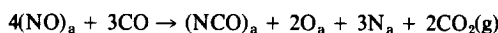


## The Reaction between NO and CO on Silica-Supported Nickel

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The reaction between NO and CO at 325 K on silica-supported Ni has been studied using infrared spectroscopy and a vacuum microbalance. Adsorbed NO [mainly as Ni(NO)<sub>2</sub>] reacts with CO to form adsorbed isocyanate (-NCO) and gaseous CO<sub>2</sub>. Preadsorbed CO is displaced by excess NO and no further reaction occurs but with a small dose of NO, CO is only partially displaced and isocyanate and CO<sub>2</sub> are generated. Data indicate that the reaction is initiated by the direct interaction of adsorbed CO and NO and that the rate of reaction is probably inhibited by strongly adsorbed isocyanate. No definite mechanism can be devised but the apparent overall reaction stoichiometry after the reaction has gone to completion (5 hr) is



where the subscript a indicates an adsorbed species and at least one step involves adsorbed CO. During reaction a weakly held form of adsorbed CO is generated which has been attributed to an (NCO)<sub>a</sub>-(CO)<sub>a</sub> interaction on adjacent Ni sites.

## INTRODUCTION

The transition metal catalyzed reaction between NO and CO leading to the formation of adsorbed isocyanate species has been extensively studied (1-8). In many cases the reaction occurs to a significant extent only if the temperature is in the 200-400°C range, and there is considerable evidence that if supported metal catalysts are used, the adsorbed isocyanate species sometimes is attached to the support rather than the metal (6). Prior to our work, Ru was the only metal which was found to catalyze this reaction at ambient temperatures and the isocyanate species is attached to the metal rather than the support (2, 3). In a brief early communication (8), and in the paper preceding this one (1), we also reported that a similar reaction occurs at ambient temperatures over silica-supported nickel. This paper is concerned with a more detailed study of the reaction between NO and CO on this catalyst using infrared spectroscopy and a vacuum microbalance.

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## EXPERIMENTAL

Experimental details are given in the paper preceding this (1). Several different catalyst samples were used in this work, all prepared from the same Ni(NO<sub>3</sub>)<sub>2</sub>-SiO<sub>2</sub> mixture, and no differences were noted from sample to sample; in one instance the same catalyst was used for 3 years with reproducible results.

Reactions were studied at 325 K for reasons discussed in the preceding paper (1). Our vacuum microbalance (Sartorius model 4433) has a symmetrical two pan arrangement and 130 mg of the same Ni/SiO<sub>2</sub> catalyst was placed on one side with either tare weights or pure silica (no differences) on the other side. Both quartz pans could be heated up to 673 K for sample regeneration or pyrolysis, and they were kept at 325 K during NO/CO experiments. The MS-10 mass spectrometer was connected with about 1 m of pyrex tubing to the reference side of the balance so that "instantaneous" MS analyses were not possible. A McLeod gage was used for pressure measurements in the 0.01 to 1.0

Torr range. The volume of the total isolated system was 2.355 liter. Weight changes could be measured to an accuracy of 1  $\mu\text{g}$ .

## RESULTS

### Spectroscopic Data

As reported in the preceding paper (1), the infrared spectrum of a large dose of NO ( $\sim 192 \mu\text{mole/g}$  of catalyst) adsorbed on silica-supported nickel has an intense ( $\sim 1.4$ – $1.6$  absorbance) asymmetric band at  $1864 \text{ cm}^{-1}$  which has been assigned to surface  $\text{Ni}(\text{NO})_2$  species. When excess CO was subsequently added, this band slowly decreased in intensity over a 5-hr period (where its intensity was halved) and new bands appeared at  $2201$  and  $2082 \text{ cm}^{-1}$  which have been attributed to adsorbed isocyanate ( $\text{NiNCO}$ ) and carbon monoxide, respectively (see Fig. 3 of that paper). A mass spectrometric (MS) analysis of the gas phase after 5 hr showed that only  $\text{CO}_2$  and CO were present, and when  $\text{C}^{18}\text{O}$  was used,  $\text{NiNC}^{18}\text{O}$ , adsorbed  $\text{C}^{18}\text{O}$ , and an exact 1:2:1 mixture of  $\text{C}^{16}\text{O}_2$ ,  $\text{C}^{16}\text{O}^{18}\text{O}$ , and  $\text{C}^{18}\text{O}_2$  was detected. We now report further details of this reaction.

The intensity of the  $1864 \text{ cm}^{-1}$  band was approximately halved ( $0.7$ – $0.9$  absorbance) when  $0.7$ – $1$  Torr of NO was added to the ir cell ( $300 \text{ ml}$  volume). After evacuation and addition of  $0.5$ – $1.0$  Torr of CO the intensity of the  $1864 \text{ cm}^{-1}$  band sharply decreased and the same new bands at  $2201$  and  $2082 \text{ cm}^{-1}$  appeared, but the latter was accompanied by a shoulder of  $2033 \text{ cm}^{-1}$ . [Spectra for adsorbed  $^{14}\text{N}^{16}\text{O}$  and  $^{12}\text{C}^{18}\text{O}$  are shown in Fig. 1. The  $2033 \text{ cm}^{-1}$  band is at  $1986 \text{ cm}^{-1}$  for  $^{12}\text{C}^{18}\text{O}$  and the other shifts are as noted in Table 1 of the preceding paper (1). For conveniences we will continue to label all bands by their  $^{12}\text{C}^{16}\text{O}/^{14}\text{N}^{16}\text{O}$  position.] After 5 hr reaction the  $2201$  band had achieved its maximum intensity, which was about 60% of that achieved using a saturation dose, but the original  $1864 \text{ cm}^{-1}$  band had disappeared. During the course of these changes, the  $2082 \text{ cm}^{-1}$  band first increased in intensity and then decreased in intensity (Fig. 1). Following evacuation, only the  $2082 \text{ cm}^{-1}$  band disappeared and the shoulder at  $2033 \text{ cm}^{-1}$  appeared as a distinct but weak band (Fig. 1F). MS analysis of the gas phase revealed that only  $\text{CO}_2$  and traces of CO were present, and when

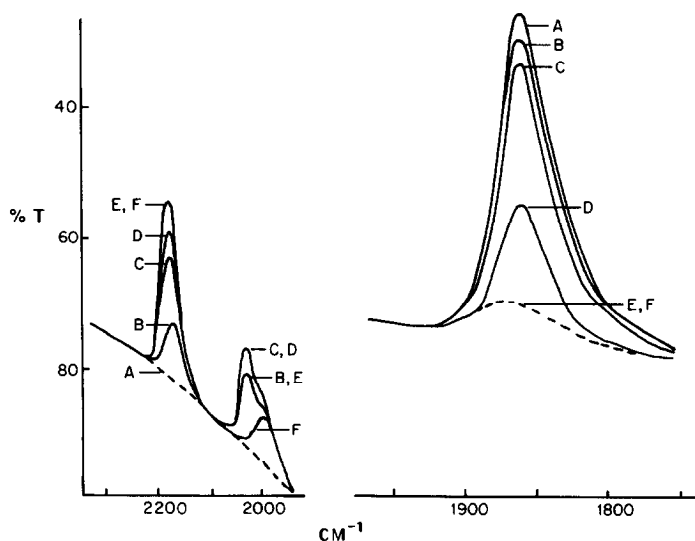


FIG. 1. (A) Infrared spectrum of adsorbed NO ( $\sim$  half coverage) on Ni. Spectra after adding 0.5 Torr of  $\text{C}^{18}\text{O}$  to (A) after (B) 2 min, (C) 20 min, (D) 50 min, (E) 180 min. (F) Evacuation of  $\text{C}^{18}\text{O}$ .

$C^{18}O$  was used, traces of  $C^{18}O$  and the 1:2:1 mixture of  $^{16}O/^{18}O$  labeled  $CO_2$  was detected after the reaction was completed.

For a similar small initial dose of NO but with excess CO (5–10 Torr), the final intensity at  $2201\text{ cm}^{-1}$  was about the same as was achieved using saturation dose of NO but the intensity of the  $2082\text{ cm}^{-1}$  band (Fig. 2) was about three times greater than that shown in Fig. 1, and its intensity continually increased during reaction. (Curves showing the intensity *vs* time profile will be described later.) Under such conditions the shoulder at  $2033\text{ cm}^{-1}$  was masked, but it was observed (as in Fig. 1) if the CO was evacuated briefly. Again, when  $C^{18}O$  was used, only  $C^{18}O$  and 1:2:1  $CO_2$  was detected after completion of the reaction. This was always the case regardless of the proportions of NO and  $C^{18}O$  used. However, a different result was obtained if rapid MS analyses were obtained.

#### The NO/ $C^{18}O$ Reaction

Mass spectra were usually obtained after the reaction had proceeded for several hours, after which the reaction cell was removed from the ir spectrometer and it

was attached to one of the mass spectrometers. In some experiments, we introduced  $C^{18}O$  to the pretreated Ni/NO surface and immediately attached the cell to the mass spectrometer, but analysis could be carried out only after about 10 min reaction time. In this case, again an exact 1:2:1 mixture of  $CO_2$  isotopes was detected.

In a different experimental arrangement the reaction cell was placed in the ir spectrometer and was connected to the vacuum line via a liquid  $N_2$  trap. Carbon monoxide- $^{18}O$  was added to the Ni/NO pretreated sample and the reaction mixture was evacuated after 40–60 sec reaction time. The trapped reaction products were then isolated, and analyzed on the MS. In all cases, the mass 46 peak [ $C^{16}O^{18}O$ ] was about 6–10 times more intense than the peaks at mass 44 and 48, the latter being of equal intensity. This suggests that  $C^{16}O^{18}O$  is the initial reaction product and that the 1:2:1 mixture simply arises from a subsequent fast exchange.

This point was confirmed in separate experiments using a 1:1 mixture of  $C^{16}O_2$  (44) and  $C^{18}O_2$  (48). After 10 min contact with a regenerated Ni sample, a 1:2:1

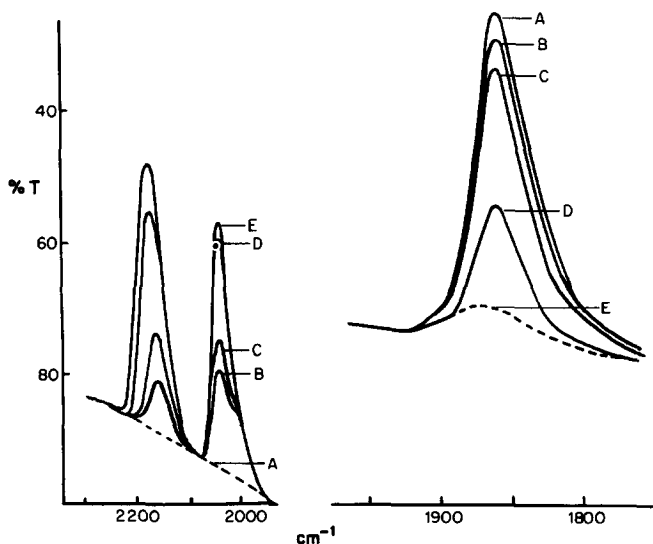


FIG. 2. (A) Infrared spectrum of adsorbed NO ( $\sim$  half coverage on Ni). Spectra after adding 10 Torr of  $C^{18}O$  to (A) after (B) 1 min, (C) 3 min, (D) 60 min, (E) 5 hr.

mixture of  $\text{CO}_2$  isotopes was detected, although no infrared bands were observed in the  $4000\text{--}1350\text{ cm}^{-1}$  range. The 1:2:1 mixture was also generated within 10 min if the 1:1  $\text{C}^{16}\text{O}\text{--}\text{C}^{18}\text{O}_2$  mixture was added (after evacuation of the reactants) to a CO/NO reacted catalyst regardless of whether the isocyanate reaction had been under way for a short time or had gone to completion. Finally, we have verified that the 1:1 mixture of  $\text{C}^{16}\text{O}_2$  and  $\text{C}^{18}\text{O}_2$  does not exchange on Pyrex or on the silica support.

#### Adsorption of CO

When 5–10 Torr of CO was allowed to react for 5 min with our silica-supported Ni sample, then after evacuation only the well known (9) bands due to linear and bridged forms of adsorbed CO were observed at 2033 and 1920  $\text{cm}^{-1}$ , respectively (see Fig. 3B for the 2033  $\text{cm}^{-1}$  band). The band intensities did not change during evacuation for 1 hr. Only if the CO contact time was greater than 1 hr and if the initial CO

pressure was greater than 25 Torr were traces of  $\text{Ni}(\text{CO})_4$  detected, either by infrared (2057  $\text{cm}^{-1}$ ) or MS analysis. [ $\text{Ni}(\text{CO})_4$  was not detected under our reaction conditions during the NO/CO reaction.] Figure 3A shows the spectrum of CO (in the presence of 5 Torr of CO) adsorbed on a catalyst which had been previously exposed to excess  $\text{O}_2$  for 5 min. The more intense band is at 2082  $\text{cm}^{-1}$  and the weaker one is at 2123  $\text{cm}^{-1}$ . The low wavenumber shifts with  $^{13}\text{CO}$  or  $\text{C}^{18}\text{O}$  of both bands were identical to that of the 2082  $\text{cm}^{-1}$  which was produced during the NO/CO reaction (see Table 1 of the preceding paper), and these shifts were similar to those of the 2033  $\text{cm}^{-1}$  band.

Whereas the 2082  $\text{cm}^{-1}$  band disappeared rapidly following evacuation in the case of the NO/CO reaction, the bands at 2123 and 2082  $\text{cm}^{-1}$  required about 1 hr evacuation before they disappeared when CO was adsorbed on preoxidized Ni.

#### Adsorbed CO + NO(g)

When a large dose of NO was added to preadsorbed CO on Ni the infrared bands of adsorbed CO at 2033 and 1920  $\text{cm}^{-1}$  immediately disappeared and a "saturation" coverage band due to adsorbed NO was observed at 1864  $\text{cm}^{-1}$ . Simultaneously an extremely weak band was observed near 2201  $\text{cm}^{-1}$  (0.01 absorbance) and only CO plus traces of  $\text{N}_2$  and  $\text{N}_2\text{O}$  were detected in the gas phase. No further changes occurred after 3 hr except for the normal slow decrease in intensity at 1864  $\text{cm}^{-1}$  (1).

However, if a low dose of NO was added, a weak band immediately appeared at 1864  $\text{cm}^{-1}$  (0.4–0.5 absorbance), a new peak band appeared at 2190  $\text{cm}^{-1}$ , the band at 2033  $\text{cm}^{-1}$  decreased in intensity, and a shoulder developed near 2082  $\text{cm}^{-1}$  (Fig. 3C). After 3 hr the 1864  $\text{cm}^{-1}$  band had disappeared, the new feature, now at 2201  $\text{cm}^{-1}$ , had intensified to a maximum value, and the shoulder at 2082 had intensified (Fig. 3D). Analysis of the gas after 3 hr when  $\text{C}^{18}\text{O}$  was used showed that an exact

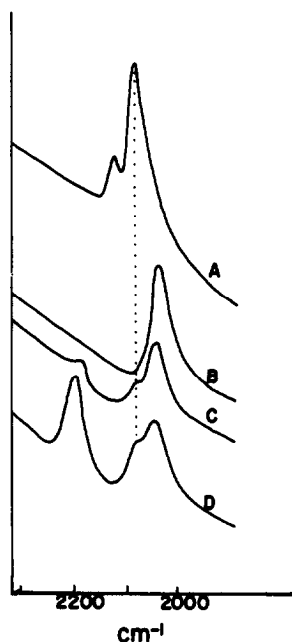


FIG. 3. (A) Spectrum of 5 Torr of CO adsorbed preoxygen treated Ni. (B) Spectrum of CO adsorbed on bare Ni. (C) Spectrum observed within 1 min of adding 0.5 Torr of NO to (B); (D) 3 hr later.

1:2:1 mixture of  $C^{16}O_2$ ,  $C^{16}O^{18}O$ , and  $C^{18}O_2$  was present, and that no  $C^{18}O$  or  $C^{16}O$  was present.

### Kinetic Data

The infrared cell has a large volume in relation to the catalyst size and it was impossible to measure the rate of change in concentration of gaseous species with time. However, it was possible to measure the intensity (absorbance) of the 1864 and 2201  $cm^{-1}$  bands as a function of time. The intensity at 2082  $cm^{-1}$  could also be measured but this band was overlapped by the 2033  $cm^{-1}$  band. In these experiments, the ir cell was fixed in the spectrometer, a specific dose of NO was added, excess was evacuated, and timing began when CO was added. Approximately 5–10 Torr of CO was used, about a 10 to 20-fold excess, so that

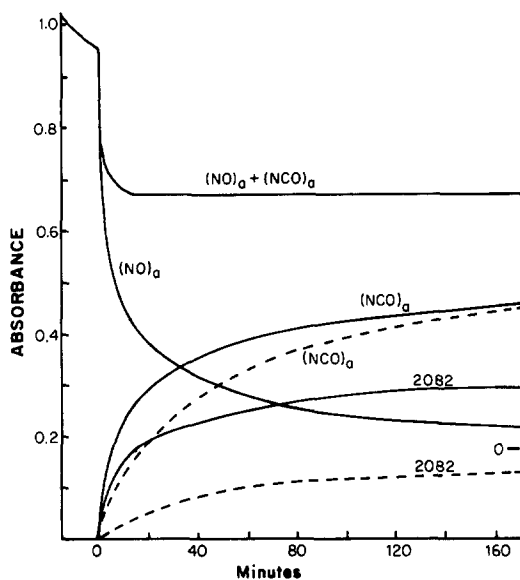


FIG. 4. Intensity vs time curves (NO/CO reaction) for adsorbed NO (1864  $cm^{-1}$ ) and isocyanate (2201  $cm^{-1}$ ) and for the 2082  $cm^{-1}$  band due to adsorbed CO. The solid and dashed curves are for moderate and near saturation initial NO coverage, respectively. Time zero refers to the introduction of CO into the ir cell, and the solid curve for  $(NO)_a$  from -10 to 0 time shows the normal slow decay in the absence of CO. The absorbance values for  $(NO)_a$  are real instrumental readings and the "zero" or background absorbance at 1864  $cm^{-1}$  is indicated at the left.

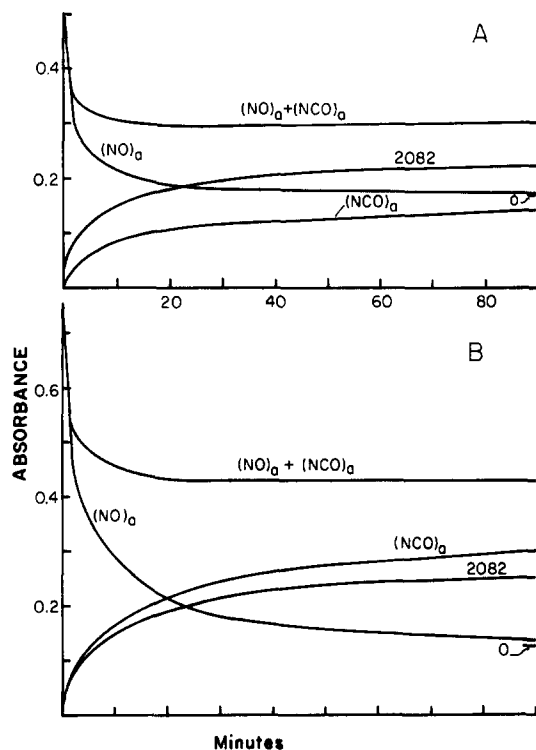


FIG. 5. Intensity vs time curves (NO/CO reaction) for (A) low and (B) intermediate coverage of NO. The absorbance values for  $(NO)_a$  are real instrumental readings, and the "zero" or background absorbance at 1864  $cm^{-1}$  is indicated at the left.

the CO pressure was effectively constant during the course of the reaction. Some typical curves showing the absorbance at 1864 (NO), 2082 (CO), and 2201 (NCO)  $cm^{-1}$  for varying initial absorbance at 1864 (i.e., for varying initial coverage of NO) are shown in Figs. 4 and 5. For moderate initial NO coverage (0.5–1 absorbance) we could accurately follow the decay in the 1864  $cm^{-1}$  band during reaction and we have also plotted the sum of the absorbances of the bands at 2201  $cm^{-1}$  (NCO) and 1864  $cm^{-1}$  (NO). For large initial NO coverage (1.4–1.6 absorbance) the intensity at 1864  $cm^{-1}$  could not be accurately measured since our spectrometer operates only in the transmittance mode and we used logarithmic (absorbance) chart paper. Further, even after 5 hr reaction when NCO formation had

ceased, the peak absorbance at 1864 was still about 0.8–0.9 (see Fig. 3 of the preceding paper). Several general features of these curves are to be noted:

(1) Although the 1864  $\text{cm}^{-1}$  slowly decreases in intensity in the absence of CO [see Fig. 2 of the preceding paper, and the solid curve for NO in the present Fig. 4 before CO is added] upon introduction of CO there is a very large increase in the rate of disappearance of this band.

(2) The initial extent of disappearance of adsorbed NO exceeded the extent of formation of adsorbed NCO, but after about 10–15 min the sum of the absorbances was linear, indicating a correlation between the rates of these two processes. That the sum curve was also nearly horizontal is a coincidence and has no significance without knowledge of the extinction coefficients. As far as could be determined, even for a very large initial coverage of NO, the sum of the absorbances of these bands was also constant (1.2–1.4 depending on conditions) to within  $\pm 0.04$  during the period 15 min–5 hr reaction time.

(3) The initial rate of growth of the 2082  $\text{cm}^{-1}$  band, and its maximum intensity, was larger when the initial coverage with NO was lower, and in most cases the rate of growth of this band decreased more rapidly than that of NCO formation.

(4) For low to moderate initial coverage with NO [up to about 0.75 of maximum as judged by the maximum attainable absorbance at 1864  $\text{cm}^{-1}$ ] the 1864  $\text{cm}^{-1}$  band eventually disappeared, but for higher coverage ( $\sim 0.90$ ) the intensity was approximately halved for 5 hr when the reaction ceased.

It is apparent from the curves shown in Figs. 4 and 5 that at least after 10 min reaction there is a correlation between the rate of disappearance of adsorbed NO (1864) and the rate of formation of isocyanate (2201). We further found (after 10 min) that the rate of formation of NCO could be reasonably well fitted to either of the following rate equations;

$$(A) \text{ rate} = k_a[\text{NO}]^2$$

$$(B) \text{ rate} = k_a \frac{[\text{NO}]}{[\text{NCO}]}$$

where [NO] and [NCO] represent the peak absorbances at 1864 and 2201  $\text{cm}^{-1}$ , respectively, and  $k_a$  is an apparent rate constant. However, we believe that this kinetic analysis is misleading because the reaction rate is very temperature dependent insofar as the heat generated by the ir source accelerates the rate where it strikes the sample. This is, the sample (which is black) is not at a truly uniform temperature, supposed to be about 325 K, and small variations in relative peak heights (6–8%) were observed if the cell position was moved during the course of reaction. The variations indicated that the rate was slightly slower on the "cooler" portions of the catalyst. Nonetheless, in numerous kinetic experiments using the same spectrometer (which has a low current Nernst source with a presample chopper) our results were very reproducible.

Finally, although we always used an excess of CO ( $P = 5\text{--}10$  Torr), we did verify that the rate appeared to be independent of CO pressure in separate experiments where this was varied from 2 to 400 Torr.

#### *Microbalance Experiments*

For reasons stated earlier, both the sample and reference pans of the balance were heated to  $325 \pm 3$  K in order to duplicate the temperature which pertained in the infrared experiments. A saturation dose of NO produced a weight increase of about 750  $\mu\text{g}$  ( $I$ ) and in most NO/CO experiments we added a dose of NO which would produce a weight increase in the 400–600  $\mu\text{g}$  range since the ir experiments indicated that, under these conditions, the 1864  $\text{cm}^{-1}$  band due to  $\text{Ni}(\text{NO})_2$  would have disappeared after 5 hr reaction with excess CO. For measurement of the quantity of  $\text{CO}_2$  produced during a reaction between preadsorbed NO and excess CO, the mixture was slowly pumped through a glass bead packed

liquid N<sub>2</sub> trap and the trapped CO<sub>2</sub> was expanded into a known volume for *P* measurement. Independent experiments with known CO/CO<sub>2</sub> mixtures showed that our trap was 100% efficient. The sample was then heated in vacuum for 1 hr at 400°C after evacuation of the CO/CO<sub>2</sub> mixture, and the gas phase was analyzed by MS, the total pressure was measured, and the final weight (at the original reaction temperature under vacuum) was recorded.

The results can be summarized as follows:

(1) The sample weight during reaction increased by 2–6% relative to the weight, in vacuum, of adsorbed NO.

(2) The weight after evacuation of excess CO plus reaction products was 3–5% lower than the weight, in vacuum, of the initially adsorbed NO.

(3) The ratio of the number of moles of NO adsorbed to CO<sub>2</sub> produced during reaction was  $2.0 \pm 0.2$ .

(4) After pyrolysis, only N<sub>2</sub> and CO<sub>2</sub> were detected in the gas phase and the mole ratio N<sub>2</sub>/CO<sub>2</sub> was  $2.0 \pm 0.3$ . The mole ratio of N<sub>2</sub> + CO<sub>2</sub> after pyrolysis to NO adsorbed was  $0.6 \pm 0.15$ .

(5) The weight of the catalyst after pyrolysis (in vacuum at the original reaction temperature) was between 12 and 18% of the weight of the originally adsorbed NO.

Some experiments were also carried out using the ir cell where a measured dose of NO was allowed to react completely with the Ni/SiO<sub>2</sub> sample. The reaction was allowed to proceed with the sample in the furnace region of the cell at 325 K. After reaction, the infrared spectra were identical to those described earlier (for similar doses of NO) and the data obtained under 3 and 4 above were identical, including the spread. Further, after pyrolysis at 400°C, all infrared bands disappeared.

Finally, when a very low dose of NO (~100 μg) was used in the balance, the sample weight immediately increased to about 200 μg when CO was added. The weight remained constant over a 5-hr per-

iod, even after the CO was evacuated. Infrared experiments carried out under similar conditions revealed that a near maximum coverage of NiCO (2033 cm<sup>-1</sup>) resulted, and we assume that the approximate 100 μg increase above is also due to adsorbed CO.

## DISCUSSION

As described in the preceding paper (1), the reaction between CO and adsorbed NO on Ni produces adsorbed isocyanate and gaseous CO<sub>2</sub>. Without regard to the nature of adsorbed NO [i.e., Ni(NO)<sub>2</sub>], we originally thought that the overall reaction stoichiometry could be represented by the equation



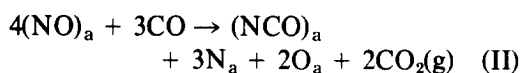
This is consistent with the data obtained from the use of C<sup>18</sup>O where NiNC<sup>18</sup>O and C<sup>16</sup>O<sup>18</sup>O are formed, and the latter subsequently exchanges to give the 1:2:1 mixture of C<sup>16</sup>O<sub>2</sub>, C<sup>16</sup>O<sup>18</sup>O and C<sup>18</sup>O<sub>2</sub>.

However, the intensity vs time curves (Figs. 4 and 5) indicate that, in the early stages of reaction, NO decomposition is faster than NCO formation and the microbalance data are not consistent with scheme (I) which predicts that the ratio of NO adsorbed to CO<sub>2</sub> generated should be 1 and not, as measured,  $2.0 \pm 0.2$ . Such a reaction stoichiometry should also cause a weight increase of 40% (NO = 30, NCO = 42) instead of a weight loss of 4%. Further, it would be difficult to explain why the ratio N<sub>2</sub> to CO<sub>2</sub> was  $2.0 \pm 0.3$  after pyrolysis. Therefore, we will first discuss the results in terms of a stoichiometry which fits the data, and we will conclude with some mechanistic comments.

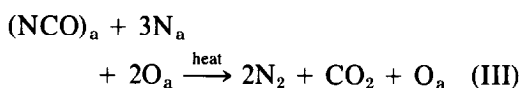
### *Stoichiometry*

In the following discussion we will indicate an adsorbed species with the subscript *a* so as not to imply any particular surface configuration, e.g., NiNO<sub>*a*</sub> as opposed to

$\text{Ni}(\text{NO})_2$ . A plausible stoichiometry which fits the quantitative data is



This scheme predicts the following; (a)  $(\text{NO})_a/\text{CO}_2 = 2.0$ ; (b) ratio of catalyst wt after reaction to that before reaction = 116/120, a decrease of 3.3%; (c) after pyrolysis of the adsorbed species we assume the following reaction



so that  $\text{N}_2/\text{CO}_2 = 2.0$ , the ratio of  $\text{N}_2 + \text{CO}_2$  to  $(\text{NO})_a$  is 0.75, and the catalyst weight after pyrolysis is 16/120 or 13.3% of the weight with the originally adsorbed NO.

Given the large scatter in the data concerning the quantities of gaseous molecules evolved in various steps, we do not believe that scheme (II) has any mechanistic significance, but that it represents a plausible average surface composition. We will consider the nature of adsorbed NO and the question of dissociation in more detail in connection with the infrared results. Further, the latter also showed that after evacuation of the reactants (the 2082  $\text{cm}^{-1}$  band disappears) there was a residual very weak band at 2033  $\text{cm}^{-1}$  due to NiCO, and this will also make a small contribution to the final weight of the catalyst.

### The 2082 $\text{cm}^{-1}$ Band

In the preceding paper (1) we argued that NO alone dissociates on Ni, and we concluded that surface oxide and nitride-like species were formed. The infrared band observed at 2082  $\text{cm}^{-1}$  during the NO/CO reaction is at the same frequency as the main band which was observed when CO was adsorbed on oxygen treated Ni (Fig. 3) and this could also be evidence for the presence of surface oxide.

However, the following experiment illustrates that this assignment may be incorrect. A low dose (about 25% of saturation)

of  $(\text{NO})_a$  was allowed to dissociate for 3–4 hr until the 1864  $\text{cm}^{-1}$  band had disappeared, and presumably only  $\text{N}_a$  and  $\text{O}_a$  were present (1). After addition of CO, no  $(\text{NCO})_a$  was formed, and no band at 2082  $\text{cm}^{-1}$  was observed, although one was observed at 2033  $\text{cm}^{-1}$ , characteristic of CO adsorbed on bare Ni. Also recall that no high wavenumber component at 2123  $\text{cm}^{-1}$  was present during the NO/CO reaction as opposed to CO adsorbed on oxidized Ni (Fig. 3A) and that the 2082  $\text{cm}^{-1}$  band disappeared rapidly following evacuation of CO (NO/CO reaction) whereas about 1 hr evacuation was required to effect this for CO on oxidized Ni. The above suggests that the 2082  $\text{cm}^{-1}$  band may not be an indication of the presence of surface oxide.

Although our argument is weak, but will develop further when we consider the mechanistic details, we believe that the 2082  $\text{cm}^{-1}$  band represents a weakly held form of adsorbed CO which is adjacent to a  $(\text{NCO})_a$  site. Just as an electron withdrawing oxide causes a high frequency shift in  $\nu(\text{CO})$  (10, 11), this is equally possible with adsorbed NCO. [The 2082  $\text{cm}^{-1}$  band is not likely due to  $(\text{CO})_a$  perturbed by  $(\text{NO})_a$  since its intensity by and large continued to increase as  $(\text{NCO})_a$  was formed, even if  $(\text{NO})_a$  was entirely consumed.] The large initial intensity at 2082  $\text{cm}^{-1}$  for low initial NO coverage might be a reflection of the larger number of vacant Ni atoms adjacent to each  $(\text{NCO})_a$  site, the reverse being the case for high initial  $(\text{NO})_a$  coverage. For intermediate coverage, the bands at 2082 and 2201  $\text{cm}^{-1}$  grew in intensity more or less in unison.

### Preadsorbed CO

Excess gaseous NO completely displaced preadsorbed CO (2033  $\text{cm}^{-1}$ ) and virtually no  $(\text{NCO})_a$  was formed. With a less than saturation dose of NO, the band at 2033  $\text{cm}^{-1}$  was reduced in intensity (Fig. 3C), a weak shoulder appeared at 2082  $\text{cm}^{-1}$ , and a weak band due to  $(\text{NO})_a$  was observed. Over a period of hours, both the



2033 and  $1864\text{ cm}^{-1}$  band decreased in intensity, a small quantity of  $(\text{NCO})_a$  was formed ( $2201\text{ cm}^{-1}$ ), and the  $2082\text{ cm}^{-1}$  band intensified (Fig. 3D).

In a separate experiment, very small doses of NO ( $\sim 0.5\ \mu\text{mole}$ ) were successively added (15 sec exposure followed by evacuation) to preadsorbed CO (Fig. 6). The intensity of the  $2033\text{ cm}^{-1}$  band steadily decreased, eventually disappearing after 15 doses (Fig. 6F) and a weak band due to  $(\text{NCO})_a$  grew. During this sequence the  $1864\text{ cm}^{-1}$  band due to  $(\text{NO})_a$  reached a final absorbance of 0.5. If excess CO was again added, the normal reaction proceeded [ $(\text{NO})_a \rightarrow (\text{NCO})_a$ ] as shown in Figs. 6G and H, accompanied by the growth of the usual band at  $2082\text{ cm}^{-1}$ .

Both experiments suggest that the initiat-

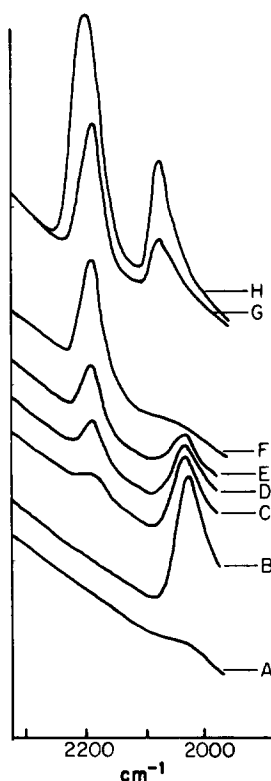


FIG. 6. Background spectrum (A) and spectrum of adsorbed CO (B). Spectra after adding successive ( $\sim 0.5\ \mu\text{mole}$ ) doses of NO; (C) first dose, (D) fifth dose, (E) tenth dose, (F) fifteenth dose. Spectrum after 1 min (G) and 3 hr (H) of adding excess CO to (F).

ing step in the reaction involves NiCO ( $2033\text{ cm}^{-1}$ ) plus  $(\text{NO})_a$ . It further implies that in the case of preadsorbed NO, some sites capable of adsorbing CO are necessary for the reaction to proceed.

In the latter connection, we note that the disappearance of  $(\text{NO})_a$  after adding CO was never complete if a large dose of NO was initially added. But by this technique alone, we never achieved a "no reaction" situation. Even if we allowed 30 Torr of NO to interact with the catalyst for 30 min prior to evacuation and addition of CO, some adsorbed CO appeared and the reaction to form  $(\text{NCO})_a$  proceeded, but of course, not to completion. It may be that the slow dissociation of NO alone will always mean that some free sites are available for CO adsorption. However, if we used the following sequence: adsorption of excess CO, evacuation of CO, adsorption of excess NO (which displaces CO), evacuation of NO, and addition of excess CO, then no adsorbed CO formed, although a very weak (0.04 absorbance) band due to  $(\text{NCO})_a$  was observed. Evidently most sites for CO adsorption were blocked. This additionally shows that the initiation of the reaction does not simply involve an encounter between gaseous CO with  $(\text{NO})_a$ .

#### Mechanistic Considerations

In spite of a considerable accumulation of data it is not possible to devise a mechanism which will account for the stoichiometry in scheme (II). Part of the difficulty lies in the fact that the slower  $(\text{NO})_a$  dissociation is possibly occurring in parallel with the  $(\text{NCO})_a$  reaction, and that more than one mechanism may be operative in the first 10 min (see kinetic data). Therefore, scheme (II) may simply represent the sum of these processes. It is also unfortunate that the kinetic data are not accurate enough to allow us to distinguish between the two plausible rate laws, and that the spectroscopic data do not allow us to conclusively assign the  $2082\text{ cm}^{-1}$  band. How-

ever, we can suggest a probable path for isocyanate formation.

Although we were not able to determine whether the initial rate of CO<sub>2</sub> evolution followed the fast (NO)<sub>a</sub> decomposition or the slower (NCO)<sub>a</sub> formation, some unique features are apparent when we consider the reaction between preoxidized Ni and CO. The oxidation of CO on nickel oxide occurs at an appreciable rate in the 150–250°C range (12, 13) but we looked at this process only at the temperature of the NO/CO reaction, 325 K, and found the following: (a) the quantity of CO<sub>2</sub> produced (~1–1.5 μmole), using excess CO, was about 10% of that which was produced during the NO/CO reaction, (b) when excess CO was added to an O<sub>2</sub> saturated sample (40 μmole of O atoms) the weight immediately increased by 70 μg (2.5 μmole of adsorbed CO) and remained constant over 5 hr, and (c) with <sup>18</sup>O<sub>2</sub>/C<sup>16</sup>O or <sup>16</sup>O<sub>2</sub>/C<sup>18</sup>O a random (i.e., not 1:2:1) but equilibrated [i.e. (C<sup>16</sup>O<sup>18</sup>O)<sup>2</sup>/(C<sup>16</sup>O<sub>2</sub>)(C<sup>18</sup>O<sub>2</sub>) = 4.0] mixture of isotopic CO<sub>2</sub> molecules and some C<sup>16</sup>O was detected. Thus, CO removes very little O<sub>a</sub> at 325 K.

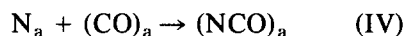
By contrast, a much larger quantity of CO<sub>2</sub> was generated in the NO/CO reaction (10–12 μmole), with C<sup>18</sup>O this was only C<sup>16</sup>O<sup>18</sup>O which subsequently rearranged to give an exact 1:2:1 mixture, no C<sup>16</sup>O was detected, and only (NC<sup>18</sup>O)<sub>a</sub> was formed. This suggests that CO<sub>2</sub> formation follows a very specific mechanism which does not involve bulk O<sub>a</sub>.

At this point it is appropriate that we comment on the results of earlier studies of the NO/CO reaction on supported Ru (2, 3). The spectra of adsorbed NO on Ru differs from our spectra (1) in that there were clear differences in the region of the ν(NO) vibration (1900–1800 cm<sup>-1</sup>) which could be correlated with the dissociation of NO to yield a partially oxidized surface. At no stage in this work did the band shape (1864 cm<sup>-1</sup>) change with time of exposure, preoxidation of the catalyst, or during the reaction with CO. Although we have sug-

gested that dissociation does occur, evidently new bands due to NO on partially oxidized Ni are not observed.

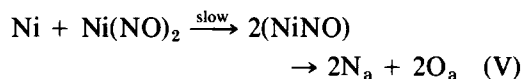
In this context, Davydov and Bell (3) suggested that (NCO)<sub>a</sub> on Ru was formed following the dissociation of NO after which N<sub>a</sub> simply reacted with gaseous CO to yield (NCO)<sub>a</sub> [the intensity of the band due to (NCO)<sub>a</sub> depended on the CO pressure]. But Brown and Gonzalez (2) suggested that the primary step involved a direct interaction between adsorbed CO and NO because the addition of small doses of NO to preadsorbed CO lead to (NCO)<sub>a</sub> formation, a result somewhat disputed by Davydov and Bell (3).

This also occurred in our experiments with preadsorbed CO on Ni where we also suggest that (NCO)<sub>a</sub> formation requires a specific interaction between CO (2033 cm<sup>-1</sup>) and (NO)<sub>a</sub>. We do not think (NCO)<sub>a</sub> formation simply involves the reaction



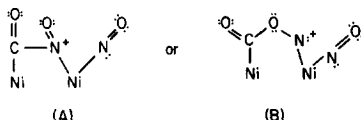
because (NCO)<sub>a</sub> formation did not occur if CO was added after (NO)<sub>a</sub> had completely dissociated. In the light of this information we will now consider how NO and CO may react.

In the absence of CO, the dissociation of (NO)<sub>a</sub> might involve the relatively slow process

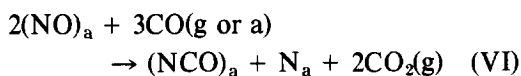


which consumes bare Ni sites. The 1864 cm<sup>-1</sup> band does not completely disappear in the absence of CO, with moderate to high initial coverage. Because the rate of decrease in the intensity of the 1864 cm<sup>-1</sup> band is so rapid within seconds of introducing CO (Figs. 4 and 5), it is unlikely that the process illustrated in (V) is simply accelerated because new bare sites are created after some O<sub>a</sub> reacts with CO or (CO)<sub>a</sub> to form gaseous CO<sub>2</sub>. [Also recall that the quantity of CO<sub>2</sub> produced after reaction with (NO)<sub>a</sub> is far greater than when CO

reacts with preoxidized Ni.] That is, we believe that there must be a specific initial reaction between  $(\text{CO})_a$  and  $(\text{NO})_a$ . [The rate or extent of reaction does not depend on the CO pressure.] It is not profitable to speculate about the details of this mechanism since many plausible roots to product formation can be envisaged, and at least two initial  $(\text{CO})_a/(\text{NO})_a$  interactions could be visualized



where (A) is similar to that suggested by Brown and Gonzalez (2). We do not know whether  $\text{CO}_2$  or  $(\text{NCO})_a$  formation occurs first, but by a multitude of paths perhaps now involving gas phase CO, it is conceivable that  $\text{CO}_2$  ( $\text{C}^{16}\text{O}^{18}\text{O}$  if  $\text{C}^{18}\text{O}$  is used),  $(\text{NCO})_a$ ,  $(\text{N}_a)$ , and  $(\text{CO})_a$  ( $2082\text{ cm}^{-1}$ ) could be generated. In view of the overall stoichiometry [scheme (II)] it may be that the second NO above simply dissociates into  $\text{N}_a$  on  $\text{O}_a$  after  $(\text{NCO})_a$  or  $\text{CO}_2(\text{g})$  is formed. That is, the apparent stoichiometry after 3–5 hr of reaction be the result of the normal slow  $(\text{NO})_a$  dissociation (scheme V) plus the  $(\text{NCO})_a$  reaction



Further speculation is unwarranted.

We have not considered the question of mobility of adsorbed species. The dissociation of  $(\text{NO})_a$  [scheme (V)] possibly involves some mobility of NO between Ni sites and in view of the ease with which adsorbed CO (which is responsible for the  $2082\text{ cm}^{-1}$  band) can be desorbed upon evacuation, this species may also be highly mobile. However, the band due to  $(\text{NCO})_a$  does not change even following 24 hr evacuation and it may be that isocyanate is a strongly adsorbed immobile species. Under such circumstances  $(\text{NCO})_a$  could act as a poison in the NO/CO reaction and this could explain why the time rate of growth

curve for the  $(\text{NCO})_a$  band at  $2001\text{ cm}^{-1}$  approximately follows that to be expected for an inhibited first order reaction. [The curves for a second-order reaction and for an inhibited first-order reaction are very similar and we have acknowledged the inaccuracy of our kinetic data.] Thus,  $(\text{NCO})_a$  may simply block potential sites for the  $(\text{NO})_a$  and  $(\text{CO})_a$  interaction. That all  $(\text{NO})_a$  does not completely react with CO at high initial NO coverage may be a reflection of this poisoning effect and again illustrates that adsorbed CO (and not gaseous CO) is necessary for the reaction to proceed. It can also be seen in Fig. 4 that the initial rate of formation of  $(\text{NCO})_a$  is greater for lower initial coverage of NO, which is reasonable since there are more Ni sites initially present for the adsorption of CO.

Finally, although we have used the symbol  $(\text{NCO})_a$  so as not to specify a particular surface stoichiometry, the isocyanate is almost certainly attached to Ni and not to the support, as has been found for the NO–CO reaction over supported Pt(4–6, 14, 15) where the  $\nu(\text{NCO})$  frequency is near  $2300\text{ cm}^{-1}$ , as is the case when isocyanate is attached to various support materials in the absence of a metal catalyst (6, 16). The frequency is generally much lower ( $2150$ – $2220\text{ cm}^{-1}$ ) for transition metal isocyanate complexes (17), as it is in this work, and for the supported ruthenium system (2, 3).

## CONCLUSIONS

In spite of a considerable accumulation of data it is unsatisfying not to be able to be more definitive about a reaction mechanism. Part of the difficulty lies in the uncertainties associated with the kinetic data (localized heating), a problem which would be more severe with other modern infrared spectrometers which emit much higher levels of infrared energy. Further, with the microbalance apparatus we were not able to measure the rate of formation of  $\text{CO}_2$  or of the amount of CO consumed, problems which will have to be overcome in future studies. Finally, in spite of these technical

problems, we still cannot differentiate between the  $(\text{NCO})_a$  formation reaction and the normal  $(\text{NO})_a$  decomposition reaction described in the preceding paper (1) insofar as the ir experiments reveal details of the isocyanate formation reaction but the gravimetric data reflect the total surface composition which may involve many processes.

We conclude with a brief summary of our findings.

(1) Preadsorbed NO on Ni reacts with CO to form  $\text{CO}_2$  and adsorbed isocyanate  $(\text{NCO})_a$  at 325 K.

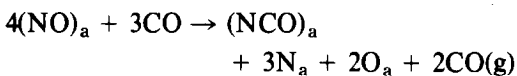
(2) Preadsorbed CO on Ni is displaced by excess NO and no isocyanate is formed, but with a small dose of NO, adsorbed CO reacts to form isocyanate.

(3) When  $\text{C}^{18}\text{O}$  is used, only adsorbed  $\text{NC}^{18}\text{O}$  is formed, but the initially desorbed carbon dioxide is  $\text{C}^{16}\text{O}^{18}\text{O}$ , and no CO exchange occurs.

(4) The isocyanate reaction appears to be initiated by a specific interaction between adsorbed CO and adsorbed NO, but gas phase CO may be involved in subsequent steps.

(5) Different mechanisms may be operative at various stages of the reaction (including normal NO decomposition in the absence of CO) but after about 10 min reaction time there was a correlation (not necessarily 1:1) between NO decomposition and NCO formation.

(6) The apparent reaction stoichiometry after completion of the reaction was



where CO may represent adsorbed and gas phase species.

(7) Surface nitride from the decomposition of NO does not react with CO to form NCO.

(8) The reaction does not go to completion for high initial coverage with  $(\text{NO})_a$ , possibly because the strongly adsorbed NCO acts as a poison or inhibitor by blocking bare Ni sites.

#### ACKNOWLEDGMENT

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