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Reactions of CO and CO_2 on Ni/SiO_2 above 373 K as Studied by Infrared Spectroscopic and Magnetic Methods

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Reactions of CO and CO_2 on Ni/SiO_2 catalysts have been studied in the 373–700 K range by ir, magnetic (saturation magnetization), and volumetric measurements. At room temperature, CO is adsorbed as a mixture of the linear form, $Ni–CO_{ads}$, and the bridged form, Ni_2CO_{ads}. Upon heating the system beyond 400 K, these forms are irreversibly transformed into new CO adspecies bonded to four Ni atoms, Ni_4CO_{ads}, with a ν_{CO} frequency at about 1830 cm^{-1}. This multibonded species is in equilibrium with gaseous CO_2 according to the reaction $2\ CO \rightleftarrows CO_2 + C$; the remaining carbon atom is reversibly dissolved into the bulk in an interstitial position. This CO disproportionation is assumed to occur via the C–O rupture of Ni_4CO_{ads} with formation of a surface carbon atom bonded to three nickel atoms Ni_3C_{surf} and an oxygen atom bonded to one nickel atom. CO_2 is dissociated on pure nickel into CO, adsorbed as Ni_4CO_{ads}, and adsorbed oxygen atoms.

I. INTRODUCTION

In previous papers (*1*, *2*) it was shown that CO was chemisorbed below 373 K on Ni/SiO_2 catalysts mainly as a mixture of linear and bridged molecular species, with a surface concentration ratio which is independent of nickel particle size in the 2.5- to 9.5-nm range, and also independent of CO coverage and temperature (273–373 K); addition of Cu (alloys) or presence of unreduced residues (partially reduced samples) leads to a lower concentration of the bridged species, which is probably associated with a changed surface geometry resulting from a dilution of the nickel phase.

In the literature, CO chemisorption is generally considered to be completely nondissociative. Recent results obtained by electron spectroscopy and ion mass spectroscopy on polycrystalline nickel above 373 K, however, are interpreted as reflecting thermally induced dissociation of the adsorbed CO (*4–6*). From the catalytic standpoint, the existence of CO rupture on polycrystalline surfaces is of importance since it provides a possible path for the methanation reaction on nickel catalysts (often considered as polycrystalline Ni surfaces).

This is the reason why we have undertaken a study of the CO reaction on a completely reduced Ni/SiO_2 catalyst above 373 K, with the help of the infrared spectroscopic and high field magnetic methods described in previous papers (*1*, *2*).

II. METHODS

Most of the experiments were performed on a Ni/SiO_2 catalyst prepared by reduction (at 650°C for 15 hr in an H_2 flow) of a precursor obtained by addition of silica to a solution of nickel nitrate hexammine [precursor A, reduction proce-

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dure 1 in reference (*2*)]. The reduction was shown to be complete, and nickel particle diameters calculated from magnetic measurements were approximately equal to 6 nm. The volume of adsorbed hydrogen at room temperature and 760 Torr was 37 ml NTP/g of Ni (*2*).

The experimental methods were the same as those described in previous papers (*1*, *2*). The nickel magnetization was measured using the Weiss extraction method. The saturation magnetization decreases upon gas chemisorption. This decrease enables us to calculate n, the magnetic "bond number" by dividing α, the decrease of the saturation magnetization (in Bohr magnetons, BM) per adsorbed molecule, by μ, the magnetic moment per nickel atom, assuming that nickel atoms involved in the bonding cease to participate in the collective ferromagnetism (*1–3*). Infrared spectra were run at room temperature on a Fourier transform spectrometer (*1*, *2*). After heat treatments, samples were cooled to room temperature for infrared and magnetic measurements; thus the observed results do not necessarily reflect the situation of the adsorbed species at higher temperatures.

III. RESULTS

In earlier experiments, CO was chemisorbed at room temperature, and the system was heated stepwise up to 700 K. Large amounts of evolved CO_2 were observed which were partly readsorbed during cooling to room temperature to perform magnetic and infrared measurements. This CO_2 evolution made the interpretation of the results rather difficult. It was then decided to simplify the system by trapping CO_2 by cryopumping, and the corresponding experimental results are reported in Section 1. They afford a better understanding of earlier experiments (system heated without cryopumping) which are described in Section 2. Finally, this work was made complete by the study of CO_2 chemisorption which is reported in Sections 3 and 4.

1. Heat Treatment of Chemisorbed CO with Cryopumping of Evolved Gases

About 7.5 and 15 ml NTP of CO/g of Ni were chemisorbed at room temperature. Higher coverages were not studied owing to the fact that they could lead to $Ni(CO)_4$ formation. The system was heated in steps up to 700 K, and evolved gases were trapped in a liquid nitrogen system. Results obtained for both coverages were found to be very similar. From infrared spectra, it was observed that the chemisorbed CO band vanished completely (Fig. 1). The volume of trapped gas,

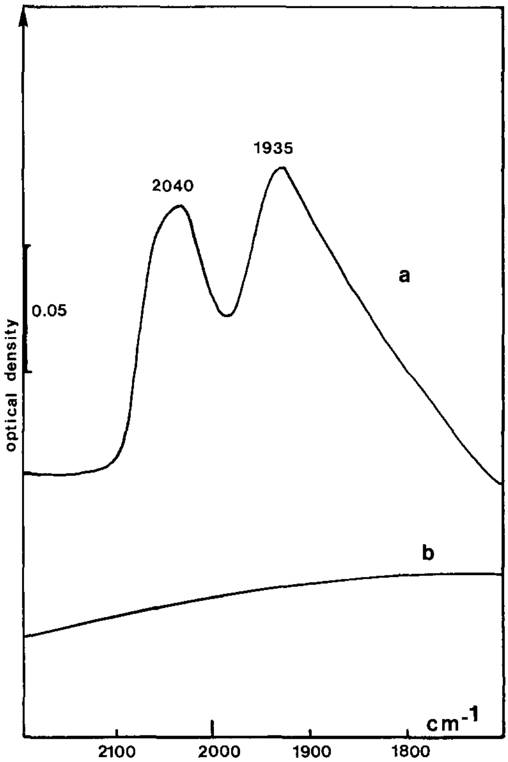


FIG. 1. Infrared spectra obtained during heat treatment of chemisorbed CO with cryopumping of evolved gases. (a), 15 ml of CO/g of Ni adsorbed at 300 K; (b), previous sample treated at 600 K for 2 hr (evolved gases were trapped in a liquid nitrogen-cooled system).

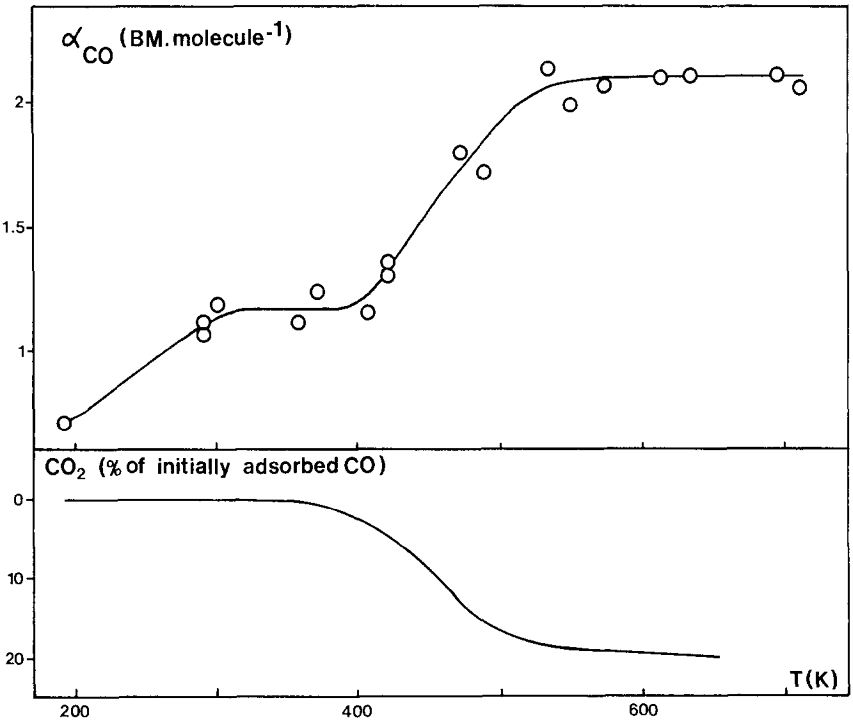


FIG. 2. Variations of α_{CO} in Bohr magnetons (BM) and of the CO_2 content in the gas phase (expressed as a percentage of the initial adsorbed CO) against the holding temperature T.

which was shown to be mainly CO_2, was found to be equal to half the volume of initially adsorbed CO, indicating that the reaction was probably the disproportionation of CO into C and gaseous CO_2:

$$2CO_{ads} \rightarrow CO_{2\ gas} + C. \quad (1)$$

Since the deposited carbon decreases the saturation magnetization by, respectively, 3.4 and 3.1 BM per C atom for low and high initial CO coverages, it is likely to be interacting chemically with the nickel.

A linear extrapolation to zero carbon concentration gives $\alpha_C = 3.7 \pm 0.3$ BM per atom.

2. Heat Treatment of Adsorbed CO without Cryopumping

Results obtained for both coverages ($v_{CO} = 7.5$ and 15 ml NTP g^{-1} of Ni) were also found to be very similar. Figure 2 shows the variations of α_{CO} with the holding temperature.

The plateau observed between 300 and 400 K was discussed earlier (*2*): CO was chemisorbed as a mixture of linear (ir band at 2070–2040 cm^{-1} denoted $NiCO_{ads}$) and bridged species (1935 cm^{-1} denoted Ni_2CO_{ads}) with a small shoulder at about 1800 cm^{-1} still not identified. The corresponding average bond number was 1.85. At higher temperatures, a second plateau at $\alpha = 2.1$ BM was detected beyond 530 K; about 23% of the carbon initially adsorbed as CO was converted into gaseous CO_2 indicating that the same amount (23% of the initial CO) was converted into carbon remaining in the catalyst. The magnetic effect due to this carbon was assumed to be equal to that previously observed in Section 1. Then, the saturation magnetization decrease calculated for the remaining ($100 - 2 \times 23 = 54\%$) CO was $\alpha_{CO} = 2 \pm 0.2$ BM/molecule with a corresponding bond number $n_{CO} = 3.3 \pm 0.3$. In this calculation, no speculation whether

CO was dissociated or not was made. It indicated that the nature of the adsorbed species was drastically changed by such a heat treatment.

Figure 3 shows the ir spectra of CO adsorbed at room temperature, then heated stepwise at higher temperatures; at $T > 380$ K, the intensity of the CO bands began to decrease. This temperature corresponds to the increase in α in Fig. 2. At 600 K, the area of the CO bands surface was half that below 380 K, suggesting that 50% of CO was probably transformed into $C + CO_2$. This result is in quite good agreement with the above volumetric data.

Moreover, the spectrum of the remaining CO was markedly changed: As temperature increased, the intensity of linear forms (A bands, $\nu_{CO} > 2000$ cm^{-1}) decreased more rapidly than the intensity of multicentered forms (B bands, $\nu_{CO} < 2000$ cm^{-1}) in such a way that the ratios of optical density decreased from $r = A_A/(A_A + A_B) = 0.35$ at 300 K to $r = A_A/(A_A + A_B) = 0.15$ at 600 K.

Inside the A and B bands, frequency and relative intensity changes were also observed upon heating: The band at 2035 cm^{-1} was shifted down to 2005 cm^{-1}. The intensity of the B_1 band at 1935 cm^{-1}, assigned to the bridged species, decreased approximately to zero, and the intensity of the B_2 band at 1820 cm^{-1} was enhanced. One can calculate the corresponding bond number of the B_2 species, taking into account that $n_{CO} = 3.3 \pm 0.3$ previously calculated from magnetic data, was in fact an average bond number corresponding to 15% of linear species and 85% of the B_2 species according to ir optical densities. One obtains for the B_2 species $n_{CO(B_2)} = 3.7 \pm 0.4$.

This sample covered with 15 ml of CO NTP/g of Ni at room temperature, then subsequently heated at 580 K, was submitted to a further CO adsorption at room temperature. The corresponding ratio $A_A/(A_A + A_B)$ was 0.35. Since the initial ratio was 0.15, the calculated ratio corresponding to the further adsorption was found to be equal to 0.6, indicating a predominant adsorption of CO in the linear form. Carbon incorporation in the surface should lead to a greater relative abundance of isolated sites or small nickel ensembles which can only adsorb CO in linear form.

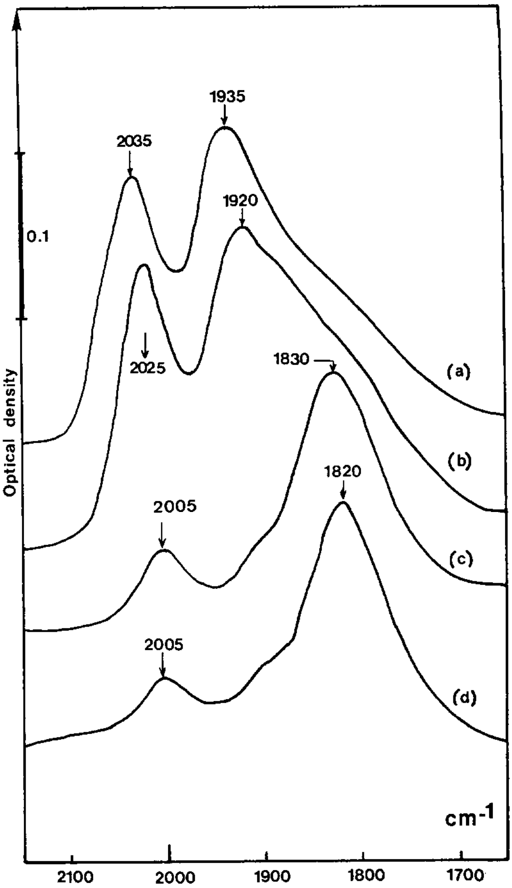


FIG. 3. Infrared spectra obtained during heat treatment of chemisorbed CO without cryopumping of evolved gases. (a), 15 ml of CO/g of Ni adsorbed at 300 K, then heat treatment in closed system; (b), for 1 hr at 380 K; (c), for 2 hr at 480 K; (d), for 1 hr at 600 K.

3. CO_2 *Chemisorption on a Ni + C Catalyst*

After the complete disproportionation of chemisorbed CO by heating and trapping evolved CO_2 (Section 1), CO_2 was allowed

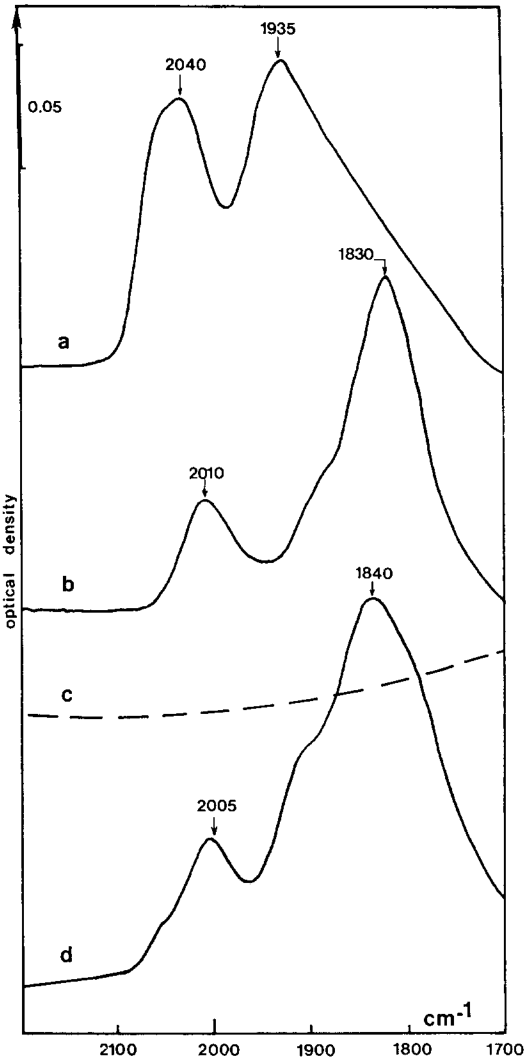


FIG. 4. Infrared spectra of CO_2 adsorbed on (Ni + C) catalysts. (a), 15 ml of CO/g of Ni adsorbed at 300 K; (b), heat treatment in closed system for 2 hr at 600 K; (c), identical to (b), but with trapping the evolved gases; (d), CO_2 adsorbed at 600 K onto sample (c).

to react with the nickel surface, first at 700 K, then at lower temperature during the cooling down to 300 K, by removing the liquid nitrogen trap. Approximately half the quantity of trapped CO_2 was adsorbed by the catalyst. The CO_2 volume remaining in the gas phase was nearly equal to that observed after the treatment described in Section 2 (heat treatment of chemisorbed CO without cryopumping and subsequent cooling at room temperature). The corresponding infrared spectrum which is shown in Fig. 4 is very similar to that observed after heat treatment of chemisorbed CO without cryopumping. The observed bands were assigned to ν_{CO} vibrations, from which it was deduced that the reverse reaction of the disproportionation was occurring as follows:

$$CO_{2\text{gas}} + C \rightarrow 2CO_{\text{ads}}. \qquad (2)$$

The most intense band was situated at 1835 cm^{-1} (the B_2 species), and the ratio $r = A_A/(A_A + A_B)$ was nearly equal to 0.15.

CO_2 chemisorption on the Ni + C catalyst gives rise to a decrease of saturation magnetization: $\alpha_{CO_2} = 1$ BM per molecule.

This decrease is in fact the result of an increase due to the consumption of C by CO_2 ($\alpha_C = 3.4$ BM/C atom; see Section 1) and of a decrease due to the chemisorption of the two CO molecules thus obtained. This decrease due to CO chemisorption may be readily calculated: $\alpha_{CO} = (3.4 + 1)/2 = 2.2$ BM per molecule, and the corresponding bond number is $n_{CO} = 3.7$.

As in Section 1, this bond number is in fact an average value: From ir data it corresponds to a mixture of 15% of the linear form and 85% of the B_2 species. Hence, the bond number for the B_2 species is $n_{CO(B_2)} = 4.2$. This bond number is very close to that observed in Section 2 ($n_{CO(B_2)} = 3.7$).

From volumetric, ir, and magnetic data the situation obtained after this procedure (CO chemisorption at 300 K, heat treatment at 580 K with trapping of evolved CO_2, subsequent CO_2 chemisorption) is very similar to that described in section 2 (CO chemisorption at room temperature, heat treatment at 580 K without trapping CO_2, cooling down to 300 K). In addition a second cycle may be performed: CO_2 can be again trapped in a quantitative

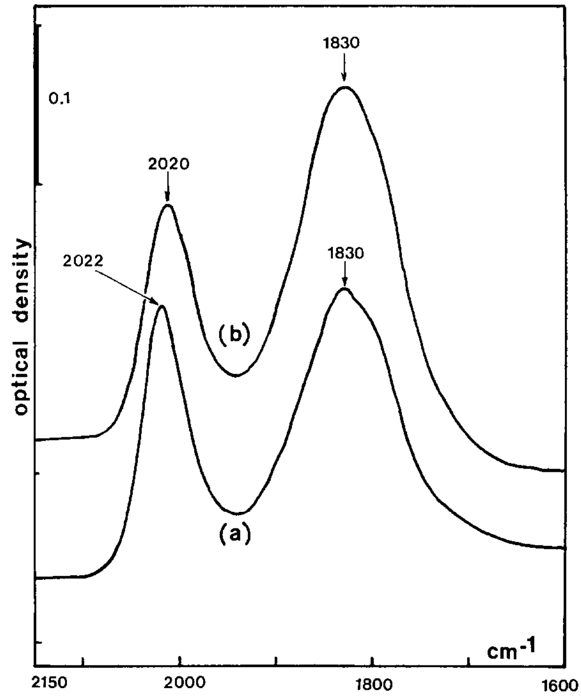


FIG. 5. Infrared spectra of CO_2 adsorbed on pure Ni/SiO_2 catalysts. (a), CO_2 adsorbed at 300 K under 1 Torr of equilibrium pressure; (b), sample (a) heated in closed system for 2 hr at 600 K.

way, and magnetic measurements show that the situation thus obtained is similar to that described after the first treatment. Trapped CO_2 may be readsorbed, and so on.

4. CO_2 *Chemisorption on Pure Nickel*

Figure 5 shows the ir spectra of the nickel catalyst saturated with chemisorbed CO_2 at 300 and at 580 K. Neither carbonate nor carboxylate bands were detected. The two bands observed at 2020 and 1835 cm^{-1} were attributed to ν_{CO} vibrations. CO_2 chemisorption probably resulted from the following dissociation:

$$CO_{2\,gas} \rightarrow CO_{ads} + O_{ads}. \qquad (3)$$

Spectra thus obtained were qualitatively similar to those observed upon CO_2 chemisorption on Ni + C catalysts (Section 2); the only difference was that the concentration of the linear species was larger on pure nickel. Observed ratios $A_A/(A_A + A_B)$ at 300 and 580 K were, respectively, 0.34 and 0.23, whereas for the system CO_2 + (Ni + C) this ratio was 0.15. Figure 6 shows the variations of α_{CO_2} and n_{CO_2} with the holding temperature (adsorbed volume 6 ml NTP/g of Ni). From this curve, it can be seen that α and n increase slightly with the holding temperature. This increase is likely to be due to the change in the relative concentration of the B_2 species evidenced by infrared experiments (the ratio decreases from 0.34 to 0.23). From α_{CO_2} in Fig. 6, one can calculate α_{CO} assuming that the contribution of O at 300 K is equal to that observed from O_2 chemisorption at 300 K (7), i.e. $\alpha_O = 0.7$ BM per atom. One obtains at 300 K: $\alpha_{CO} = \alpha_{CO_2} - \alpha_O = 1.9$ BM per molecule and $n_{CO} = 3.2$.

From ir data, this average bond number corresponds to 34% of the linear form and 66% of the B_2 form. Thus, the bond number which can be attributed to the B_2 species is $n_{CO(B_2)} = 4.3 \pm 0.5$. This value is in good agreement with those

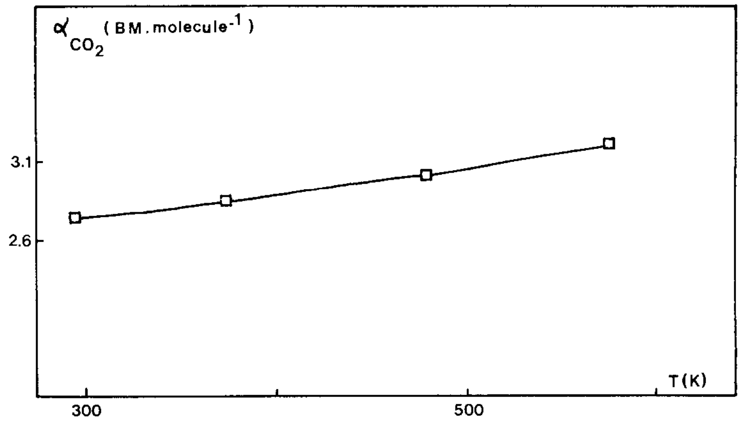


FIG. 6. Adsorption of CO_2 on pure Ni: Variations of α_{CO_2} against the holding temperature.

obtained from direct CO chemisorption at high temperatures described in Sections 2 and 3.

Reaction (3) is reversible: It has been shown that 60 and 100% of the chemisorbed CO_2 are removed by pumping at 470 and 570 K, respectively, according to reaction (4):

$$CO_{ads} + O_{ads} \rightarrow CO_{2\ gas}. \qquad (4)$$

It can be asked whether the chemisorption of CO and of O_2 would give the

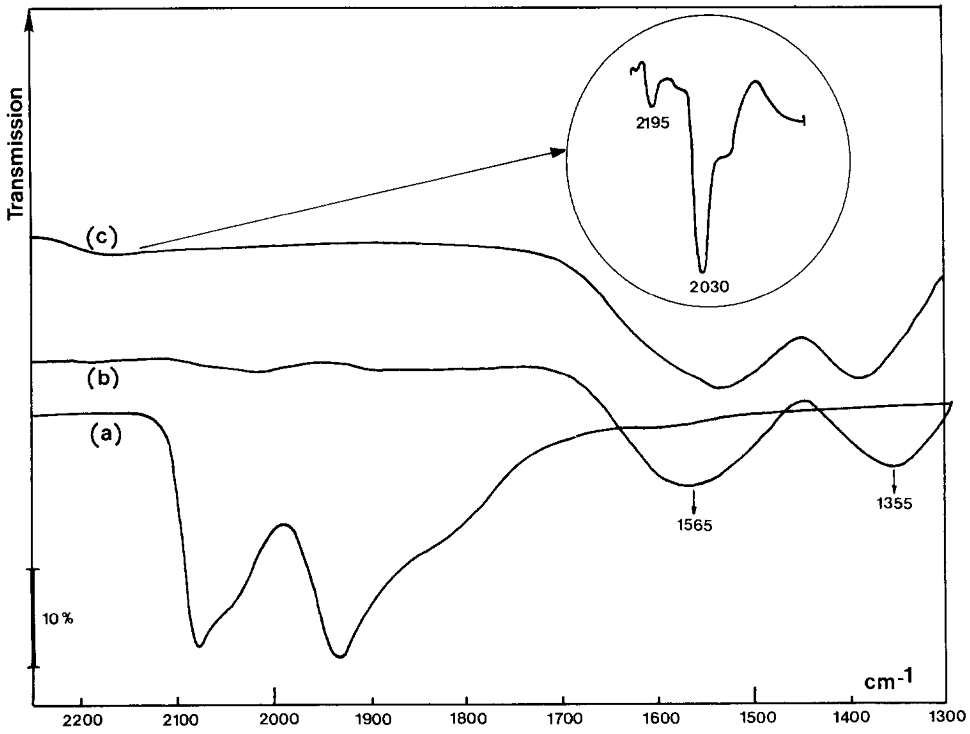


FIG. 7. Infrared spectra obtained during the oxidation of adsorbed CO by gaseous oxygen at 300 K. (a), CO adsorbed on Ni/SiO_2 catalyst (reduction level = 100%; particle size = 6.5 nm.); (b), O_2 admitted at 300 K on sample (a); (c), evacuation of the gas phase and introduction of CO at a pressure of 1 Torr (circled spectrum corresponds to the automatic scale expansion of the 2250- to 2000-cm^{-1} region).

same results as direct CO_2 chemisorption; the answer is no (Fig. 7): At room temperature, the preadsorbed CO bands vanish as O_2 is adsorbed, and bands at 1565 and 1355 cm^{-1} which can be attributed to carboxylate species bonded to Ni appear. When CO is subsequently admitted, a very small amount is chemisorbed, mainly as linear species on Ni but to a smaller extent on NiO (2195 cm^{-1}).

IV. DISCUSSION

1. *Nature of Observed Species*

The carbon which is formed from CO disproportionation at 580 K decreases the saturation magnetization by 3.7 ± 0.3 BM/C (Section 1). This magnetic effect is very similar to that observed by Cadeville *et al.* (*8*) for carbon interstitially dissolved in bulk nickel. These authors have interpreted their results assuming that the carbon impurity which has a charge difference of Z = four electrons with the metal is screened to satisfy the classical law of electric neutrality in conducting metals (*9*). The screen is situated in the d band for transition metals. In the case of ferromagnetic nickel, the screening of C is coming from the two spin subbands $\sigma\uparrow$ and $\sigma\downarrow$ with $Z\uparrow = 0.2$ and $Z\downarrow = 3.8$, so that the Friedel sum rule is satisfied ($Z = Z\uparrow + Z\downarrow$ = four electrons) and the observed decrease of saturation magnetization is accounted for ($\alpha = Z\downarrow - Z\uparrow = 3.6$ BM). In that case, the screening comes mainly from the minority-spin band ($Z\downarrow = 3.8$). In our case, it seems reasonable to make the same hypothesis and to assume that the carbon atom is also in an interstitial position. In our experiments the total amount of C which is dissolved is nearly equal to the solubility of carbon in bulk nickel (*8*). This carbon will be denoted $C_{interst.}$ in further discussions. It should not be confused with another form of carbon in nickel catalyst observed by complete craking of hydrocarbons at temperatures around 370 K and characterized by $\alpha = 1.8$ BM/C and $n = 3$.

This form probably corresponds to a nickel carbide, Ni_3C, located on the nickel surface, and be denoted $Ni_3C_{surf.}$. It has been shown that this surface carbide may undergo a dissolution into the bulk at temperatures higher than 370 K (*10*). The reversible reaction seems probable, and it can be written:

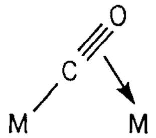
$$C_{interst.} \overset{Ni}{\rightleftarrows} Ni_3C_{surf.} \qquad (5)$$

Another species that has been evidenced in this work is that corresponding to the CO band at about 1830 cm^{-1} with a bond number nearly equal to 4 (Sections 2, 3, and 4). The observed frequency is characteristic of a carbonyl species; hence C and O are not separated. Various models may be proposed to account for the observed bond number:

(i) The first one would consist of an erect adsorbed molecule with the carbon atom bonded to four nickel atoms. Such a model has never been detected in coordination compounds: The carbon atom of the CO molecule is generally bonded to one, two, or in some cases to three metal atoms. This cannot be considered as a definitive proof that such a model would not exist on a metallic surface, however.

(ii) Coordination chemistry suggests another possible model (*11*, *12*): In $W(CO)_5PPh_3$, $EtAlCl_2$ or $Mo(phen)(PPh_3)_2(CO)_2$, $AlEt_3$ complexes, the carbon and oxygen atoms are bonded to the two metallic atoms of the complex. In our case, C and O could be also bonded to the nickel atoms of the surface.

(iii) From coordination chemistry, a third model can be proposed: In dimanganese clusters (*13*, *14*), one of the metal atoms forms a normal two-electron metal–carbon dative bond with a possible π component, while the other metal bonds to the C≡O bond as it would in heteroolefin; the model may be written in the following way:



This system has been shown to be labile: The two metallic atoms have a similar role due to the rapid movement of CO. It may be supposed that on a nickel surface (which can be considered as a metallic cluster with a large number of metallic atoms) this lability could be extended to a larger number of metallic atoms, giving rise to bond numbers higher than 2. Such a hypothesis has already been proposed in the case of benzene chemisorption on nickel (*15, 16*).

It might be objected that the stretching frequency of the adsorbed species (1830 cm^{-1}) is much higher than that corresponding to the metal carbonyl Lewis acid complexes [1633–1731 cm^{-1} (*11*) and 1667 cm^{-1} (*12*)] and to the dimanganese complex (1645 cm^{-1}). It should be recalled, however, that when the number of metallic atoms increases in a cluster or when one goes from the cluster to the metal, the CO frequency increases to a large extent (*1*). Thus, this objection may be rejected.

It is clear that models, different from those suggested above may be imagined, but whatever the exact model, the main facts are that CO is bonded to four nickel atoms (this species will be noted $Ni_4\text{–}CO_{ads}$ in the following discussion) and that the ir stretching frequency of CO is lowered indicating a weakening of the C–O bond.

2. Reactions and Intermediates Involved

(i) The first reaction that has been reported is the thermal disproportionation of CO initially adsorbed at room temperature mainly as a mixture of linear and bridged species (reaction 1 in Section 1):

$$Ni\text{-}CO_{ads},\ Ni_2CO_{ads} \rightarrow CO_{2\ gas} + C_{interst.} \qquad (1)^*$$

This reaction probably involves intermediate steps that we can try to elucidate.

(ii) First of all, this reaction is not reversible, in the sense that when CO_2 is allowed to react with the nickel catalyst containing interstitially dissolved carbon (Section 3), a new adspecies is detected, $Ni_4\text{–}CO_{ads}$. This adsorbed form can be easily transformed again in the $CO_{2\ gas}$ and dissolved carbon as shown by the second cycle described in Section 3.

The reversible reaction corresponding to these transformations may be written:

$$Ni_4\text{–}CO_{ads} \rightleftarrows CO_{2\ gas} + C_{interst.} \qquad (6)$$

As $Ni\text{–}CO_{ads}$ and $Ni_2\text{–}CO_{ads}$ are transformed upon heating into $Ni_4\text{–}CO_{ads}$ (Section 2), we can assume that one of the intermediate species in reaction (1*) is $Ni_4\text{–}CO_{ads}$, and the combination of Equations (1*) and (6) would give:

$$Ni\text{–}CO_{ads},\ Ni_2\text{–}CO_{ads} \rightarrow Ni_4\text{–}CO_{ads} \rightleftarrows CO_{2\ gas} + C_{interst.} \qquad (7)$$

This hypothesis seems reasonable since $Ni_4\text{–}CO_{ads}$ is thermodynamically more stable than the mixture of linear and bridged species (the lower the ir C–O stretching vibration frequency, the stronger the carbon–metal bond and the weaker the C–O bond). Another argument in favor of this hypothesis is that of all the adsorbed species detected in this work, $Ni_4\text{–}CO_{ads}$ has the weakest C–O bond, making it the most prone to be disrupted into carbon and oxygen, a necessary path in the disproportionation reaction.

(iii) It is interesting now to speculate on the intermediate steps in the disproportionation reaction itself (reaction 6). It has been seen that disproportionation requires a rupture of the C–O bond, and that $Ni_4\text{–}CO_{ads}$ is energetically the most probable precursor. It can be asked what is the exact nature of the fragments involved in this rupture. The carbon fragment is probably the surface carbide, bonded to three nickel atoms, since it is the only carbon surface species we have detected. The oxygen atom is likely to be bonded to one nickel atom as in molecular gaseous oxygen adsorption on nickel (*7*). These fragments require together four nickel atoms, just as $\mathrm{Ni_4{-}CO_{ads}}$. This geometrical consideration may be considered as an additional proof that the precursor in the C–O rupture is $\mathrm{Ni_4{-}CO_{ads}}$. The cracking reaction would be:

$$\mathrm{Ni_4{-}CO_{ads}} \rightleftarrows \mathrm{Ni_3C_{surf.}} + \mathrm{Ni{-}O_{ads}}. \qquad (8)$$

It should be noted that Eq. (8) has not received direct experimental verification in this work; however, it is consistent with all our experimental data. The beginning of the CO cracking would correspond to the formation of gaseous CO_2, i.e., beyond 380 K, in agreement with results obtained by other techniques (*4–6*).

Finally, combining Eqs. (8) and (7) and assuming that the surface carbon may be dissolved into the bulk [Eq. (5)], one obtains the overall process (*9*):

$$\begin{aligned} &\mathrm{Ni{-}CO_{ads}},\ \mathrm{Ni_2{-}CO_{ads}} \rightarrow \mathrm{Ni_4{-}CO_{ads}} \rightleftarrows \\ &\qquad \mathrm{Ni_3C_{surf.}} + \mathrm{Ni{-}O_{ads}} \rightleftharpoons \tfrac{1}{2}\mathrm{CO_{2\,gas}} \\ &\qquad\qquad + \begin{array}{c}\mathrm{Ni_3C_{surf}} \\ \downarrow\uparrow \\ \mathrm{C_{interst.}}\end{array} \qquad (9)\end{aligned}$$

A point which remains obscure is how C and O fragments are reacting to give gaseous CO_2. There are at least two possibilities: Either one oxygen atom reacts with $\mathrm{Ni_4{-}CO_{ads}}$, or one carbon reacts with two oxygen atoms.

If there is no direct proof for the latter scheme, the former hypothesis is invoked in the case of CO_2 adsorption onto pure nickel. In Section 4, it was concluded that gaseous CO_2 may be split on pure nickel into adsorbed oxygen and $\mathrm{Ni_4{-}CO_{ads}}$. The reaction was shown to be reversible by pumping back CO_2 according to the following reaction:

$$\mathrm{CO_{2\,gas}} \overset{\mathrm{Ni}}{\rightleftarrows} \mathrm{Ni{-}O_{ads}} + \mathrm{Ni_4{-}CO_{ads}}. \qquad (10)$$

This overall process is of importance owing to the problem of the CO disproportionation, and also of methanation. Certain questions remain. Is hydrogen reacting with carbon, as suggested in recent papers (*17*, *18*), or with adsorbed CO? And if this is the case, what are the active forms? Work on this subject is in progress in our laboratory.

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