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Formation of $Ni(CO)_4$ during the interaction between CO and silica-supported nickel catalyst: an FTIR spectroscopic study

M. Mihaylov [a], K. Hadjiivanov [a,*] and H. Knözinger [b]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*
[b] *Department Chemie, Physikalische Chemie, LMU München, Butenandtstrasse 5-13 (Haus E), 81377 München, Germany*

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The formation of $Ni(CO)_4$ during interaction of CO with silica-supported highly dispersed nickel metal ($d_{av} \approx 4$ nm) was investigated by FTIR spectroscopy. At temperatures below 145 K, in addition to linear and bridged nickel carbonyls, CO adsorption on Ni^0/SiO_2 leads to the formation of $Ni(CO)_x$ ($x = 2, 3$) subcarbonyls (band at *ca.* 2090 cm^{-1}) and negligible amounts of $Ni(CO)_4$ adsorbed on SiO_2 (band at 2048 cm^{-1}). Up to this temperature CO causes no detectable erosion of the metal surface. Above 145 K the rate of interaction between CO and the nickel particles significantly increases. Until 235 K $Ni(CO)_4$ mainly remains in the adsorbed state, while at still higher temperatures the equilibrium between adsorbed and gaseous $Ni(CO)_4$ (band at 2058 cm^{-1}) is shifted towards the latter. It is assumed that subcarbonyls formed on defect sites of the metal surface are precursors of the nickel tetracarbonyl. Successive adsorption–evacuation cycles of CO at room temperature result in a decrease in the amount of the $Ni(CO)_4$ formed, probably due to a reduction of the number of defect metal sites. On the basis of ^{12}CO and ^{13}CO coadsorption, an alternative interpretation of the band at 2048 cm^{-1} to species containing isolated $Ni(CO)_3$ groups is proposed.

KEY WORDS: adsorption; carbon monoxide; FTIR spectroscopy; nickel; nickel tetracarbonyl

1. Introduction

Supported nickel catalysts are widely applied in important industrial processes, *e.g.*, in hydrogenation and hydrogenolysis [1–3]. They are also used for the steam-reforming of methane and higher hydrocarbons and for the methanation of coal synthesis gas. In these reactions carbon monoxide participates as a product or reagent, respectively. For that reason, detailed knowledge of the interaction between CO and supported nickel is needed. Also, CO is one of the most frequently used probe molecules for IR characterization of surfaces, including supported nickel [4–12]. This is due to the sensitivity of ν(CO) towards the oxidation degree of the adsorption site, its geometry and coordinative unsaturation.

A series of investigations [5,11–29] has shown that under certain conditions CO corrosively interacts with metallic nickel. This may cause both morphological changes of metal particles [12–15] and nickel loss of the catalyst [2,15]. Thus, during low-temperature (473–523 K) hydrogenation of CO on supported nickel catalysts, the so-called "chemical sintering" of the catalysts occurs [12–15]. This is assumed to be caused by nickel transport from particle to particle in the form of nickel sub/tetracarbonyls extracted from defect Ni^0 sites. These carbonyls migrate either on the support surface or through the gas phase to the (111) face which is characterized by the closest packing of atoms [12–14,16,18–20]. This leads to smoothing and growing of the metal particles. In addition, high CO pressures during hydrocarbon synthesis from synthesis gas can lead to nickel loss of the catalyst: nickel leaves the system in the form of $Ni(CO)_4$ [2,15].

The formation of $Ni(CO)_4$ is thermodynamically favoured by high pressures and low temperatures. It proceeds at pressures above *ca.* 1 Pa and temperatures below 523 K [15,19, 20]. However, from a kinetic point of view, a significant temperature decrease reduces the reaction rate. Studying a series of supported nickel catalysts, Bartholomew and Pannell [21] have not detected $Ni(CO)_4$ formation at 273 K. Under normal conditions the reaction rate is very low (of the order of 10^{-3} to 10^{-2} $Ni(CO)_4$ molecules $site^{-1}$ s^{-1}) [16,17,19,20]. The reaction rate increases with temperature and reaches a maximum at about 350–390 K irrespective of the CO pressure, and then sharply drops [15–17,19]. According to de Groot *et al.* [16] and Greiner and Menzel [17] this is not caused by an increase in rate of the back reaction (dissociation of $Ni(CO)_4$) but by the process mechanism and originates from the decreasing CO coverage on the surface. In addition, the reaction rate is very sensitive to the roughness of the metal surface and the presence of contaminants [16,17,20]. It is assumed [16,17] that carbon deposition on the surface, which may proceed simultaneously with nickel carbonylation, suppresses the reaction significantly. According to Greiner and Menzel [17], the formation rate of $Ni(CO)_4$ depends on the strength of the bonds between (i) the Ni atoms and (ii) the CO molecules with the surface.

A general aim during the synthesis of supported metal catalysts is attaining a high metal dispersion. Thus, a large part of the active phase is able to participate in the catalytic reaction. Therefore, the interaction of CO with disperse nickel catalysts is of practical importance. To pre-

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[*] To whom correspondence should be addressed.

pare highly dispersed Ni/SiO_2 catalyst we grafted Ni^{2+} ions on silica from an aqueous solution of a nickel hexammine complex [23,24]. After complete reduction the sample contains small metal particles of uniform size (average diameter ∼4 nm).

In the literature there are some contradictions with respect to the effect of the dispersion of the supported nickel on the formation of $Ni(CO)_4$. Most authors propose that the interaction is more pronounced with highly disperse catalysts [12–14,23,24] which are normally characterized by a high concentration of defect sites playing the role of active sites in the process. However, some authors [28,29] suggest that the formation of $Ni(CO)_4$ is characteristic of samples with low dispersion. In agreement with the first group of authors, our Ni^0/SiO_2 sample exhibited a strong interaction with CO at room temperature with formation of $Ni(CO)_4$ [23,24]. To the best of our knowledge, there are no detailed studies on the reaction at temperatures lower than 293 K and there are no exact data on the temperature at which this reaction begins. For this reason, the purpose of the present paper was to investigate the effect of the temperature on the interaction between CO and disperse Ni^0/SiO_2. The effect of other factors such as time and CO pressure was also studied. FTIR spectroscopy was used for the investigations. More precise identification of the surface nickel carbonyls was achieved by experiments on coadsorption of ^{12}CO and ^{13}CO.

2. Experimental

The silica used as a support was commercially available *Aerosil* with a specific surface area of 336 $m^2\ g^{-1}$.

Grafting of Ni^{2+} ions on the support was performed from a 0.1 M Ni^{2+} aqueous solution obtained from $Ni(NO_3)_2$ containing 12.5 wt% ammonia (pH 12.3). 10 g of SiO_2 were dispersed in 150 ml of this solution and the suspension obtained was stirred for 1 h. The precipitate was then filtered off, washed thoroughly with water (*ca.* 2 l), dried and calcined for 1 h at 623 K. The nickel concentration in the sample, according to the chemical analysis, was 1.72 wt% [23,24].

The IR spectra were recorded on a Bruker IFS-66 apparatus at a spectral resolution of 1 cm^{-1} accumulating 128 scans. Prior to the experiments, the sample powder was pressed to a self-supporting wafer (density 10–12 $mg\,cm^{-2}$) under a pressure of 10^6–10^7 Pa. Both the pre-treatment and the experiments were performed *in situ* using a purpose-made IR cell connected to a vacuum-adsorption apparatus with a residual pressure lower than 10^{-3} Pa. The design of the cell permitted IR measurements in the range between 85 K and room temperature. Before the experiments the sample was activated by successive thermooxidative and thermovacuum treatment (both at 673 K). The sample was then reduced for 1 h in a hydrogen flow at 873 K and evacuated for 1 h at the same temperature. Separate TPR experiments have shown that this high temperature is necessary to achieve a complete reduction of the supported nickel [23].

Carbon monoxide (>99.997%) was supplied by Linde AG, and ^{13}C-labeled CO by Aldrich Chemical Company, Inc. Its isotopic purity with respect to ^{13}C was 99 at% but it contained about 10 mol% $^{13}C^{18}O$.

3. Results and discussion

3.1. Low-temperature adsorption of CO

It may be expected that for kinetic reasons the formation of $Ni(CO)_4$ at low temperatures would be negligible. Therefore, we studied the interaction between Ni^0/SiO_2 and CO at 85 K and then at gradually increasing temperature. The IR spectrum of CO (equilibrium pressure 200 Pa) adsorbed at 85 K on the reduced Ni/SiO_2 sample showed five bands located at 2157, 2135, 2095, 2049 and 1920 cm^{-1} (figures 1 and 2, spectra (a)). The band at 2157 cm^{-1} is attributed to H-bonded CO [30] since, simultaneously with its appearance/disappearance, a red shift by -90 cm^{-1} of the silanol OH band at 3740 cm^{-1} is detected. The band at 2135 cm^{-1} characterizes physically adsorbed CO. According to literature data [5,8,9,12,23,24] the band at 2095 cm^{-1} can be assigned to $Ni(CO)_x$ ($x = 2, 3$) subcarbonyls. The band at 1920 cm^{-1} is unambiguously attributed to bridged Ni^0_2CO species [4–12,23–26,28,29]. A band with a maximum at 2049 cm^{-1} has also been observed by Mohana Rao *et al.* [27], however after $Ni(CO)_4$ adsorption on a highly dehydroxylated silicalite. These authors suggest that the band is due to the T_2 mode of physically adsorbed $Ni(CO)_4$. The interpretation is based on comparison with IR spectra of a $Ni(CO)_4$ solution. At 85 K the band characterizing nickel tetracarbonyl remained practically unchanged with time, which means that after the formation of a certain amount of adsorbed $Ni(CO)_4$ no further corrosive interaction between CO and supported Ni^0 takes place.

With rising temperature the bands of H-bonded and physically adsorbed CO decrease in intensity and disappear suc-

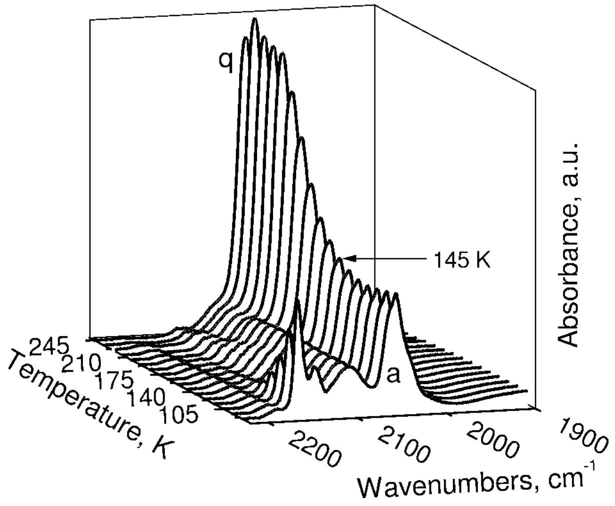

Figure 1. IR spectra of CO (200 Pa equilibrium pressure) adsorbed on Ni^0/SiO_2 at 85 K (a) and at gradually increasing temperature by steps of 10 K up to 245 K (b)–(q).

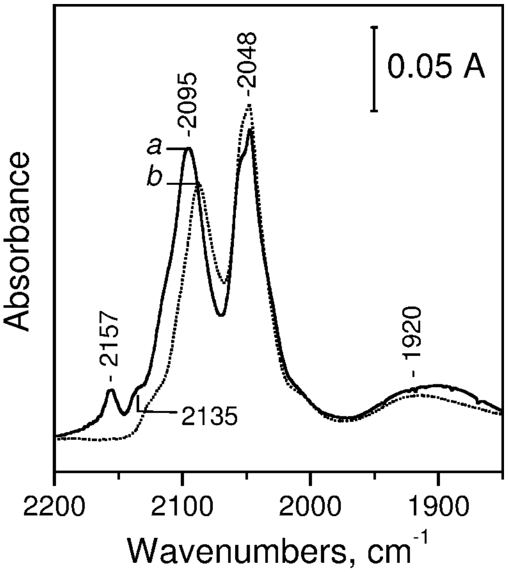

Figure 2. IR spectra of CO adsorbed at 85 K on Ni^0/SiO_2. Equilibrium pressure of 10 Pa CO (a) and after evacuation (b).

cessively at *ca.* 145 and *ca.* 115 K, respectively. The intensity of the bands of sub- and tetracarbonyls remained almost unchanged up to 145 K. Above this temperature the band arising from physically adsorbed $Ni(CO)_4$ quickly increased in intensity, reaching a maximum at about 235 K. With further increase of temperature, the intensity of the band at 2048 cm^{-1} decreases. This indicates that a measurable interaction between supported nickel and CO proceeds at temperatures above 145 K. The intensity drop of the 2048 cm^{-1} band above 235 K can be attributed to a shift of the adsorption–desorption equilibrium in the direction of gaseous $Ni(CO)_4$ because of the fact that the physical adsorption of tetracarbonyl is weak.

On the basis of these results it may be concluded that formation of significant amounts of $Ni(CO)_4$ begins above 145 K. As a result CO causes corrosion of the metal surface.

A fresh sample was reduced *in situ* in a hydrogen flow. Adsorption of CO (100 Pa) on this sample at 85 K led to a spectrum analogous to that already described (figure 2, spectrum (a)). During evacuation the bands characterizing physically adsorbed and H-bonded CO disappear, whereas the band at 2048 cm^{-1} increases in intensity at the expense of the band at 2095 cm^{-1} (figure 2, spectra (a) and (b)). This suggests that the subcarbonyls formed on defect sites of the metal surface are precursors of $Ni(CO)_4$ formation as has also been assumed by other authors [12].

3.2. Adsorption of CO at room temperature

In order to obtain more information on the effect of different factors (pressure, time of contact) on the interaction between Ni^0 and CO, additional experiments at room temperature were performed.

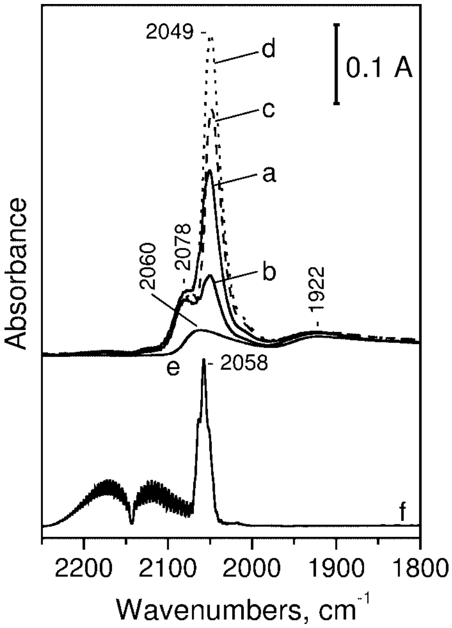

Figure 3. IR spectra of CO adsorbed at room temperature on Ni^0/SiO_2. Equilibrium pressure of CO = 1.6 kPa (a); evacuation and readsorption of 1.6 kPa CO (b); evacuation and readsorption of 20 kPa CO, spectrum recorded immediately after the introduction of CO (c) and after 10 min (d) and after subsequent evacuation (e). Spectrum of the gas phase after interaction of CO (20 kPa) with the Ni^0/SiO_2 sample (f).

Adsorption of CO (1.6 kPa) on a freshly reduced Ni/SiO_2 sample leads to the appearance of an intense band at 2049 cm^{-1} with a shoulder at 2078 cm^{-1} and a low-intensity band at 1922 cm^{-1} (figure 3, spectrum (a)). These bands were already assigned to adsorbed $Ni^0(CO)_4$, $Ni^0(CO)_x$ and Ni_2^0CO carbonyls, respectively. However, the intensity of the band at 2049 cm^{-1} is much higher than in the case of adsorption of CO at 85 K. Hence, as discussed above, the supported nickel and CO interact, forming volatile $Ni(CO)_4$. This assumption is confirmed by the spectrum of the gas phase (figure 3, spectrum (f)) in which an intense band at 2058 cm^{-1} characterizing gaseous $Ni(CO)_4$ [22,27,31] was detected.

Subsequent evacuation and adsorption of the same amount of CO results in a pronounced decrease in intensity of the 2049 cm^{-1} band and a slight decrease in intensity of the band at 2078 cm^{-1} (figure 3, spectrum (b)). This can be explained by elimination of $Ni(CO)_4$ during the evacuation. Most probably this leads to a concentration decrease of the reactive sites on which the compound is formed. As already noted, some authors [12,17,19,20] assume that these are defect sites on the metal surface and their consumption leads to smoothing of the metal surface. Another reason for the decrease of the amount of the appearing sub- and tetracarbonyl complexes might be the blocking of defect sites by carbon as a result of dissociation or disproportionation of CO. This process occurs usually at higher temperatures but may take place partially at room temperature on stepped and highly disordered surfaces [16,17,20]. However, the absence of bands in the region above 2100 cm^{-1} excludes the presence of Ni^+ and/or Ni^{2+} ions on the sample surface [6,23–26]. This suggests that under these conditions no CO dissociation has occurred, otherwise the oxygen formed would have oxidized Ni^0 [1,22–26].

The subsequent evacuation–adsorption cycle of a much larger CO quantity (equilibrium pressure of 20 kPa) leads to an intensity rise of the 2049 cm^{-1} band which is characteristic of physically adsorbed $Ni(CO)_4$ (figure 3, spectrum (c)). Obviously, this is caused by a considerable increase in the pressure of the carbon monoxide in spite of the fact that the concentration of defect sites on the metal nickel particles has decreased.

The intensity of the band at 2049 cm^{-1} slowly increases with time (figure 3, spectrum (d)). This is an indication that under the chosen conditions the system does not reach equilibrium rapidly.

After evacuation the spectrum exhibits only two weak broad carbonyl bands at 2060 cm^{-1} (Ni^0–CO) [4–12,23–29] and at 1922 cm^{-1} (Ni_2^0CO) (figure 3, spectrum (e)). It should be noted that, despite the fact that the bands of linear carbonyls and physically adsorbed tetracarbonyl almost coincide, the corresponding surface forms significantly differ in stability, the linear carbonyls being much more stable.

The results show that the interaction between CO and supported Ni^0 proceeds mainly with the participation of small nickel particles and depends strongly on the CO pressure. The rate of $Ni(CO)_4$ formation decreases with time which is likely caused by a consumption of the active sites.

3.3. Adsorption of labeled CO

Additional experiments on coadsorption of ^{12}CO–^{13}CO at 85 K were performed for an elucidation of the nature of surface $Ni_x(CO)_y$ complexes. Initially ^{12}CO (100 Pa equilibrium pressure) was adsorbed at 85 K on the sample. Bands of H-bonded CO (2157 cm^{-1}), physically adsorbed CO (2138 cm^{-1}), sub- (2094 cm^{-1}) and tetracarbonyls of nickel (2047 cm^{-1}) were observed. ^{13}CO (100 Pa) was then introduced into the IR cell. In order to achieve more complete exchange between the isotopes, the pellet was heated for a short time at room temperature, then cooled again to 85 K. The spectrum of the sample treated in this way showed nine bands (figure 4). Several of these bands can easily be ascribed to adsorption complexes with the participation of either ^{12}CO (2157, 2137, 2091 and 2047 cm^{-1}) or ^{13}CO (2109, 2091, 2047 and 2003 cm^{-1}). Some of the bands coincided. Another low-intensity band at 1963 cm^{-1} is attributed to species involving $^{13}C^{18}O$. Two additional bands at 2030 and 2017 cm^{-1} were not detected after adsorption of the pure isotopes.

Nickel tetracarbonyl is a tetrahedral molecule with one IR active mode, T_2 at 2058 cm^{-1} [22,27,31]. A stepwise exchange of $Ni(^{12}CO)_4$ with ^{13}CO molecules is expected to produce three new bands in the $\nu(^{12}CO)$ region on the place of the T_2 band. These three bands have to originate from $[Ni(^{12}CO)_3(^{13}CO)]$, $[Ni(^{12}CO)_2(^{13}CO)_2]$ and $[Ni(^{12}CO)(^{13}CO)_3]$ species, respectively. However, we detected only two bands. These results could be rationalized by the assumption that, in the adsorbed state, $Ni(CO)_4$ contains an isolated $Ni(CO)_3$ group. Thus, the bands at 2030 and 2017 cm^{-1} can be attributed to $[Ni(^{12}CO)_2(^{13}CO)]$ and $[Ni(^{12}CO)(^{13}CO)_2]$ groups, respectively. Hence, the results suggest that the adsorption of $Ni(CO)_4$ leads to fixing of one CO ligand to the support surface, the remaining part of the molecule imitating the structure of a tricarbonyl.

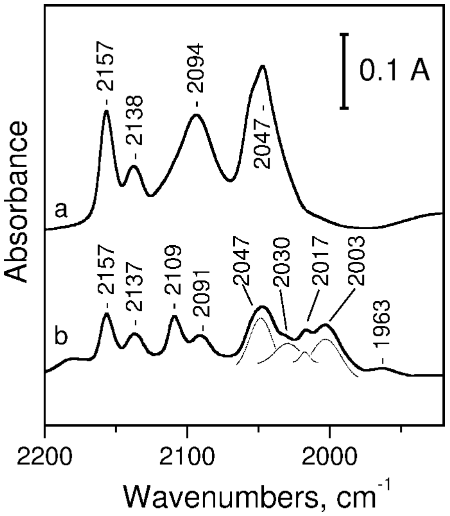

Figure 4. IR spectra of ^{12}CO (100 Pa equilibrium pressure) adsorbed on Ni^0/SiO_2 at 85 K (a) and after introduction of ^{13}CO (100 Pa equilibrium pressure), heating the sample at room temperature for 2 min and cooling again to 85 K (b).

Another possibility to explain the results obtained is the presence of $Ni(CO)_3$ entities on the sample surface. Interacting with CO, these species give $Ni(CO)_4$ which is released in the gas phase and, *vice versa*, $Ni(CO)_3$ species are produced during adsorption of gaseous $Ni(CO)_4$ on silica:

$$[\mathrm{Ni(CO)_3}]_{\mathrm{ads}} + [\mathrm{CO}]_{\mathrm{gas}} \rightleftharpoons [\mathrm{Ni(CO)_4}]_{\mathrm{gas}} \tag{1}$$

Thus, our results confirm the interpretation of the band at 2048 cm^{-1} as characterization to nickel polycarbonyls and at the same time indicate the presence of $Ni(CO)_3$ groups.

4. Conclusions

- At temperatures below 145 K the interaction between CO and Ni^0/SiO_2 is restricted to the formation of nickel carbonyls, among them very minor amounts of $Ni(CO)_4$ adsorbed on SiO_2.
- The formation rate of $Ni(CO)_4$ begins to increase rapidly above 145 K, which leads to corrosion of the metal particles.

Acknowledgement

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