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Adsorption of CO on Well-Defined Ni/SiO$_2$ Catalysts in the 195–373 K Range Studied by Infrared Spectroscopy and Magnetic Methods

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CO adsorption on Ni–SiO$_2$ catalysts has been studied by two complementary techniques, infrared spectroscopy and saturation magnetization. Special care was taken to measure the degree of reduction and the metallic particle size. Two main bands attributed to CO bonded to Ni are observed: the A band at 2070–2040 cm^{-1}, and the B band at 1935 cm^{-1} with a shoulder at 1800 cm^{-1}. For completely reduced samples, the ratio $r = A_A/(A_A + A_B)$ of the integrated intensities of A and B bands, as well as the bond number n calculated from magnetic measurements ($n = 1.85$) are particle size independent in the 2.5–9.5 nm range, temperature independent in the 20–100°C range, and coverage independent. On partially reduced samples, n is smaller and r higher.

Experimental results are fully accounted for by assuming that the A band corresponds to a linear form and that the B band is a bridged species, the shoulder at 1800 cm^{-1} being attributed to multicentered species. Ni^{2+} or NiO present on partially reduced samples acts as a diluent of metallic nickel atoms, similar to Cu atoms in Ni–Cu alloys; the stability of the concentration ratio of linear and bridged species suggests an analogy with coordination complexes. The presence of two bands in the region corresponding to linear species (2070 and 2040 cm^{-1}) with intensities ratios varying with the degree of reduction, Ni particles size, coverage, and temperature is also discussed.

INTRODUCTION

The adsorption of CO on supported nickel has received considerable attention hitherto. The first reason is that CO is involved in reactions of great economic importance, like methanation, or steam-reforming of hydrocarbons. Moreover, CO is an exceptionally good molecule for basic chemisorption studies owing to its high stability (dissociation on the surface can be generally excluded in moderate conditions).

The first description of the Ni–CO surface bond was proposed by Blyholder (*1*) using the Chatt-Dewar scheme for coordination complexes: in this model, a concerted electron transfer of the 3σ lone pair from C to metal and back donation of metal electrons to the lowest unfilled orbitals of CO (Π^* antibonding) is assumed. This basic scheme is generally accepted, and has recently been used in theoretical treatments of CO chemisorption (*2, 3, 11*). Infrared data reported in the literature are interpreted within the framework of this scheme; however, two types of interpretation are proposed to account for the observed bands:

i. according to Eischens and Pliskin (*4*), the absorption band above 2000 cm^{-1} must be ascribed to the stretching vibrations of linearly bonded CO, while the bands below this frequency are due to bridge-bonded

CO. Results obtained on Ni–Cu alloys (*5–8*) are in agreement with this view: the larger the Cu content, the smaller the relative intensity of the latter band; if this band is ascribed to bridged species, then results are fully accounted for, assuming that Cu acts as a diluent for Ni atoms. Magnetic measurements are also in good accordance with this hypothesis (*8*): the "bond numbers" corresponding to the bands above and below 2000 cm^{-1} are, respectively, 1 and approximately 2. More recently CNDO calculations were performed on the interaction of CO with (100) and (111) faces of clusters containing up to 13 Ni atoms (*9*). Two models were proposed: the first one corresponds to a CO molecule located directly over the nickel surface atom, and the second one, in a multicentered position, the carbon atom being directly over the center of the hole (this position is the most stable). CO bond order determinations allowed the 2075 and 1935 cm^{-1} bands to be attributed, respectively, to the first and to the second model (*9*).

ii. It was also suggested (*1*) that CO is bonded only to one metallic atom (linear form) and that the various C–O stretching frequencies which are observed are due to the various electronic states of the metallic surface atoms, this electronic state reflecting the geometric environment. According to this view the band above 2000 cm^{-1} is regarded as due to CO adsorbed on regular crystal faces where Ni atoms have a high coordination number, and the band around 1900 cm^{-1} corresponds to CO adsorption on sites where the Ni atoms have a somewhat low coordination number (edges, corners . . .). In a more recent paper (*10*), similar considerations are put forward, and observed frequencies are ascribed to CO adsorbed on C_9, C_8, C_7, and C_6 nickel atoms (the subscript *n* is the coordination number).

iii. Politzer and Kasten (*11*) investigated the Ni–CO system using the iterative extended-Hückel method. It was found that the high or the low frequency bands could be attributed either to linear, or to multicentered species, the number of Ni atoms involved in the interaction being a determining factor in the band position.

In most experimental studies, catalysts were not sufficiently defined from the morphological standpoint: particularly, the degree of reduction was not measured, and some of our preliminary experiments suggested that this point was of considerable importance for chemisorptive properties. Moreover, most experiments were performed at room temperature, at full coverage, using only one technique. This situation prompted us to plan new experiments on well-defined Ni/SiO_2 with the help of two complementary techniques, infrared spectroscopy and magnetic methods, and it is a part of the results which are reported here (results obtained at higher temperatures, and the interaction of $CO + H_2$ will be reported in another paper (*12*).

EXPERIMENTAL METHODS

Catalyst Preparation

Five catalysts (denoted A, B, C, D, and E) were prepared by adding Aerosil silica (surface area 380 $m^2\ g^{-1}$ for C and 200 $m^2\ g^{-1}$ for A, B, D, and E) into a solution of nickel nitrate hexammine (*13*, *14*). The concentration of the solutions was changed to vary Ni contents of the catalysts. In preparation of A, B, and C the solution was filtered; the complex adsorbed on the surface of the support was decomposed by evaporating ammonia and $Ni(OH)_2$ was precipitated. In D and E preparations, nickel hydroxide was precipitated by boiling the solution prior to filtering. In all cases, the solid was washed and dried. The sample for magnetic measurement consisted of a cylindrical pellet obtained by agglomeration under $2T/cm^2$ containing ca. 0.15 g of catalyst, 0.5 cm in diameter and 1.0 cm in length. For infrared experiments,

TABLE 1

Method of Preparation and Morphology of Catalysts

Samples	Precursor	Ni loading (%wt)	Reduc. proc.	Reduc. temp (°C)	Degree reduc. calcd	D_1 (nm)	D_2 (nm)	D_s (nm)	Δ	D_{H_2} (nm)	a_{H_2}
1	A	16	I	200	0						
2	A		I	350	0.05	3.07	2.9	2.98	0.05	6.6	0.45
3	A		I	400	0.2	3.6	3.2	3.4	0.12	5.7	0.6
4	A		I	500	0.7	5.16	4.2	4.7	0.2	4.6	1.01
5	A		I	650	1.02	7.0	5.5	6.3	0.25	5.7	1.1
6	A		I	900	1.0	11.0	8.0	9.5	0.32	9.5	1.0
7	B	4.1	II	530	0.88	3.26	2.33	2.8	0.3	3.73	0.75
8	B		I	610	1.07	3.93	2.68	3.3	0.38	3.7	0.9
9	C	4.2	III	530	1.06	2.9	2.14	2.52	0.3	2.5	1.01
10	D	4.5	I	450	0.61	2.6	2.4	2.5	0.08		
11	D		I	550	0.78	3.92	3.6	3.76	0.08		
12	E	8.7	I	450	0.23	3.3	3.2	3.25	0.03		
13	E		I	650	1.0	5.3	5.0	5.13	0.06	4.66	1.1

the solid was compressed under the same pressure, and the sample was a disc 1.8 cm in diameter (weight comprised between 0.025 and 0.040 g). Three reduction procedures were used:

i. *procedure 1*: reduction for 15 hr in a H_2 stream (2 liters/hr).

ii. *procedure 2*: outgassing of the sample at 530°C for 1 hr, and subsequent reduction at the same temperature in a 2 liters/hr H_2 flow for 3 hr.

iii. *procedure 3*: similar to 2 except that the gas flow was 50 liters/hr.

Reduction temperatures are given in Table 1.

After reduction the sample was outgassed at 450°C for 2 hr. Adsorption experiments were performed with a conventional volumetric apparatus (*14*). Volumes of adsorbed gas were calculated from the change in gas pressure measured with a Texas Instrument pressure gauge.

Apparatus

The range of interest for the CO vibration is situated between 2200 and 1600 cm^{-1}; since it coincides partly with the Si–O band of the support, an unambiguous determination of the CO band position and intensity is difficult if carried out with a classical ir spectrometer. Our spectra were generally performed at 25°C on a Fourier transform spectrometer Digilab F T S 14. The pure spectrum of CO (optical density versus frequency) was directly computed from accumulated spectra recorded before and after adsorption. In our experiments the resolution was 4 cm^{-1}; 200 scans were accumulated before computation both for the background and the catalyst covered with CO in order to improve the signal/noise ratio.

The magnetization was measured in an electromagnet (fields up to 21 kOe) at 300, 77, and 4.2 K using the Weiss extraction method. Some experiments were performed in a superconductive coil (70 kOe) at 4.2 K. The systems were calibrated using pure nickel.

Magnetic measurements give information both on the morphology of reduced catalysts (degree of reduction, metallic particle size) and on the nature of adsorbed CO. The degree of reduction was calculated from saturation data; it was assumed that saturation magnetization at low temperatures was not size dependent (equal to the bulk magnetization). This point will be discussed in detail in another paper devoted to magnetic properties and preparations of finely divided Ni particles (*15*).

Variations of saturation magnetization (ΔM_s) due to gas adsorption were calculated by plotting ΔM against $1/H$ and extrapolating to $1/H = 0$. Magnetic "bond numbers," n, were calculated assuming that nickel atoms in interaction with adsorbed molecules cease to participate in the collective ferromagnetism (*16*). The number of metallic atoms which are demagnetized by this process were obtained by dividing the change of saturation magnetization expressed in Bohr magnetons per adsorbed molecule (α) by the magnetic moment of Ni atoms also expressed in Bohr magnetons (BM): $n = \alpha/0.6$.

In a previous paper (*17*) it was shown that the decrease of saturation magnetization per adsorbed molecule was nearly independent of the temperature of measurement (300, 77, and 4.2 K) for various gas adsorptions (H_2, C_2H_4, C_6H_6 . . .). It was checked that the situation was the same for CO chemisorption. For example, decreases of saturation magnetization measured at 300, 77, and 4.2 K due to CO chemisorption at 300 K on sample 9 were found to be nearly identical within 10%. This is the reason why α values reported here were obtained by magnetic measurement at 77 K, whatever the temperature of adsorption or treatment.

Magnetic Granulometry

The specific magnetization σ of an assembly of spherical single domain particles is described by the Langevin function:

$$\sigma = \sigma_s L(a) \quad \text{with} \quad a = \Pi D^3 \rho \sigma_s H/6kT,$$

σ_s is saturation magnetization; D, particle diameter; ρ, density; H, field strength; and T, absolute temperature.

For a real catalyst, diameters are far from uniform. Let assume a distribution of particle diameters, $f_v(D)$ such that $\int_0^\infty f_v(D)dD = 1$, and $f_v(D)dD$ the volume fraction of particles having a diameter between D and $D + dD$. Then, the magnetization of such a real sample is (*16*):

$$\sigma = \sigma_s \int_0^\infty f_v(D) L(\mathrm{a}) dD.$$

Assuming that σ_s is not D dependent, this equation may be written in an approximate form at low and high fields:

$$\sigma = \sigma_s{}^2 \Pi \rho H/18kT \int_0^\infty f_v(D) D^3 dD \qquad \text{(low fields)},$$

$$\sigma = \sigma_s \left[1\text{–}6kT/\Pi \rho \sigma_s H \int_0^\infty f_v(D) D^{-3} dD \right] \qquad \text{(high fields)}.$$

Average diameters calculated from M vs H curves at low fields (D_1) and M vs $1/H$ at high fields (D_2) are:

$$D_1 = M_3{}^{\frac{1}{3}},$$
$$D_2 = M_{-3}{}^{-\frac{1}{3}},$$

with

$$M_n = \int_0^\infty D^n f_v(D) dD \quad (n\text{th order moment}).$$

The surface diameter, D_s, which corresponds to the metallic surface area, may be written $D_s = M_{-1}{}^{-1}$. We have the relation

$$M_{-3}{}^{-\frac{1}{3}} \leqslant M_{-1}{}^{-1} \leqslant M_3{}^{\frac{1}{3}}.$$

Then the surface diameter may be conveniently calculated by:

$$D_s = \frac{D_1 + D_2}{2}.$$

The difference between D_1 and D_2 gives an estimation of particle size heterogeneity: one can characterize the distribution width by the following parameter:

$$\Delta = \frac{D_1 + D_2}{D_s}.$$

EXPERIMENTAL RESULTS

Morphology of Catalysts

Figure 1 shows the magnetization of sample 8 (Table 1) as a function of applied field at 300 and 77 K. Experimental points are not exactly superimposed when plotted against H/T (Fig. 1); if correction is made for the change of saturation magnetization with T, the H/T superposition is observed, assuming that $M_s(300\ \text{K})/M_s(77\ \text{K}) = 0.87$. Similar results are obtained for other samples, with corresponding saturation magnetization ratios which are comprized between 0.9 for large particle samples and 0.8 for small particle samples.

Average diameters calculated from the $M(H)$ curves are given in Table 1. Particle diameters thus calculated are also compared to H_2 chemisorption data; H_2 saturation is considered to occur at 20°C under 750 Torr. Diameters are calculated assuming H/Ni surface = 1 and [111] and [100] planes on the metallic surface.

For partially reduced catalysts, the quantity of adsorbed hydrogen is smaller than that expected from magnetic particle size measurements. It is suggested that a part of the nickel surface is not accessible to H_2 owing to its partial coverage with unreduced residues. This allows us to define a new parameter, a_{H_2}, the degree of accessibility of the surface to H_2, which can be calculated in the following way: $a_{H_2} = D_{H_2}/D_s$ where D_{H_2} is the average diameter calculated from H_2 chemisorption.

When catalysts are completely reduced, the accordance between D_s and D_{H_2} is quite satisfying (samples 4, 5, 6, 8, 9, and 13). It should be noted that magnetic measurements give coherent values for diameters: in all cases the relation $D_1 \geqslant D_2$ is observed, in agreement with the equation $M_3^{\frac{1}{3}} \geqslant M_{-3}^{-\frac{1}{3}}$.

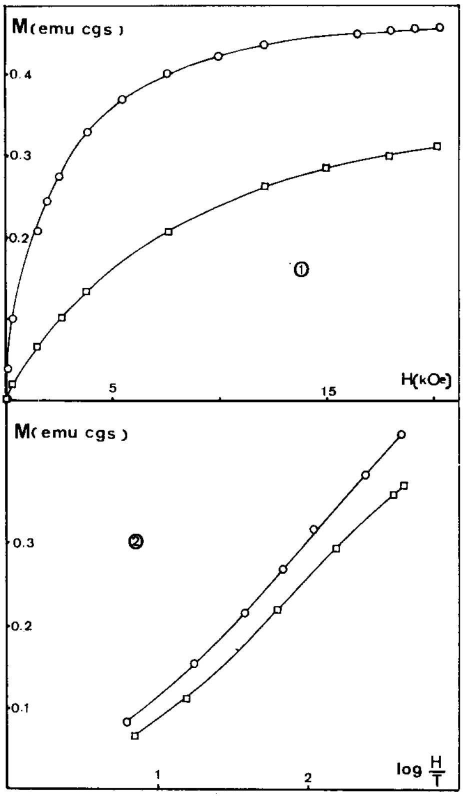

FIG. 1. Magnetization M of sample 8 at 300 (□) and 77 K (○) as a function of applied field H (curves 1) and against $\log(H/T)$ (curves 2). The weight of the sample was 0.2 g and the Ni loading 4.1% wt.

Adsorption Studied by Magnetism

Typical plots of saturation magnetization σ_s against volume of adsorbed carbon monoxide per gram of nickel at three temperatures are shown in Fig. 2 (sample 5, completely reduced). The equilibrium pressure of the gas phase is smaller than 1 Torr to prevent nickel carbonyl formation. It can be observed that at −78, 20 and 100°C the curves are linear, indicating that the nature of chemisorbed species are almost unchanged as the coverage increases. At 100°C the slope is slightly higher than at 20°C, indicating that the nature of adsorbed species does not vary greatly in the 20–100°C range (*19*).

This point was confirmed by the fact that when CO was adsorbed at −78°C and subsequently heated stepwise up to 100°C, variations of α (and n) with temperature (shown in Fig. 3) were observed with n equal to 1.3 at −78°C, increasing to ca. 1.85 at 20°C and staying constant up to 100°C, in good agreement with previous results.

Similar results are obtained on other completely reduced samples (Table 2). As an example, we have shown in Fig. 4 variations of σ_s against CO coverage for samples 5 and 6 at 20°C; magnetic isotherms are linear and have similar slopes (same adsorbed species). In Fig. 5 variations of n and α at 20°C against the diameter of nickel particles are plotted for completely reduced samples; it can be seen that n and α are independent of the particle size in the range studied. The observed bond number of sample 9 (D_{Ni} = 2.5 nm) is temperature independent in the 20–100°C range, as for sample 5.

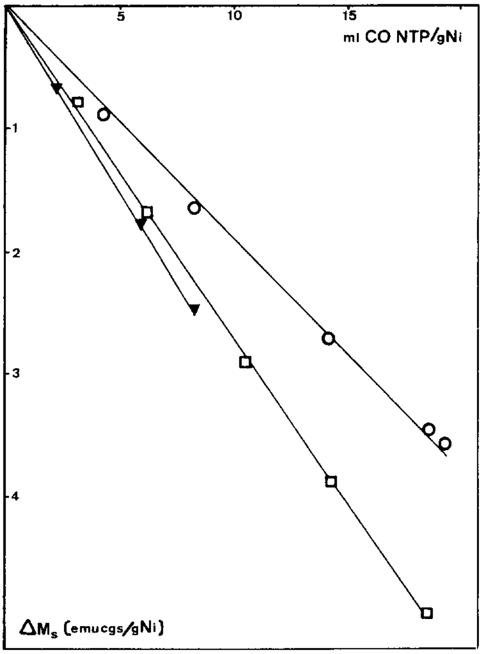

FIG. 2. Variations of M_s at 77 K (saturation magnetization) versus the adsorbed quantity of CO (sample 5) at various temperatures of adsorption: (○) −78°C, (□) +20°C, (▼) +100°C.

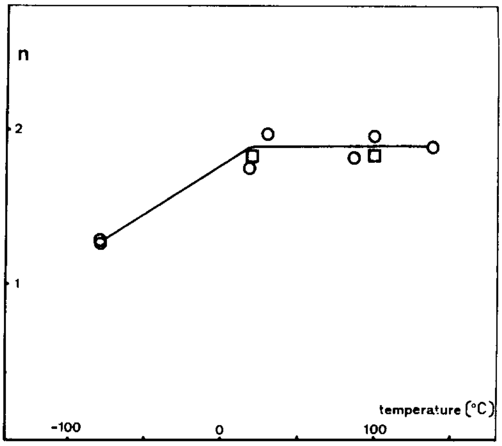

FIG. 3. Variation of n (bond number) during the adsorption of CO at various temperatures; (□) sample 9; (○) sample 5.

The slopes of magnetic isotherms for partially reduced samples are smaller, as seen in Fig. 4 and Table 2. Figure 6 shows variations of n against the accessibility of the metallic surface to H_2 (a better correlation is observed between n and a_{H_2} rather than between n and the degree of reduction). It indicates that n decreases as a_{H_2}, whatever the Ni particle sizes.

Infrared Data

Two sets of experiments were performed: in the first case large amounts of CO were introduced onto the catalyst; the pressure was generally smaller than 2 Torr and the system was rapidly evacuated by pumping to prevent important formation of nickel carbonyl. In the second case, small amounts were successively adsorbed to study the system at various coverages. This procedure was similar to that used for magnetic measurements; the pressure was smaller than 1 Torr and no nickel carbonyl was detected.

TABLE 2

Bond Numbers (n) and Ratios (r) of A and B Band Intensities

Catalyst No.	Degree of reduction	Particle size diameter (nm) D_s	Bond number (n)	$r = A_A/(A_A + A_B)$
1	0	—	No adsorption	A and B bands not observed
2	0.05	2.98	—	0.565
3	0.2	3.4	1.45	
4	0.7	4.7	—	0.38
5	1.02	6.3	1.85	0.37
6	1.0	9.5	1.9	0.368
7	0.88	2.8	1.32	0.40
8	1.07	3.3	1.61	0.33
9	1.0	2.52	1.83	0.366
10	0.61	2.5	—	0.435
11	0.78	3.76	1.76	0.368
12	0.23	3.25	—	0.432
13	1.0	5.13	1.95	0.31

Adsorption by First Procedure

Figures 7 and 8 show the spectra of CO irreversibly adsorbed at room temperature on various samples. One group of bands was observed in the 2100–2000 cm^{-1} range (A bands) and a second one in the 1950–1800 cm^{-1} range (B bands). Measurements of integrated optical densities A_A and A_B were difficult owing to the fact that A and B bands were not well separated. As a consequence, the ratios of integrated optical densities $r = A_A/(A_A + A_B)$ which are reported in Table 2, should be considered

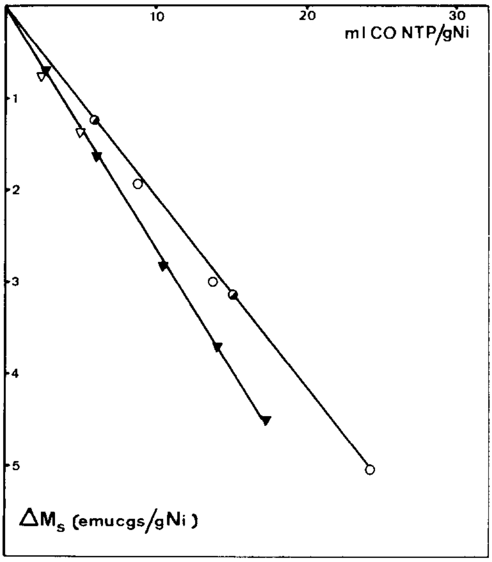

FIG. 4. Variations of M_s at 77 K vs the adsorbed quantity of CO at 20°C. (◑) Sample 3, bond number $n = 1.37$; (▼) sample 5, $n = 1.82$; (▽) sample 6, $n = 1.90$; (○) sample 7, $n = 1.32$.

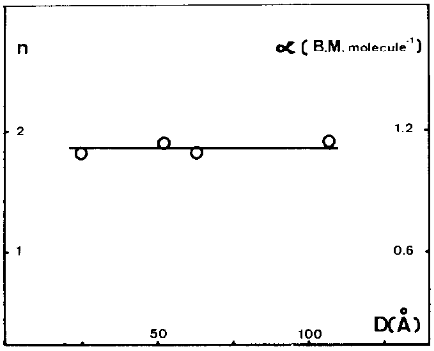

FIG. 5. Variations of n (bond number) and α (decrease of M_s in Bohr magneton per adsorbed molecule) for CO against nickel particle size.

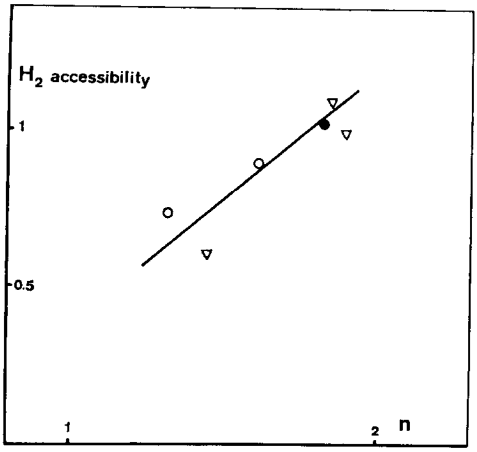

FIG. 6. Variation of n for CO against the accessibility of the metallic surface to hydrogen.

rather as a relative measurement against the reduction level, the Ni particle size, than as an accurate determination of the relative abundance of the observed species.

Another band (C) was observed at 2195 cm^{-1} on partially reduced samples (samples 1 and 12). This band was easily detected at pressures higher than 5 Torr; the higher the CO pressure, the higher its intensity. It disappeared by pumping for a long time at room temperature.

From Table 2, it can be seen that for completely reduced samples the ratio r is approximately equal to 0.31–0.38, whatever the nickel particle sizes. For incompletely reduced samples, values of r are larger.

A careful examination shows that in fact the A band absorption is made up of two bands at about 2040 (L) and 2070 cm^{-1} (H). Their relative intensity depends upon the degree of reduction and the particle size: at low reduction level, the 2070 cm^{-1} band is predominant; for completely reduced samples, the relative intensity of the 2040 cm^{-1} band increases as the nickel particle size increases (figs. 7 and 8).

Adsorption by Second Procedure

Infrared spectra recorded at various coverages at 25°C are reported in Fig. 9. It can be observed that the ratio $r = A_A/(A_A + A_B)$ does not vary significantly with the degree of coverage. Moreover the composition of the A band absorption is coverage dependent. At low coverage, only the 2040 cm^{-1} band is present; at higher degree of coverage, the relative intensity of the 2070 cm^{-1} band increases, and decreases on pumping; the A absorption bands thus obtained as well as the r values are very similar to those obtained from the first adsorption procedure.

The appearance of the 2070 cm^{-1} band at high coverage suggests that the binding energy is smaller than that corresponding to the 2040 cm^{-1} band. This fact was confirmed by a set of experiments at low temperature. A small amount of CO (10 ml/g Ni) was introduced at −196°C onto a completely reduced catalyst (sample 5). Infrared spectra were recorded during the warming of the sample up to 25°C. At low temperature, the 2070 cm^{-1} band was much more intense. When the temperature increased the 2070 cm^{-1} band disappeared and only the 2040 cm^{-1} band remained (by recooling the sample to −196°C the spectrum was not changed). This experiment showed clearly that the 2070 cm^{-1} band was less stable, which is in agreement with the fact that the corresponding frequency is higher (*1*). In another paper (*19*), it was shown that during this experiment, the ratio $r = A_A/(A_A + A_B)$ decreases as the temperature increases.

DISCUSSION

Bands Assignment

The C band at 2195 cm^{-1} which was observed only on partially reduced samples is to be assigned to CO adsorbed on Ni^{2+} or NiO species. In all our observations the larger the ratio $A_A/(A_A + A_B)$, the smaller the n value; thus, the A band may be assigned to the linear species Ni–CO for which the bond number should be equal to 1, and the B band to bridged or multi-

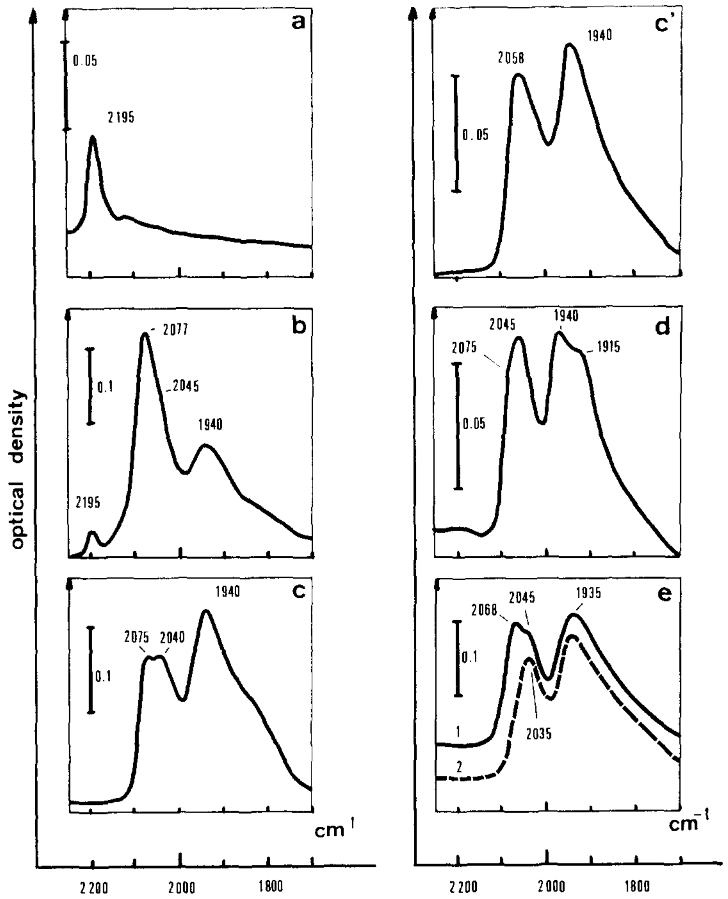

FIG. 7. Infrared spectra of CO adsorbed on various samples Ni/SiO_2. (a) sample 1 contacted with a 10 Torr CO pressure at 25°C; (b) CO irreversibly adsorbed at 25°C on sample 2; (c) and (c′) CO irreversibly adsorbed at 25°C on sample 5; (d) CO irreversibly adsorbed on sample 6 at 25°C; (e) low temperature experiments with sample 5; (1) 10 ml CO/g Ni adsorbed at −196°C, spectrum recorded between −100 and −50°C; (2) spectrum obtained warming the previous sample up to room temperature.

centered species (Ni_x–CO, $x > 1$) with a bond number $n = x > 1$. These conclusions are in complete agreement with our previous work on CO adsorption on Ni–Cu alloys (*8*) and strengthen the hypothesis of Eischens and Pliskin (*4*): it can be recalled that the B band is mainly due to bridged species ($x = 2$, $\nu CO = 1935\ cm^{-1}$), but that other multicentered species are also present (Ni_3CO, Ni_4CO, which give bands at lower frequencies, 1800 cm^{-1} for example).

Now let us focus our attention on the two bands in the range attributed to linear species (*A* absorption). Various hypotheses may be proposed to account for the observed variations of the ratio A_H/A_L with the degree of reduction and nickel particle size.

i. Electronic effects: in the system Ni/Ni^{2+}, Ni is expected to donate electrons to Ni^{2+} in order to equilibrate Fermi levels at the interface. According to the (σ, π) band scheme for CO chemisorption (*1*), the back-donation of Ni electrons to the π^* CO orbitals is decreased with consequent increasing of the CO frequency. Then, for incompletely reduced samples, bands should be shifted towards higher frequencies.

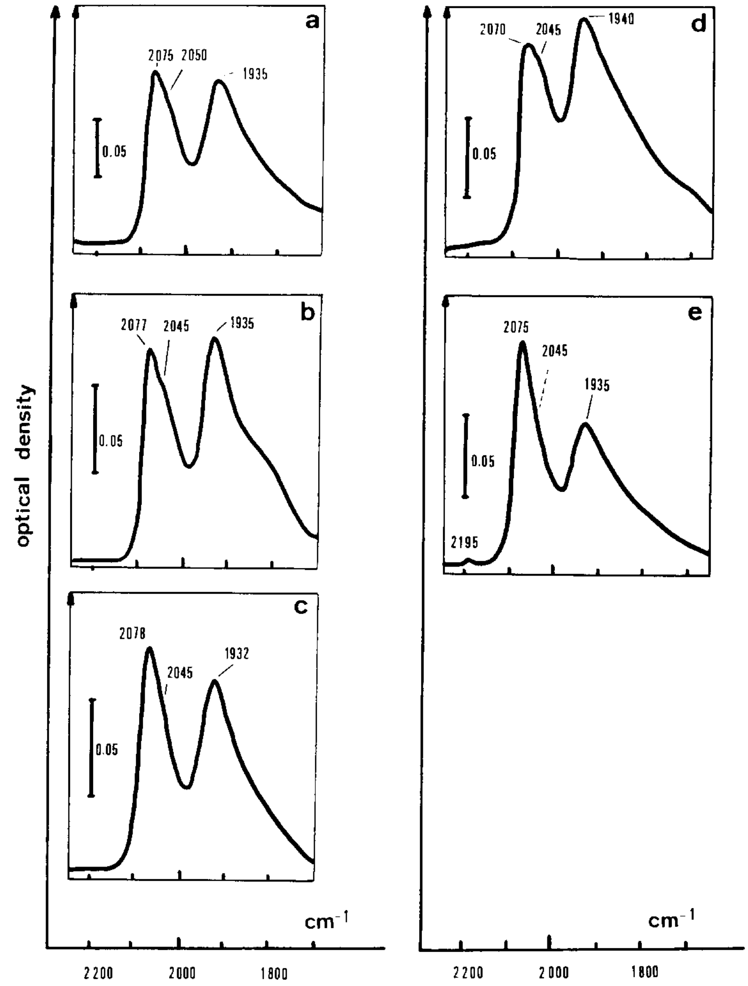

FIG. 8. Infrared spectra of CO irreversibly adsorbed at room temperature on different Ni/SiO_2 catalysts. (a) Sample 7; (b) sample 9; (c) sample 10; (d) sample 11; (e) sample 12.

For completely reduced samples, it is observed that the smaller the nickel particle size, the higher the νCO frequency for the A band; an electronic effect similar to that invoked in the case of NO adsorption on supported platinum catalysts could be postulated (*20*).

However, both explanations would lead to a continuous shift of the frequencies, and as a matter of fact, the two bands A_H and A_L remain roughly at the same position; only the ratio A_H/A_L varies with nickel particle size and reduction level. Thus, these two hypotheses may be ruled out.

ii. In a recent paper, one of us has discussed the influence of hydrogen coverage on the spectra of CO adsorbed on Ni/SiO_2 catalysts (*21*). It was shown that preadsorbed or subsequently adsorbed hydrogen increases the intensity of the 2070 cm^{-1} band. However, our catalysts were completely free from adsorbed hydrogen: samples were outgassed at 400°C and it was checked that no hydrogen was evolved after subsequent heat treatment at higher temperatures.

iii. The A_H band could be attributed to some precarbonyl species (*11*). This hypothesis is in accordance with the fact that

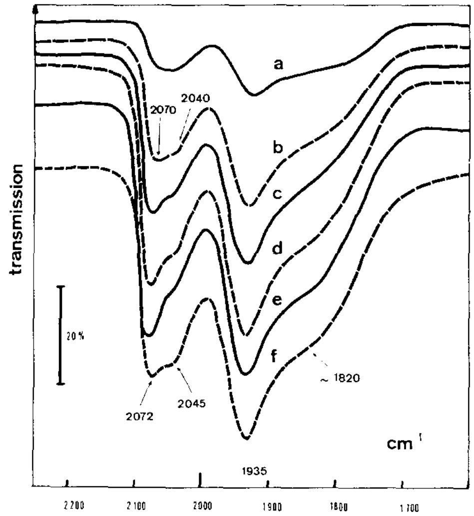

FIG. 9. Infrared spectra of CO adsorbed at room temperature on sample 5 as a function of the coverage. (a) 9.06 ml CO/g Ni; (b) 14.5 ml CO/g Ni; (c) 20.15 ml CO/g Ni; (d) 25.2 ml CO/g Ni; (e) 31.6 ml CO/g Ni; (f) after evacuation of the residual gas phase at 25°C.

the A_H band is observed at high CO coverages, but this attribution disagrees with the predominant formation of the A_H band in low temperature experiments.

iv. Another possibility is to attribute the bands at 2070 and 2040 cm^{-1} to CO linearly bonded to one nickel atom in different environments (*10, 11*). However, the existence of only two bands in the linear region would suggest only two types of geometrical environment, when it can be easily predicted that their number is greater. (It can be noted that according to the hypothesis proposed in (*10, 11*), the B band could be assigned to linear CO, which is not in agreement with our deductions, as has been shown previously).

v. The A_H band may be assigned to CO molecules linearly bonded to metallic nickel atoms in interaction with an oxide phase (unreduced nickel or silica), whereas the A_L band would correspond to CO linearly bonded to unperturbed nickel atoms. Sites corresponding to the 2070 cm^{-1} band are relatively more abundant on partially reduced samples and small nickel particles, so this hypothesis seems to be in good agreement with most of the experimental data. Further experiments are needed to confirm this hypothesis.

Geometric Effects and Nature of Adsorbed CO

On completely reduced samples, a mixture of linear and multicentered species corresponding to an average bond number equal to ca. 1.85 was observed at room temperature. This bond number (or the ratio of the concentrations of the two species) is remarkably constant: it does not depend upon

i. The temperature within the 20–100°C range;

ii. The nickel particle size (2.5–12 nm);

iii. The degree of coverage.

If linear and multicentered species are adsorbed without any interaction, then a different situation is expected: for example, a continuous increase of *n* with temperature is expected, as multicentered species are more stable (*3*). This is the reason why we suggest the existence of a stable chemical form comprising a mixture of linear and multicentered CO, similar to that observed in metallic clusters, where CO is bonded to one, two or three metallic atoms in well-defined proportions (*22*).

The hypothesis of this complex, which requires more than 2 adjacent nickel atoms, enables us to propose a possible explanation for the fact that the multicentered species concentration decreases much more rapidly than the probability to have two adjacent atoms in the case of Ni–Cu alloys (*8*): as a matter of fact this complex requires more than two nickel atoms. Of course, other hypotheses may be proposed: for example, more than two nickel atoms are necessary for the formation of a Ni_2CO, because all Ni atoms are not equivalent (*23*) in the alloy. The problem still remains open.

The relative abundance of the bridged

species is smaller on partially reduced samples; moreover, on this sample the accessibility to H_2 adsorption is smaller than 1, suggesting that the surface is partially occupied by unreduced residues. Then, geometric effects similar to those invoked previously (*7*) in the case of Ni–Cu alloys may be proposed to account for this observation: these unreduced residues would decrease the probability to have adjacent Ni atoms on the surface, thereby decreasing the relative concentration of the bridged species.

CONCLUSION

In this study, magnetic measurements and infrared spectrometry gave consistent results showing once again that the two techniques are complementary. On nickel, CO is adsorbed as linear ($n = 1$, νCO $= 2075–2045$ cm^{-1}) and multicentered forms ($n \geqslant 2$, νCO $= 1935–1800$ cm^{-1}), in agreement with the Eischens and Pliskin's hypothesis.

On completely reduced samples, the observation of a mixture of linear and multicentered species with a constant concentration ratio, suggests an analogy with coordination complexes.

On partially reduced samples, the relative abundance of multicentered species is decreasing, suggesting that unreduced surface residues play the same role as copper in Ni–Cu alloys. The dilution factor seems to be of primordial importance for the nature of the adsorbed species. This last point shows the necessity of a complete knowledge of the catalyst morphology (reduction level, particle size, etc.).

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