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The Adsorption of NO and NO_2 on Silica-Supported Nickel

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The adsorption of NO and NO_2 on reduced silica-supported nickel at 325 K has been studied using infrared spectroscopy and a vacuum microbalance. For all NO coverages, a single infrared band at 1864 cm^{-1} was observed which was asymmetric to low wavenumber. From the isotopic shift data using $^{14}NO/^{15}NO$ mixtures, this has been assigned to the symmetric (strong, 1864 cm^{-1}) and antisymmetric (weak, 1820–1840 cm^{-1}) NO stretching modes of a surface $Ni(NO)_2$ species. The infrared and gravimetric data indicate that NO also dissociates to yield surface oxide and nitride species, as has been found using other techniques, and the $Ni(NO)_2$ species resides on a partially oxidized surface. An identical infrared band was observed for NO adsorbed on a preoxidized surface, and for a less than saturation dose of NO_2 adsorbed on bare Ni. However, with a large exposure to NO_2, surface nitrate-like species were produced. Finally, the 1864 cm^{-1} band from either adsorbed NO or NO_2 slowly disappeared when CO was added and new bands at 2201 and 2082 cm^{-1} appeared due to adsorbed isocyanate and CO, respectively. This reaction is discussed in detail in the paper following this.

INTRODUCTION

There have been many infrared spectroscopic studies (*1–13*) and UHV [LEED, Auger, XPS, UPS] studies (*14–20*) of the adsorption of nitric oxide on Group VIII metals. The object has mainly been to determine how NO adsorbs on a given metal (*1–3, 7, 14–18*) or to determine how adsorbed NO reacts with other molecules such as CO, H_2 and CH_4 (*4–13, 19*). Particular attention has been devoted to studies of isocyanate formation during the catalyzed reaction between CO and NO (*4–12*).

The present paper is concerned with an infrared study of the adsorption of NO and NO_2 on silica-supported nickel, and its subsequent reaction with CO. Further details of the latter reaction are given in the paper following this. Earlier infrared studies have been carried out by Blyholder and Allen (*1*), Batychko *et al.* (*2*), Terenin and Roev (*3*) and Ito *et al.* (*7*) and recent UHV studies have been done by Price *et al.* (*14*), Conrad *et al.* (*15*) and Brundle (*16*). This work will be discussed in more detail below. A preliminary account of a portion of the present work has also been published (*21*).

EXPERIMENTAL

Catalyst preparation. A brief description of the technique used to prepare some silica-supported group VIII metals has been described previously (*22*). A unique feature of our technique was the use of dry acetone as an impregnation solvent. This prevented extensive rehydration of the silica and we obtained improved infrared transmission in the 3700–3200 cm^{-1} spectral region (*23, 24*).

In the present work, 1 g of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 50 ml of dry acetone, to which was added 2 g of Cab-O-Sil HS-5 silica (BET surface area 320 m^2 g^{-1}) which had been previously heated for 12 hr in a furnace at 700°C. Two hundred milligrams of the dried powder was pressed into a 25-mm-diameter disc using about 500 lb pressure for 2–3 sec. The disc was heated in air at 350°C for 5 hr, was placed in the reaction cell [which has been described elsewhere (*22*)], was evacuated at 50°C until the pressure dropped to about 10^{-3} Torr, and was

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reduced in H_2 at 400°C over a 4-hr period. The resulting sample contained 9.2% Ni by weight and the infrared transmission at 2200 cm^{-1} was about 90% with no compensation in the reference beam. However, since the background spectrum of silica fluctuates in the 2100–1350 cm^{-1} spectral region a compensating disc of pure silica was placed in the reference beam so as to yield a relatively flat baseline.

Equipment and materials. Infrared spectra were recorded on a modified Perkin-Elmer model 13G spectrometer. Band positions were accurately calibrated with respect to the known spectra of a variety of gases (usually DCl and H_2O) and spectral slit widths were always chosen to be less than the half band widths of surface species. Mass spectra were run on either an *in situ* A.E.I. MS 10 mass spectrometer or a MS 9 high-resolution mass spectrometer. In all cases where more than one suspected product would have the same mass number (e.g., CO and N_2), then either the appropriate isotopically labeled reactants were used, and/or the high-solution instrument was used. For gravimetric work a Sartorius model 4433 microbalance was used and this was also directly coupled with the MS10 mass spectrometer and a vacuum line such that gas pressures, mass spectra, and catalyst weight changes could be measured simultaneously. Approximately 130 mg of catalyst was used and weight changes of $\pm 1400\ \mu g$ could be measured with an accuracy of $\pm 1\ \mu g$.

Because the Ni/SiO_2 samples were black, some heat is absorbed from the ir beam and we have determined that sample temperature was about 325 K. Accordingly, the microbalance experiments were carried out with the sample heated to 325 K. The infrared results described below were identical if the sample disc was kept at 325 K while the cell was not situated in the infrared spectrometer.

Nitric oxide (Matheson) was dried by passing the gas through P_4O_{10} on the vacuum line followed by several trap to trap distillations; a colorless solid could be condensed at 77 K whereas a bluish solid, presumably due to traces of N_2O_3 (*25*), was obtained if the gas was trapped directly from the cylinder. Hydrogen (Matheson U.H.P.) was passed through a Deoxo purifier, then through two glass bead-packed liquid N_2 traps prior to use. Other gases used "as received" were ^{16}CO (Matheson assayed Research grade), ^{13}CO (Merck, 90% ^{13}C), $C^{18}O$ (Prochem, 99% ^{18}O), $^{18}O_2$ (Prochem, 99% ^{18}O), D_2 (Matheson, 99%), and ^{15}NO (Merck, 98.8% ^{15}N).

RESULTS

In studies of adsorption on supported metal catalysts, difficulties can arise if the support itself is also active. Thus, whereas alumina is often an active adsorbate by virtue of its Lewis acid centers, silica is generally considered inert, at least if it has not been subjected to a vacuum degassing treatment at temperatures above 400°C (*26*). In the present work we have verified using infrared spectroscopy and the vacuum microbalance that none of N_2O, NO, or NO_2 adsorbs on silica provided that the vacuum degassing treatment was below 400°C, and only NO_2 was chemisorbed if temperatures above 400°C were employed (*27*).

Adsorption of NO

The infrared spectra obtained after adding nitric oxide at varying pressures (cell volume 300 ml) to silica-supported nickel are shown in Fig. 1. Only one band was observed throughout the 4000–1350 cm^{-1} spectral region, centered at 1864 cm^{-1}, and this was slightly asymmetric to the low wavenumber side. [The background spectrum of silica has a strong broad band at about 1880 cm^{-1}. In most experiments it was difficult to achieve perfect double beam compensation with the reference SiO_2 disc, and the background rise shown in Fig. 1 is due to SiO_2.] The maximum intensity at 1864 cm^{-1} was generally achieved using a dosing pressure of 1.5–2.0 Torr, and no

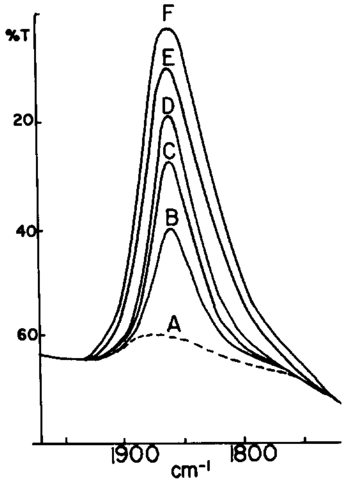

FIG. 1. Infrared spectra of adsorbed NO on Ni after admitting gaseous NO at various pressures for 1 min and evacuating the excess for 1 min. (A) Background; (B) 0.5 Torr; (C) 0.7 Torr; (D) 1.0 Torr; (E) greater than 2 Torr.

changes resulted if up to 20 Torr were added. (Hereafter, a dose in excess of 4 Torr will be referred to as a saturation dose, and, as will be seen, corresponds to about 192 μmole of adsorbed NO per g of catalyst.) When ^{15}NO was used, the peak position shifted to 1829 cm^{-1} and the band shape was the same.

When a relatively small dose of NO was added (0.4–0.7 Torr), a mass spectrometric (MS) analysis of the gas phase after 5 min reaction showed that a trace (<1 μmole) of N_2 was present. If a saturation dose of NO was added the MS anlaysis showed that in addition to a large quantity of residual NO, traces of N_2 and N_2O were present, in roughly equal proportions. Regardless of the dose of NO added, the intensity of the 1864 cm^{-1} band slowly decreased with time until it reached a constant value after about 2 to 3 hr. Some curves showing this decrease are shown in Fig. 2. For a very small dose the 1864 cm^{-1} band disappeared entirely after 2 hr and only a trace of N_2 was present. The curves shown in Fig. 2 could be obtained whether or not the cell had been evacuated after the addition of NO. After the intensity of the 1864 cm^{-1} band had reached a constant value, it further decreased in intensity only if the sample was heated in the 150–200°C range, and it disappeared rapidly if heated at 220°C. After heating at 400°C, only N_2 was detected in the gas phase.

The 1864 cm^{-1} band was not affected if 10 Torr of H_2 was added at 20°C, but it disappeared rapdily if the sample temperature was increased to 60°C and no new ir bands were detected. The major desorption products which could be detected with a mass spectrometer where H_2O and N_2 (confirmed by the use of $D_2/^{15}NO$), The 1864 cm^{-1} band disappeared immediately if 1.4 Torr of O_2 was added at 20°C and again, no new ir bands were observed. No changes resulted if CH_4 was added at 20°C although the 1864 cm^{-1} band disappeared if the sample was heated in CH_4 at 220°C and the infrared spectrum of gaseous CO_2 was observed.

Finally, when NO was added to a catalyst which had been preexposed to 10 Torr O_2 for 5 min followed by evacuation for 5 min, the spectrum was identical to that just described for NO on the non-O_2 treated catalyst.

With a 130-mg Ni/SiO_2 sample in the vacuum microbalance, the weight increase after admitting a 10-fold excess of CO, NO,

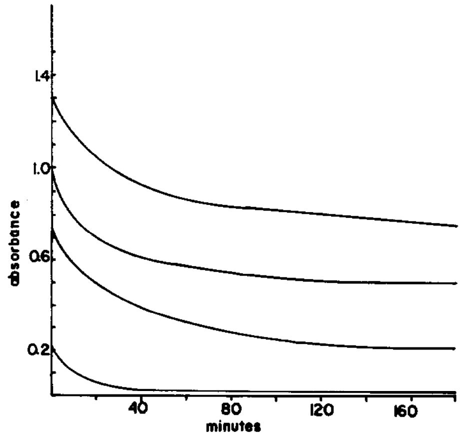

FIG. 2. Decay of the 1864 cm^{-1} band (absorbed NO) as a function of time for varying initial NO coverage.

or O_2 to a regenerated sample for 5 min followed by evacuation until the pressure dropped to 10^{-4} Torr was about 125 ± 15 μg (CO), 750 ± 50 μg (NO), and 700–900 μg (O_2). The weight did not increase with further exposure with CO or NO, but it did continue to increase slowly with time with O_2. The absolute weight of adsorbed CO or NO varied somewhat depending on the history of a given sample (some catalysts were used for 3 years) and we have indicated this ± variation above. A saturation dose of NO of 750 μg corresponds to 192 μmole/g of catalyst.

After any exposure of NO in the 200–800 μg range, virtually no weight change (±10 μg) was detected with time if the balance was continually evacuated, or if it was isolated from the vacuum system. In the latter cases, traces of N_2 or N_2O were detected by MS and the pressure rise indicated that about 0.5 to 1 μmole of gaseous products was present. Evidently little NO decomposes to yield gaseous products. However, after pyrolysis at 673 K and cooling to 325 K, only N_2 was detected by MS, pressure measurement indicated that the number of moles of N_2 liberated to NO adsorbed was 0.45 ± 0.05, and that the final evacuated catalyst weight was approximately halved.

Absorbed NO + CO (g)

When gaseous carbon monoxide (10 Torr) was added to preadsorbed NO (saturation, evacuated 5 min), the intensity of the 1864 cm^{-1} band immediately decreased and new sharp but weak bands appeared at 2191 and at 2082 cm^{-1}. The 2191 cm^{-1} band reached its maximum intensity after 5 hr of CO contact and now was centered at 2201 cm^{-1}. Little change occurred at 2082 cm^{-1}, and the intensity of the 1864 cm^{-1} band had about halved (Fig. 3). No further changes occured after 24 hr contact time. An MS anlaysis of the gas phase after 5 hr reaction showed that only CO and CO_2 were present. After 10 min evacuation the band at 2082 cm^{-1} disappeared and no further spectral changes occurred with up to 18 hr evacuation. If the CO had been evacuated before the 2201 cm^{-1} band had achieved its maximum intensity, then the 2082 cm^{-1}

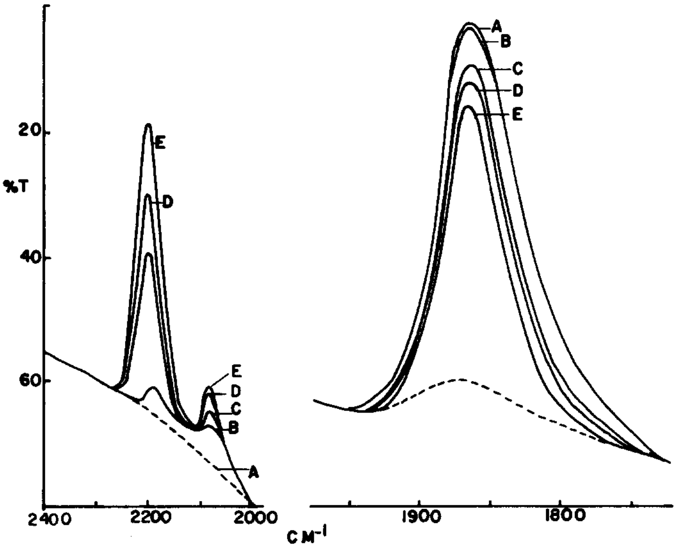

FIG. 3. The dashed curve is the background spectrum of Ni/SiO_2 and curve (A) is the spectrum obtained after adsorption of 10 Torr of NO followed by evacuation. Spectra obtained after adding 10 Torr of CO after (C) 15 min, (D) 45 min, and (E) 300 min reaction.

band again disappeared and no further spectral changes (4000–1350 cm^{-1}) resulted after up to 18 hr evacuation.

The peak position of the 2201 cm^{-1} band shifted to lower wavenumber when the following reactants were used, $^{13}CO/NO$, $CO/^{15}NO$, or $C^{18}O/NO$. Although the shift is reported (Table 1) for the new band after at least 3 hr reaction, slight differences in peak positions were noted from experiment to experiment and the data are probably only reliable to within ±2 cm^{-1}. [Peak positions for a given situation were calibrated with respect to gaseous DCl to about 0.2 cm^{-1} accuracy.] The band at 2082 cm^{-1} shifted to lower wavenumber only when ^{13}CO or $C^{18}O$ was used. Finally, when the combination $C^{18}O/N^{16}O$ was used, only the oxygen-18 shifted 2201 and 2082 cm^{-1} bands were detected but the gas phase contained, in addition to unreacted $C^{18}O$ (but no $C^{16}O$), an exact 1 : 2 : 1 mixture of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$.

Adsorption of N_2O and NO_2

When N_2O was added to silica-supported Ni at any pressure, no spectral features were detected and no further examination of this system was carried out.

When 0.5–1 Torr of NO_2 was used, the only spectral feature noted was a strong band at 1864 cm^{-1} of intensity comparable to that achieved using a similar dose of NO, i.e., about half saturation. When CO was added, again bands at 2201 and 2082 cm^{-1} appeared and reached maximum intensity after 5 hr. When $C^{18}O$ was used, only a 1 : 2 : 1 mixture of isotopically labeled CO_2 was detected in addition to residual $C^{18}O$.

TABLE 1

Infrared Band Positions (cm^{-1}) after Reaction of Adsorbed NO with CO[a]

CO/NO	$CO/^{15}NO$	$^{13}CO/NO$	$C^{18}O/NO$
2201	2188	2138	2182
2082	2082	2030	2035
2033[b]	2033[b]	1983[b]	1986[b]

[a] Normal isotopes (C-12, 0-16, N-14) are unlabeled.

[b] Due to the linear form of adsorbed CO on bare Ni.

If a saturation dose of NO_2 was added, a very weak band was observed at 1864 cm^{-1} accompanied by a pair of strong bands at 1555 and 1440 cm^{-1}. When any dose of CO was added, no spectral changes resulted and only gaseous CO was detected in the gas phase.

DISCUSSION

Spectroscopic Result

An early infrared study of the adsorption of NO on nickel was carried out by Blyholder and Allen (*1*) who studied the reaction on oil-suspended Ni particles and on silica-supported nickel. Using oil-suspended Ni, the low-frequency region was available for spectroscopic examination, and they observed three bands at 1840, 650, and 625 cm^{-1} (1840 cm^{-1} only for Ni/SiO_2) which they attributed to a linear neutral NiNO species. In other early infrared work, Terenin and Roev (*3*) also reported a band at 1850 cm^{-1} due to this species for NO on Ni, whereas Batychko *et al.* (*2*) reported a strong band near 1860 cm^{-1} and a weak shoulder near 1820 cm^{-1} for NO on Ni/SiO_2. The former was assigned to NiNO and the latter was attributed to NO adsorbed on nickel oxide.

The single band observed in the present work at 1864 cm^{-1} is probably due to the same species. Detailed arguments for an assignment to linear neutral NiNO are well established (*1–13*), and the slight shift to higher wavenumber could be due to differences in average particle size (*13*, *28*) or to the amount of surface oxygen or nitrogen from the dissociation of NO (see below).

However, Ito *et al.* (*7*) recently studied the infrared reflectance spectrum of NO adsorbed under UHV conditions on evaporated Ni films and assigned a band at 1820 cm^{-1}, which was observed only with low NO coverage, to an NiNO monomer, whereas a pair of stronger bands which appeared at 1860 and 1750 cm^{-1} with higher coverages was assigned to an adsorbed *cis* dimer of NO. In our work, apart from the asymmetry associated with the 1864 cm^{-1} band no additional bands were observed although we acknowledge that the low wavenumber antisymmetric ν(NO) mode of an adsorbed dimer is expected to be relatively weak (*7, 24, 29*). We will show below that there is considerable evidence which suggests that our 1864 cm^{-1} band contains two components which can be assigned, not to a *cis* dimer, but to a geminal $Ni(NO)_2$ surface species.

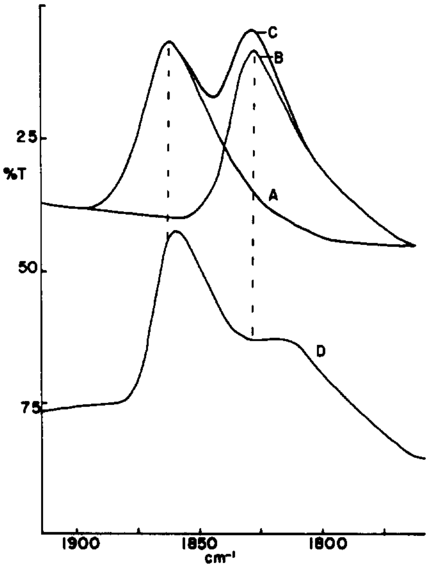

FIG. 4. Infrared spectrum of adsorbed ^{14}NO (A) and ^{15}NO (B) at low initial coverage. Curve (C) is the reconstructed sum of (A) and (B). Curve (D) is the spectrum obtained after the adsorption of a 1 : 1 mixture of ^{14}NO and ^{15}NO. The percentage T scale refers to curve D.

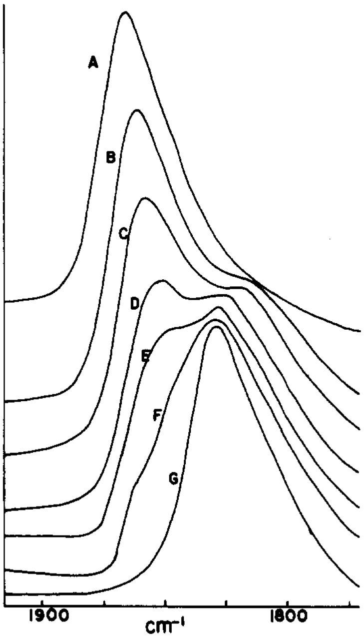

FIG. 5. (A) Spectrum of absorbed ^{14}NO. (B–F) Spectra observed after adding successive small doses (~0.1 Torr) of ^{15}NO to (A). (G) Spectrum of adsorbed ^{15}NO.

Firstly, the vacuum microbalance experiments (using the same Ni catalyst which was transferred from the ir cell) showed that far more NO was chemisorbed than CO. Although part of this could be due to extensive NO dissociation into adsorbed nitride and oxide as has been found in other studies (*14–16*), it could also be partially due to the formation of species in which more than one NO is bonded to each surface Ni atom. In order to test the latter idea, a 1 : 1 mixture of $^{14}NO/^{15}NO$ was adsorbed. If monomeric NiNO was the sole form of adsorbed NO, then two bands of equal intensity at 1864 and 1829 cm^{-1} would be expected, and a reconstructed composite is shown in Fig. 4C. The spectrum observed was considerably different (Fig. 4D) having a strong maximum at 1858 cm^{-1} and a weak broad shoulder between 1815 and 1825 cm^{-1}. The relative intensities and peak positions did not depend on the amount of NO added. Figure 5 shows the sequence of spectra obtained when small doses of ^{15}NO were added to preadsorbed ^{14}NO. When the intensities of the two bands were approximately equal (Figs. 5D and E) the peak positions were near 1853 and 1825 cm^{-1}.

The results suggested that a simple monomeric NiNO is not responsible for the 1864 cm^{-1} band. Further, since the overall profile does not depend on coverage, as has been found for adsorbed $^{12}CO/^{13}CO$ on Pt

(*30, 31*), this suggests that dipole–dipole perturbation effects are not responsible for the unusual spectrum. It is also unlikely that we have an adsorbed *cis* dimer, $(NO)_2$, in spite of the absence of a band near 1750 cm^{-1} since one would expect a band midway between 1864 and 1829 cm^{-1} for the $^{14}NO^{15}NO$ species (*32*). The data instead indicate that a new band exists near 1855 cm^{-1}, and perhaps below 1825 cm^{-1}.

Although we were never able to resolve a distinct shoulder, for either ^{14}NO or ^{15}NO, the 1864 or 1829 cm^{-1} band was always asymmetric to the low-frequency side, and this asymmetry was independent of coverage. If two NO molecules were adsorbed on each Ni atom, then symmetric and antisymmetric ν(NO) modes would be expected, the latter being very much less intense than the former due to surface dipole imaging (*7, 24, 29*). Further, the coupling between these modes would be weaker than for a *cis* dimer and the frequency separation would be small, as is found in many transition metal nitrosyl compounds which contain $M(NO)_2$ groups (*33*). Using standard techniques (*24, 32*) we have calculated expected position of the ν_a and ν_s band of adsorbed $^{15}NO/^{14}NO$ and $(^{15}NO)_2$ dimers as a function ν_a for $(^{14}NO)_2$ which, from the band profile, might lie in the range 1815–1850 cm^{-1} [see Ref. (*32*) for details of the technique as applied to $(NO)_2$]. That is, the data for ν_s (1864 cm^{-1}) and ν_a (1815–1850) were used to determine the NO stretching force constant ($14.90–15.18 \times 10^5$ dyn cm^{-1}) and the coupling constant ($0.38–0.094 \times 10^5$ dyn cm^{-1}) from which the expected positions for the isotopic species were calculated. The results are plotted in Fig. 6. The symmetric $\nu(^{15}NO)_2$ mode remained constant at 1830 cm^{-1} which is very close to the experimental value of 1829 cm^{-1}, whereas $\nu_s(^{14}NO/^{15}NO)$ varied only slightly between 1852 and 1859 cm^{-1}, again in line with experimental observation. Further, $\nu_a(^{14}NO/^{15}NO)$ lies below the strong band at 1829 cm^{-1} due to $\nu_s(^{15}NO)_2$, which, if overlapped with the latter band, could account for the apparent shift to lower wavenumber when all isotopic species are present (Figs. 4 and 5).

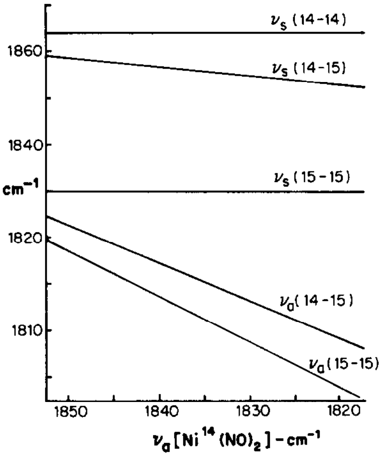

FIG. 6. A plot of the calculated frequencies of the symmetric (ν_s) and antisymmetric (ν_a) NO stretching mode of dimeric $Ni(NO)_2$ assuming that ν_s (14–14) [for $Ni(^{14}NO)_a$] was fixed at 1864 cm^{-1} and ν_a (14–14) ranged from 1817 to 1853 cm^{-1}.

With a 1 : 1 mixture of adsorbed ^{14}NO and ^{15}NO, there would be twice as many mixed (14/15) dimers as (14/14) or (15/15) dimers. Although the band intensities may not follow that 1 : 2 : 1 pattern, we have attempted to reconstruct the experimental band shape by drawing with equal intensity, the separate observed band shapes for adsorbed ^{14}NO and ^{15}NO (1864 and 1829 cm^{-1}) with a Lorentzian profile for $\nu_s(^{14}NO/^{15}NO)$ of twice the peak height at 1854 cm^{-1} (Fig. 7). By inserting a second Lorentzian curve for $\nu_a(^{14}NO/^{15}NO)$ at 1816 cm^{-1}, one can approximately reproduce the experimental shape. Note that the apparent maximum is now higher than 1854 cm^{-1}. Also, when relatively less adsorbed ^{14}NO is present (Fig. 5D and E) the observed maximum is nearer 1854 cm^{-1}.

In consideration of the preceding we believe that undissociated NO on our nickel catalyst exists mainly as the $Ni(NO)_2$ species. We had earlier (*21*) assigned the 1864 cm^{-1} band to monomeric NiNO, a conclusion which was reached before we had used the microbalance and the mixed isotopic

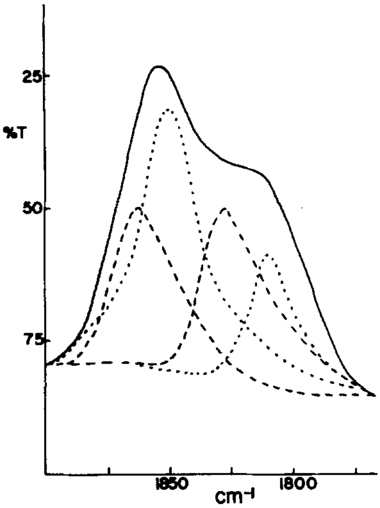

FIG. 7. (---) Observed infrared spectrum of adsorbed ^{14}NO and ^{15}NO. (....) Lorentzian curves centered at 1854 and 1816 (see text). (———) The sum of the above curves. Note that the sum curve is drawn on a percentage T scale for comparison with the experimentally obtained spectra.

nitric oxides. We do not believe that the asymmetry to the low wavenumber side of the main peak can be attributable solely to NO on nickel oxide since the same band profile was observed if NO was adsorbed on preoxidized Ni. However, as will be expanded upon below, we must conclude that our Ni(NO)$_2$ species nonetheless resides on a partially oxidized surface. Therefore, our results do not necessarily contradict those of Ito *et al.* [the *cis* dimer], since their experiments were carried out under UHV conditions with a low coverage of NO.

To conclude this spectroscopic discussion, a major point of difference between our work and that reported by Blyholder and Allen (*1*) and Batychko *et al.* (*2*) was that both groups reported observing an additional band near 2200 cm^{-1} following the adsorption of NO on bare Ni. This band was not observed by Terenin and Roev (*3*). Blyholder and Allen (*1*) found that this band (2205 cm^{-1}) formed after adsorption at 20°C on both Ni/SO$_2$ and Ni–hydrocarbon suspensions, whereas Batychko *et al.* (*2*) reported that this band (2190 cm^{-1}) formed only if adsorption was carried out at 150°C. Both groups attributed this additional feature to an "activated" form of NiNO, possibly adsorbed on edge or corner sites. However, Batychko *et al.* (*2*) found that this band could be produced at 20°C when CO was added to adsorbed NO, and Blyholder and Allen (*1*) found that their 2205 cm^{-1} band appeared at 2180 cm^{-1} with greatly enhanced intensity when CO was added to preadsorbed NO.

The above behavior when CO is present is similar to that found in the present work and we believe that species responsible for our 2201 cm^{-1} band was also generated by Blyholder and Allen (*1*) and by Batychko *et al.* (*2*). The 2201 cm^{-1} band underwent an appreciable isotopic shift when any of ^{13}C, ^{18}O, or ^{15}N were substituted (Table 1), so it cannot be assigned to an activated form of NiNO or to Ni(NO)$^+$. In view of the large ^{13}C shift, it would be more reasonable to assign this band to a surface nickel isocyanate (NiNCO). Both the peak position and the isotopic shifts are in the range which has been reported for other surface metal–isocyanate species (*4–6, 8–12*) and for surface SiNCO (*34*). Although metal isocyanates in most other work have been generated only after a high temperature (150–400°C) reaction between NO and CO over a catalyst, Brown and Gonzales (*6*) and Davydov and Bell (*10*) recently reported that RuNCO was formed at room temperatures using virtually the same reaction conditions as ourselves. It would appear then that at least under the conditions where CO and NO were intentionally present, NiNCO surface species were also generated in the work described by Blyholder and Allen (*1*) and by Batychko *et al.* (*2*). The reaction between NO and CO is considerably more complex than indicated and is discussed in detail in the following paper. At this time the nature of the 2082 cm^{-1} band (adsorbed CO) will also be discussed. For comparison in Table 1 we have also indicated the band position for the linear form of adsorbed CO on Ni (*35*) and as can be seen, the ^{18}O and ^{13}C isotopic shifts of this band (2033 cm^{-1} for $^{12}C^{16}O$) and the 2082 cm^{-1} band are virtually identical.

The Dissociation of NO

We have implied that NO probably dissociates on nickel and that the spectroscopic features might be more correctly attributed to NO adsorbed on a partially oxidized surface. Support for this comes from the following observations; (a) an identical 1864 cm^{-1} band was observed for NO adsorbed on a preoxygen-treated catalyst, (b) the intensity of the 1864 cm^{-1} band slowly decreased with time (Fig. 2), and (c) after NO adsorption only traces of N_2 desorbed, and there was very little weight change with time in the microbalance experiments. All of this suggested that at 325 K, NO on nickel slowly dissociates to yield oxide and nitride type species.

This is also consistent with the relative adsorption capacity for CO, NO, and O_2 as measured with the balance. The large weight increase for O_2 as opposed to that for CO is consistent with the know ability of oxygen to form a relatively thick oxide layer (*36–38*). However, even assuming one-half of the CO is attached to a single Ni atom and the other half is attached to two Ni atoms (bridged CO), the adsorption capacity of NO is greater than would be predicted by assuming that each surface Ni atom contained two NO molecules, i.e., we have a partially oxidized surface.

This finding is consistent with results obtained using other techniques. Conrad *et al.* (*15*) using LEED, AES, and UPS found that NO readily dissociated on NI(111) into adsorbed N and O atoms, even in the presence of preadsorbed oxygen. Brundle (*16*) using XPS/UPS found that both NO and NO_2 dissociatively adsorbed on Ni films at 300 K to yield surface oxide and nitride and various NO states and that little gaseous N_2 desorbs. He further found that the percentage dissociation increased with time of contact in vacuum as found in this work. Conrad *et al.* (*15*), Brundle (*16*), and Price *et al.* (*14*) all found that extensive liberation of gaseous N_2 did not occur until the Ni sample was heated considerably above 325 K (~800 K) a result which is qualitatively consistent with the present results in that extensive liberation of N_2 occurred if samples were heated at 673 K in our case, although the lower temperature limit for this process was not thoroughly investigated. [From the microbalance pyrolysis data, we assume that most of the original nitrogen is liberated as N_2 leaving oxide behind.] Therefore, we conclude that our own surface at 325 K is similar to that described by Brundle (*16*) in that surface oxide and nitride are present, except the major NO species is in the form of $Ni(NO)_2$.

Adsorbed NO_2

The spectrum obtained after the addition of a saturation dose of NO_2 is the same as that which has been previously observed by Blyholder and Allen (*39*) following the adsorption of 10 Torr of NO_2 on silica-supported Ni (see their Fig. 7). The strong bands at 1555 and 1440 were assigned to surface nitrate species and the weak band at 1850 cm^{-1} (1864 cm^{-1} here) indicated that a small quantity of adsorbed NO was present. We found that this "saturated" surface was unreactive toward CO.

With a less than saturation dose of NO_2 (not investigated by Blyholder and Allen) the spectrum obtained was identical to that obtained using NO and NiNCO and CO_2 were also produced if CO was subsequently added. We must assume that at low coverage NO_2 dissociates to yield adsorbed NO (as $Ni(NO)_2$) and oxide. A similar conclusion was reached by Brundle in his XPS and UPS study (*16*) of the adsorption of NO_2 on Ni films.

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