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Desorption of Carbon Monoxide from Nickel Using Mercaptans

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The displacement of CO chemisorbed on nickel (as evaporated films and silica-supported samples) by 1-propyl, 2-propyl, 1-butyl, 2-butyl, and *tert*-butyl mercaptan was studied using infrared spectroscopy. The CO was gradually displaced as the mercaptan pressure increased. When using Ni/SiO_2 adsorbents, some of the bridge-bonded CO is first converted to a linear species and then displaced. Also the poisoned Ni/SiO_2 surfaces would readsorb CO; however, only the linear species was stable enough to withstand evacuation.

INTRODUCTION

Since Eischens *et al.* original paper (*1*) using infrared spectroscopy to elucidate surface structures, a large number of other studies have been published employing the same technique. Many of these (*2–7*) have dealt with the structure of carbon monoxide chemisorbed on nickel. It is evident from these papers that the structure of CO on nickel is equivocal, and all would agree a variety of surface structures must exist. Eischens *et al.* (*1*) originally proposed two basic structures, CO bonded linearly to a single nickel atom and CO bridge bonded to two separate nickel atoms. Using a molecular–orbital model, Blyholder (*8*) rationalized the infrared spectra of chemisorbed CO on the basis of a single structure, i.e., linearly bonded CO. This model, which was adapted from MO theory for coordination complexes, described the role of various atomic and molecular orbitals in charge transfer to and from the metal and the consequences thereof. Since this work appeared, several other publications have sought to clarify the uncertainty (*9–14*) and it is evident that most authors now prefer at least two structures.

In 1956 Eischens *et al.* (*1*) reported the effect of surface coverage on the spectrum of CO on silica-supported nickel. Other authors (*6, 7, 15–17*) have used different molecules to selectively poison the nickel surface and to study the influence of the poison on the spectrum of chemisorbed CO. These investigations all used silica-supported nickel samples.

This paper describes an infrared study showing the effect of adding several different mercaptans to nickel samples that were covered with preadsorbed CO. It is well known that mercaptans are strongly adsorbed by nickel and it has been shown (*18*) that they can be used to displace chemisorbed carbon monoxide from the metal. The metal samples were prepared either as silica-supported nickel or evaporated nickel films. Therefore it is possible to compare the results and evaluate the effect of the support.

METHODS

The nickel samples were prepared using established procedures. The nickel films were evaporated from a resistively heated tungsten filament in the presence of a small pressure of helium. The specific technique was first introduced by Blyholder (*19*) and uses a thin film of hydrocarbon oil on the inside of the cell windows.

The silica-supported samples were prepared using the impregnation method. The cell design and reduction procedure are described elsewhere (*20*). The silica was supplied by G. L. Cabot Corporation (Cab-O-Sil M-5) and the nickel was impregnated

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using nickel(II) nitrate (J. T. Baker, reagent grade). Supported samples were prepared that contained 5, 10, and 20 wt% metal upon reduction. Other suppliers include A. D. Mackay Inc. (tungsten and nickel wire for the films), Air Reduction Company (CO, C.P. grade), and Big 3 Industries (high-purity H_2 and He). The mercaptans were supplied by Eastman Organic Chemicals (1-propanethiol) and Aldrich Chemical Company (2-propyl, 1-butyl, 2-butyl, and *tert*-butyl mercaptan). The mercaptans were subjected to several freeze–thaw cycles with pumping and stored in glass vessels on the vacuum system.

Infrared spectra of the films were recorded using a Beckman IR-10 spectrophotometer. Useful spectra of films were recorded over the region 4000 to 400 cm^{-1} while spectra of silica-supported nickel were recorded from 4000 to 1300 cm^{-1}. All spectra of the supported samples were recorded using a Beckman IR-4240 spectrophotometer.

After preparing the samples, a background spectrum was recorded. Subsequently the cell was returned to the vacuum system and carbon monoxide at approximately 3 Torr (1 Torr = 133.3 N m^{-2}) was added to the cell. After 10 min the gas-phase CO was removed by pumping and another spectrum was recorded which exhibited the absorption bands due to chemisorbed CO. The mercaptan was added to the cell at the lowest pressures first and then the cell was isolated from the vacuum system after each addition of the mercaptan. All observable changes were complete after 30 min when using this procedure and all spectra were recorded after waiting 1 hr to make sure all changes were complete. After recording the spectrum for each mercaptan pressure the cell was returned to the vacuum system and evacuated to remove gases. After evacuation, additional mercaptan at a greater pressure was admitted to the cell and the process repeated. This procedure was used throughout most of the study.

RESULTS

Although only a narrow portion of the infrared spectrograms are presented, in each case the total spectrum was recorded. Absorption bands are evident in these spectra which are characteristic of the way absorbent is prepared. After addition of the mercaptan, absorption bands are observed which could be ascribed to the newly formed surface species. These are in agreement with those reported elsewhere (*18, 21*).

Evaporated Nickel Films

All spectra recorded using evaporated metals contain several absorption bands that are due to the presence of oil in the cell as explained in the methods section. These occur in the following regions: 3000–2800, 1480–1360, and 720 cm^{-1}. The presence of these bands does not interfere with the spectral regions of interest in this study. In Fig. 1, the "background" represents the spectrum corresponding to carbon monoxide chemisorbed on a freshly prepared sample. Two absorption bands characteristic of CO chemisorbed on nickel are readily apparent. These are located at 2040 and 1900 cm^{-1} and are assigned to the C–O stretching motion of linearly and bridge-bonded carbon monoxide (*1*).

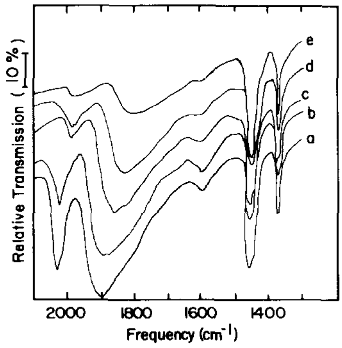


FIG. 1. Displacement of CO from a nickel film by 2-propanethiol. (a) Background with chemisorbed CO. The mercaptan pressures in the cell were: (b) 7.3 × 10^{-3} Torr, (c) 7.4 × 10^{-2} Torr, (d) 7.8 × 10^{-1} Torr, (e) 5 Torr.

Figure 1 is typical of the spectra that are observed using the different mercaptans to displace the CO from the surface. Since the various spectra are so similar only one is shown to illustrate the observations. This figure presents the results of adding 2-propanethiol at various pressures up to 5 Torr. Spectrum (a) corresponds to the background and was recorded at a cell pressure of 5 × 10^{-5} Torr. Spectra (b), (c), (d), and (e) correspond to mercaptan pressures of 7.3 × 10^{-3}, 7.4 × 10^{-2}, 7.8 × 10^{-1}, and 5 Torr, respectively. The high-frequency band shifts from 2040 to 2000 cm^{-1} and is almost gone when the mercaptan pressure reaches 5 Torr. However, the low-frequency band is still prominent in the spectrum. This latter band also shifted toward lower energy as the mercaptan pressure was increased. This peak shifted from 1900 to 1820 cm^{-1}. There was evidence for some chemisorbed CO remaining at the highest pressure for each mercaptan used. This same behaivor was observed in each case.

Silica-Supported Nickel Adsorbents

The study was repeated using silica-supported nickel in order to determine if the supported metal would behave in the same way. It was thought that perhaps the gradual displacement of CO, as the mercaptan pressure increased, might be an artifact due to the solubility and diffusion of the poison into the oil as opposed to a direct interaction effect with the adsorbent.

Figure 2 is typical of the spectra that are obtained using the Ni/SiO_2 adsorbents. All spectra indicate that CO displacement for these samples occurs differently than for the evaporated films. This figure presents the results of adding 2-propanethiol at various pressures up to 1 Torr. Spectrum (a) corresponds to the background while spectra (b), (c), (d), and (e) correspond to mercaptan pressures of 0.1, 0.2, 0.5, and 1.0 Torr, respectively. It should be noted that for the first few additions (spectra (b) and (c)) of the mercaptan the 1925-cm^{-1} band decreased in intensity and shifted little in position while the 2060-cm^{-1} absorption experienced an increase in intensity and shifted to 2075 cm^{-1}. Further additions of the mercaptan simultaneously decreased both bands and the high-energy band shifted back to 2050 cm^{-1} as the CO was displaced in the last stages of the process. This effect was observed for each mercaptan used in the study.

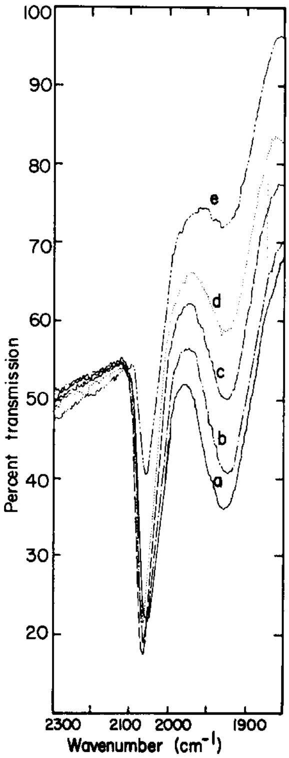


FIG. 2. Displacement of CO from Ni/SiO_2 by 2-propanethiol. (a) Background with chemisorbed CO. The mercaptan pressures in the cell were: (b) 0.1 Torr, (c) 0.2 Torr, (d) 0.5 Torr, (e) 1.0 Torr.

Possible effects of metal concentration in the adsorbents were also studied. Impregnated samples were prepared that contained 5, 10, and 20 wt% nickel on reduction. Little difference could be detected in the resulting spectra. For the 5 wt% samples the high-frequency band shifted from 2060 to 2040 cm^{-1} while the low-frequency band shifted from 1925 to 1900 cm^{-1}, as the mercaptan pressure in the cell was increased. For the 10 and 20 wt% samples the high-wavenumber band shifted from 2050 to 2075 cm^{-1} then back to 2050 cm^{-1} with increasing mercaptan pressure while the low-frequency absorption exhibited little if any shift in its position. The increase in intensity of the 2060-cm^{-1} band accompanied by a decrease in the 1920-cm^{-1} band (for the first few additions of the mercaptan) was noted for all three loadings.

The procedure normally followed in adding mercaptan to the cell involved isolating the cell from the vacuum system once a specific mercaptan pressure was attained. No changes were observed in the spectra after about 30-min exposure following this procedure. However, when the cell was left open to the whole vacuum system, at a particular mercaptan pressure, the absorption maxima continued to change for much longer periods. This is shown in Fig. 3. This figure illustrates what was observed when a 10 wt% nickel sample was exposed to a 0.1-Torr pressure of *n*-butanethiol with the cell left open to the whole vacuum system. Spectrum (a) corresponds to the background of the freshly reduced sample, while (b) indicates the results of chemisorbing carbon monoxide. Spectra (c), (d), and (e) were recorded after 5 min, 45 min, and 24 hr, respectively. It is obvious that the intensity of the 2060-cm^{-1} band increases in time and shifts to 2070 cm^{-1} while the 1940-cm^{-1} band decreases and shifts to about 1915 cm^{-1}. After 24-hr exposure, the cell was evacuated for 2 hr at 1 × 10^{-5} Torr and spectrum (f) recorded.

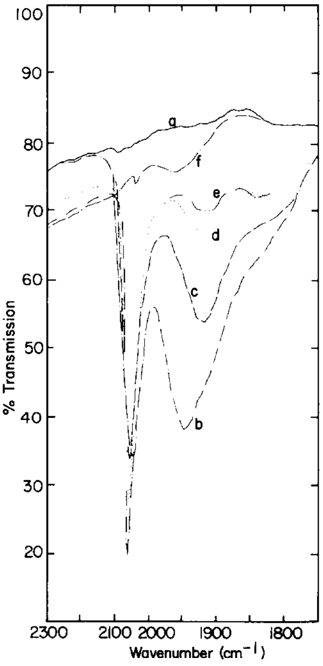


FIG. 3. Slow displacement of CO as a function of time at a fixed pressure of 0.1 Torr 1-butanethiol. (a) Background, (b) chemisorbed CO, (c) 5-min exposure, (d) 45-min exposure, (e) 24-hr exposure, (f) evacuation at 1 × 10^{-5} Torr for 2 hr.

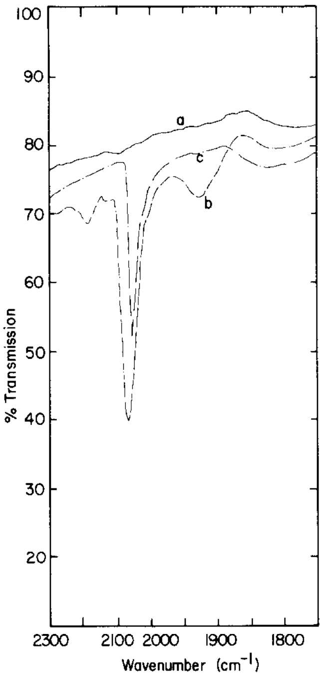


FIG. 4. Effect of adding CO to the sample in Fig. 3. (a) Background as in Fig. 3, (b) addition of 5 Torr CO, (c) evacuation at 1 × 10^{-5} Torr for 1 hr.

This shows evidence of a very small band at 2040 cm^{-1} and a slightly larger one at 1960 cm^{-1}, which indicate a very small amount of CO was still on the surface although most of it pumped off under these conditions. Subsequent additions of CO at 5 Torr gave rise to two bands at 2065 and 1922 cm^{-1} as can be seen in Fig. 4(b). Evacuation at 1 × 10^{-5} Torr for 1 hr resulted in the spectrum shown in Fig. 4(c).

Only one absorption band is evident in this spectrum located at 2060 cm^{-1}.

DISCUSSION

It is well known that mercaptans are strongly adsorbed on nickel surfaces poisoning those surfaces for carbon monoxide chemisorption (*16–18, 21*). In all but one of these studies (*18*), the surfaces were poisoned before exposure to the carbon monoxide. For the purposes of this study the reverse procedure was followed, i.e., CO displacement using mercaptans, to see if the two procedures would produce similar results. It is possible to conclude that the mercaptans used in this study do displace chemisorbed carbon monoxide from evaporated nickel films and Ni/SiO_2 absorbents. This is seen in Fig. 1–4.

The position of the absorption maxima vary slightly from sample to sample and has been noted before. The exact positions of the chemisorbed CO bands have evoked considerable discussion and have provided the basis for several studies (*2, 3, 8, 13, 22–27*). The positions of the two bands using evaporated film adsorbents usually occur at frequencies slightly lower than the corresponding bands on the Ni/SiO_2 substrates. Also the relative intensities of the two bands are dependent on the nature (as a film or supported) of the particular absorbent. For the evaporated films the ratio of the intensities of the high-frequency band to the low-frequency band is smaller than it is for the Ni/SiO_2 samples. This means that more bridging CO species exist on the films while the linear structures are more abundant on the Ni/SiO_2 absorbents. This may be due to a contamination effect of the oil support where some of the isolated linear sites are blocked by a residue. It may also be due to the fact that the films are amorphous and more surface sites for birdge bonding exist.

Nickel Films

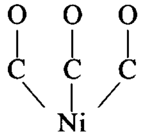
Figure 2 shows that as the mercaptan pressure is increased, the two CO absorption bands decrease in intensity in proportion to one another. A shift in the positions of the two absorption maxima accompanies the gradual dispalcement. This was observed for all the evaported films.

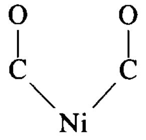
Blyholder (*8*) has suggested it is possible to infer the Ni–C bond strength of the surface species by observing the position of the corresponding CO stretching frequency. Using synergic bonding arguments he said that a lower CO frequency implied a stronger Ni–C bond strength and vice versa.

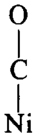
The shift in the frequencies of the two CO bands (2040 to 2000 cm^{-1} and 1900 to 1820 cm^{-1}) indicates that as the CO is removed from the surface of the films the remaining surface structures are more strongy held. That is, a greater Ni–C bond strength is implied by a weakening of the CO bond as reflected in the shift of the corresponding CO frequencies. This observation is complicated by the electronic effect of the added mercaptans. When the mercaptan is adsorbed on the metal, it donates electron density to the nickel which can then be back-donated into the Ni–C π bond. This back-donation of electron density stabilizes the remaining chemisorbed CO, and one would expect to observe a corresponding shift in the absorption maxima to lower energy. Therefore it is not possible to sort out these two effects using this technique. The overall effect is probably a combination of the two since it is well known that the heat of absorption for CO on nickel is a function of the surface coverage which implies the surface is heterogeneous and the resulting surface structures are not independent of each other.

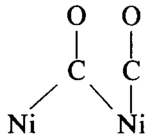
Silica-Supported Nickel

For the Ni/SiO_2 samples a surprising result was noted. The observation that the high-frequency band always increased in intensity while the other band decreased (as the mercaptan was first introduced to the cell) was unexpected. The low-frequency

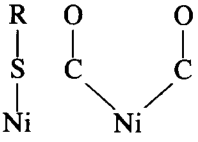

(I)


(II)


(III)


(IV)

band is attributed to bridge-bonded CO which requires two adjacent nickel atoms. As the mercaptan initially adsorbs, it appears to do so at one of these sites which causes the bridged species to rearrange to a linear species without being displaced from the surface. If any CO was displaced to the gas phase its concentration was too low to be detected. This shift in intensities was only observed for low coverages of the mercaptan since the two bands decreased in intensity at about the same rate after the first few additions of the thiol. The shift in the frequency of the high-energy band is consistent with an increase of the number of linearly bound species. Rochester and Terrell (*17*) reported a similar effect in their studies using samples poisoned with mercaptan before addition of the CO. The position of the adsorption due to the linear structures, formed after addition of the mercaptan, indicates they are more weakly held than the linear structures which are formed when CO is chemisorbed on a freshly prepared Ni/SiO$_2$ sample. When the cell is evacuated after each addition of mercaptan (with corresponding spectra recorded before and immediately after evacuation) the result is a significant intensity decrease of the high-frequency band. Also the position of the absorption maximum shifts from the higher frequency back to 2060 cm^{-1}. The CO chemisorbed on a freshly prepared Ni/SiO$_2$ sample is not so easily removed as evacuation at 10^{-6} Torr for 24 hr does not result in a significant change in the observed spectrum. Therefore the surface species responsible for the 2075-cm^{-1} band is less strongly held than the structures that give rise to the band in the region 2050–2060 cm^{-1}. Rochester and Terrell (*17*) suggested the 2075-cm^{-1} band could be due to the presence of a subcarbonyl species such as (I) or possibly (II) whereas the band near 2050 cm^{-1} is attributed to structure (III). Species (II) could be formed from a structure such as (IV) when the mercaptan is adsorbed on one of the nickel atoms involved in the bridge-bonded CO, e.g.,



It is this process that is thought to occur during the initial dosing of the mercaptans into the cell.

The metal concentration seems to have little influence on the results of the displacment. For the 5 wt% samples the results indicate that the samples are becoming more like the films in their behavior. That is, the two bands shift toward lower wavenumber as the mercaptan is added. Unlike the films, however, the high-energy band again increases in intensity for the first two mercaptan doses indicating an increase in the number of linearly bound CO molecules. Therefore at very low coverages of mercaptan the results indicated the chemisorbed CO is not necessarily being displaced into the gas phase, but certainly some of the bridge structures are converted into linear ones until a certain critical stage is reached after which subsequent additions of the mercaptan remove the CO from the surface.

If the reaction cells were exposed to a larger volume of a mercaptan at a specific pressure, the spectra indicate CO is displaced continuously for up to 24 hr as can be seen in Fig. 3 which illustrates the increase of the high-frequency band as the second one decreases. Figure 3(e) indicates considerable CO is still bound to the surface although it is almost exclusively in the linear form. This material is not strongly bound to the surface as evacuation results in almost the complete loss of the spectral bands (Fig. 3(f)). The resulting surface would readsorb CO, as shown in Fig. 4(b), although the amount that would chemisorb was less than that normally observed. Evacuation resulted in spectrum (c) of Fig. 4. This spectrum indicates that although some bridge-bonded CO was formed in the presence of excess CO, the structure was only weakly bound and could be easily pumped off, whereas only part of the linear species was removed by the evacuation. This would suggest that the number of adjacent nickel atoms, capable of bridge-bonding CO, are drastically reduced when compared with the number expected on a freshly prepared Ni/SiO_2 adsorbent.

ACKNOWLEDGMENTS

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