Cu to Ni decreases the rate of methanation dramatically, owing to the number of deposited C atoms being decreased. It is known that addition of Cu to Ni eliminates CO adsorption in the multiply coordinated form (1955 cm^{-1}) under the limit of detection by infrared absorption (5).

In this paper we have observed by infrared spectra that an Ni-Cu 50/50 alloy which according to other measurements (9, 10) has about 15–20% Ni atoms in the surface reveals a separated CO adsorption on Ni (2030 cm^{-1}) and Cu (2130 cm^{-1}) atoms. When this alloy stays in CO

($p_{\text{CO}} \sim 6$ Torr) for a certain time (of the order of hours) at room temperature, the adsorption on Ni increases clearly while on Cu it is diminished slightly (Fig. 3). We attribute the effect to the gas induced segregation, a phenomenon already observed by other methods (11). As will be shown in later papers (3, 12), this phenomenon is essential for understanding the volumetric measurements of CO adsorption on Ni-Cu alloys.

CO can be dissociated also on Ni-Cu alloys but under the same conditions to a much lower extent than on pure Ni (4). The infrared spectra revealed that the deposited carbon also decreases the intensity of the high-frequency infrared band similar as on pure Ni after the maximum on the curve in Fig. 2 has been passed.

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