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Study of the Formation of Isocyanate Surface Complexes on Pt/Al_2O_3 Catalysts

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The interaction of NO, CO and NO + CO with 5% Pt/Al_2O_3 was investigated by adsorption, thermal decomposition and infrared spectroscopic measurements in the temperature range 25–400°C. It was found that the extent of adsorption of NO + CO gas mixture was roughly 1.5–2 times larger above 200°C than the sum of the separately adsorbed gases, and that the preadsorbed NO promoted the adsorption of CO. Infrared spectroscopic studies revealed the formation of surface isocyanate at 2267 cm^{-1} under these conditions. The formation of surface isocyanate was followed as functions of time, temperature and partial pressure of reacting gases. It was found that the isocyanate complex at 2267 cm^{-1} occurred at the remarkably low temperature of 150°C, and it formed at maximum intensity at about 320°C. The composition of the reacting gas greatly influenced the intensity of the band; it was also detected in high intensity in the presence of an excess of NO and even on oxidized surfaces. The change in intensity of the band due to isocyanate with time indicated that isocyanate reacted with NO at higher temperatures and in an NO excess.

It is proposed that the dominant route for the formation of surface isocyanate is the reaction between gaseous CO and the adsorbed N formed in the dissociation of adsorbed NO at elevated temperature, but the possibility of molecular surface interaction between NO and CO at lower temperature, as the precursor of isocyanate formation, is also considered.

INTRODUCTION

While investigating the adsorption and surface interaction of NO and CO on different solid surfaces recently, we observed that preadsorbed NO promotes the uptake of CO on many oxide surfaces (*1–3*) and also on Pd/Al_2O_3 catalysts (*4*). This phenomenon was attributed to the formation of surface isocyanate complexes.

Isocyanate intermediates were first identified by means of infrared spectroscopy by Unland (*5–7*) on noble metal catalysts and by London and Bell (*8*) on copper catalysts. Unland suggested that an isocyanate intermediate could be responsible for the formation of NH_3 in the presence of water at 400°C during the NO–CO reaction. Direct evidence for the occurrence of this reaction was provided by our study of the surface reaction of the NCO complex on Pd/Al_2O_3 with water, using a combined infrared and mass spectrometry technique (*4*).

Clarification of the relative importance of the surface isocyanate complex in the NO–CO reaction and in the reactions leading to NH_3 in water-containing NO–CO mixtures requires further research, primarily with regard to the formation and reactivity of NCO intermediates. In the present paper a study is made of the surface interaction of NO with CO, and of the formation of NCO intermediates on Pt/Al_2O_3 catalysts. In the next paper we wish to report on the reactions of surface isocyanate complexes with different gases.

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TABLE 1

Characteristic Data of NO Adsorption[a]

T_0 (°C)	q_0 (μmole/g)	$q_{(90)}$ (μmole/g)
25	0	100
100	7.83	20.8
200	21.33	41.7
300	32.50	36.7
400	19.50	34.1

[a] q_0 = the amount of instantaneous adsorbed NO; $q_{(90)}$ = the amount of gas uptake in 90 min.

EXPERIMENTAL METHODS

Material

The Pt/Al_2O_3 sample was prepared by impregnation of Al_2O_3 (Degussa P 110 C1) in a solution of $H_2PtCl_6 \cdot 6H_2O$ (Reanal). The well-homogenized suspension was dried at 100°C for 16 hr. A self-supporting plate was made from this sample by compressing 30 mg powder under a pressure of 1670 atm. The sample thickness was estimated as 10 mg/cm^2. For adsorption and desorption measurements small fragments of this plate were used. The procedure of pretreating the Pt/Al_2O_3 sample prior to measurements was almost the same as that used by Unland:

i. Heating the sample to 400°C under evacuation.
ii. Treating with 100 Torr O_2 for 30 min at 400°C.
iii. Evacuating at 400°C for 15 min.
iv. Adding H_2 for 30 min at 400°C.
v. Evacuating the sample at 400°C for 15 min.

Nitric oxide (Matheson Co.) was of commercial purity (99%). It was purified by bulb-to-bulb distillation before use. The mass spectrum did not show the presence of NO_2 or N_2O_3. Carbon monoxide was prepared by reacting formic acid with sulfuric acid at 83°C. The other gases used were also of commercial purity.

Methods

The adsorption measurements were conducted in a Sartorius microbalance.

The thermal desorption of the NO was investigated in a catalytic reactor described earlier (*2*). The reactor was combined with the ion source of an MS 10 mass spectrometer. Infrared spectra were recorded with a Specord 71 IR (Zeiss) double beam spectrophotometer with an NaCl monochromator at a scan rate of 1 or 5 wave-numbers/sec. All spectra were recorded as linear absorbance vs frequency. Slits were programmed to obtain constant energy in the reference beam. The instrument was calibrated periodically against a 0.02 mm polystyrene film. Accurate band positions were obtained from spectra recorded with the frequency scale expanded fourfold. The accuracy is judged to be better than ±5 cm^{-1}. Some preliminary experiments were carried out with a Spektromom 2000 (MOM) double beam spectrophotometer with NaCl optics.

A greaseless vacuum infrared cell similar to that described by Karge (*9*) was constructed and used in conjunction with a conventional vacuum and gas handling system capable of evacuation to 10^{-4} Torr.

The formation of isocyanate complexes was studied in the following way: 45 Torr of a gas mixture of NO (5%), CO (10%) and N_2 (85%) was admitted to the pretreated Pt/Al_2O_3 at the reaction temperatures. After a certain time the catalyst sample was moved to the cold part of the cell. Following cooling, the gas pressure was reduced to 10^{-1} Torr. The spectrum was taken at the temperature of the infrared beam, about 50°C.

RESULTS

Adsorption Studies

The primary aim of our adsorption studies was to see whether there is any indication of the formation of a surface complex between NO and CO and of promoted adsorption. The adsorption of the individual components was first investigated.

The adsorption of NO (10 Torr) started with a very fast initial uptake, the extent of which increased with the temperature (Table 1). The subsequent slow chemisorption process was evaluated with the integrated form of the Elovich equation

$$q = (2.3/\alpha) \log (t + t_0) - (2.3/\alpha) \log t_0,$$

where $t_0 = 1/a\alpha$ is an integration constant. Since $t_0 \ll t$, the above equation can be reduced to

$$q = (2.3/\alpha) \log t - (2.3/\alpha) \log t_0.$$

The Elovich plots consist of two linear segments with a distinct break between them (Fig. 1). Some characteristic data for the adsorption of NO are given in Table 1.

It can be seen that the initial adsorption increases rapidly with temperature in the range 25–200°C, but afterwards the increase is very slight. The study of the uptake of NO was extended to higher temperatures, up to 400°C, where a considerable further interaction occurred between NO and Pt surfaces.

No products of the surface reaction between NO and Pt/Al_2O_3 at 25°C were detected by mass spectrometric analysis during the adsorption of NO. At 100°C, however, a very small amount of N_2O was found. At 250°C 8×10^{-3} Torr O_2 and 3×10^{-2} Torr N_2O also appeared in the gas phase at the very beginning of the adsorption, their partial pressures not changing subsequently. At 400°C the decomposition of NO occurred at a measurable rate, yielding N_2O, O_2 and N_2. The extent of decomposition of NO in 30 min was about 15%.

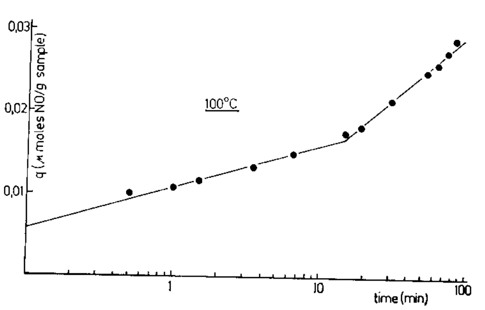


FIG. 1. Elovich plot in integrated form for NO adsorption on 5% Pt/Al_2O_3 sample at 100°C. q = the amount of NO adsorbed. The sample was cleaned at 400°C before the measurement.

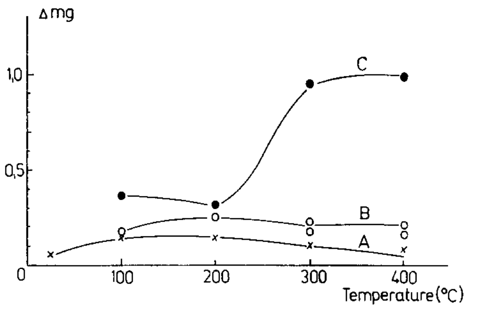


FIG. 2. The amount of gas uptake from gas mixture of CO (20 Torr) + N_2 (10 Torr) (A); NO (10 Torr) + N_2 (20 Torr) (B) and NO (10 Torr) + CO (20 Torr) (C) at different temperatures. The adsorption time was 90 min. The sample was cleaned at 400°C before each adsorption measurement.

The adsorption of CO on the same surfaces was also investigated; it was always less than that of NO.

Measurements were also made on an oxidized surface, which adsorbed much less NO at a very low rate.

The coadsorption of NO + CO was studied at the same temperatures. The amounts of gases adsorbed in 90 min are plotted in Fig. 2. From a comparison of the three curves it appears that the extent of adsorption above 200°C was roughly 1.5–2 times larger than the sum for the separately adsorbed gases. This phenomenon was apparent in the instantaneous adsorption processes, too. Mass spectrometric analysis of the gas phase indicated that above 300°C a reaction between NO and CO set in, yielding CO_2, N_2 and a small amount of N_2O. We note here that the adsorption of these gases themselves above

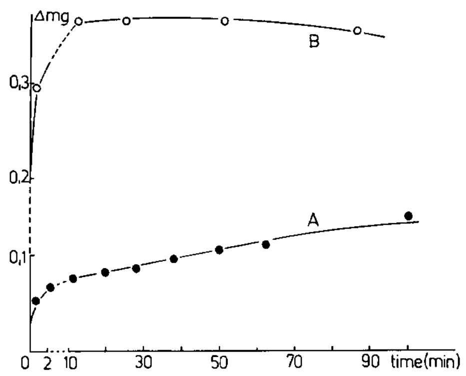


FIG. 3. The effect of preadsorbed NO on the subsequent adsorption of CO at 200°C. (A) Adsorption of CO on clean Pt/Al_2O_3; (B) adsorption of CO on Pt/Al_2O_3 treated in 10 Torr NO at 400°C for 30 min, cooled to 200°C and then evacuated for 5 min. The sample was cleaned at 400°C before each measurement.

300°C is relatively slight, so that the large adsorption observed from an NO + CO mixture cannot be accounted for by the adsorption of these products of the NO–CO reaction. It is important to mention that the gases adsorbed from the NO + CO mixture are held on the surface much more strongly than any of the individual gases studied here.

In subsequent experiments the effect of a preadsorbed gas (NO or CO) was investigated on the adsorption of the other gas. It was found that preadsorbed CO does not promote the adsorption of NO at 200–400°C. No promoted adsorption of CO was observed when NO was adsorbed first and, after a short evacuation, CO was admitted onto the surface at the same temperature. Moreover, CO reacted with the preadsorbed gas at 300–400°C, as indicated by a decrease in the weight of the sample. A strong promotion of CO adsorption was exhibited when NO was adsorbed on the reduced surface at 400°C, the sample was then cooled down in an NO atmosphere to 100–200°C and the gases were pumped off for 1 min before CO adsorption (Fig. 3). When NO was preadsorbed below 300°C no such promoted adsorption was observed.

Thermal Desorption Studies

Some measurements were carried out concerning the thermal desorption of NO from a Pt/Al_2O_3 surface. NO (10 Torr) was adsorbed at 400, 250 and 25°C for 30 min on the fractions of Pt/Al_2O_3 discs (used for infrared studies) pretreated in the usual way. The sample was cooled to room temperature, then evacuated for 10 min and heated at a rate of 10°C/min. The gases desorbed were analyzed by mass spectrometry.

The characteristics of the desorption curves depended sensitively on the adsorption temperature. A very small amount of NO was desorbed after the adsorption at 25°C, in agreement with our finding that the adsorption of NO is mainly reversible at this temperature. The partial pressure of NO increased up to 150°C, afterwards decreased and N_2 and N_2O began to form. After adsorption at 250°C the pressure of NO increased only up to 260°C, and then decreased (Fig. 4). N_2, N_2O and O_2 desorbed from 190, 200 and 300°C, respectively. A sudden increase in the formation of O_2 and N_2 began at 360°C.

When NO was adsorbed at 400°C and the catalyst subsequently cooled, the partial pressure of NO increased linearly with the temperature up to 400°C. The partial pressures of other gases were very small over the whole temperature range. N_2 appeared first at 130°C; its partial pressure slowly increased with the temperature. N_2O and O_2 appeared at 170°C. An increase in the O_2 pressure was observable from 330 to 430°C. The results are shown in Fig. 5.

Some measurements were also performed on the thermal desorption of the separate gases CO, CO_2, N_2O and N_2 adsorbed previously at 400°C. The slow desorption

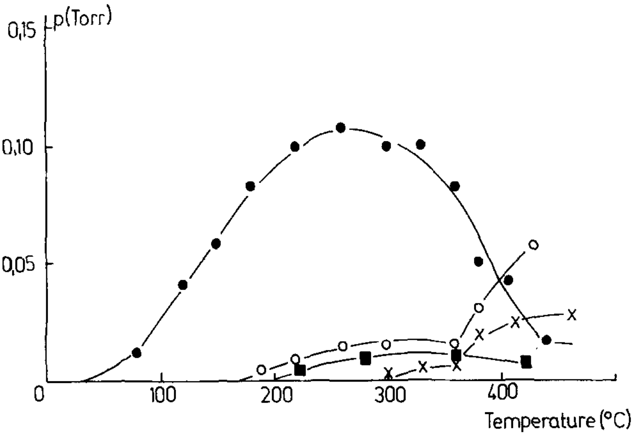


Fig. 4. Thermal desorption of gases after the adsorption of 10 Torr NO at 250°C for 30 min. (●) NO; (○) N_2; (■) N_2O; (X) O_2. The cooling of the sample was performed in NO atmosphere. The gases were pumped off at 25°C for 5 min. Heating rate was 10°C/min. The sample was cleaned at 400°C before the measurement.

of CO started from 100°C; it became faster from 250°C. Above 300°C readsorption of CO was observed. The desorption of CO_2 started from 50°C. No readsorption of CO_2 occurred. In the case of N_2, desorption of gases was not detected up to 400°C.

Infrared Spectroscopic Measurements

Our knowledge concerning the formation of isocyanate complexes on Pt surfaces is very limited. Unland (*5–7*) reported the effects of temperature and the variation of the reaction mixture. He found that:

i. The strong band at 2267 cm^{-1}, which was assigned to covalently bonded isocyanate [–NCO], did not appear until the sample temperature was raised to 300°C. The medium-intensity band at 2148 cm^{-1}, assigned tentatively to anionic isocyanate, [NCO]$^-$, first appeared at 400°C.

ii. Formation of both bands required excess CO.

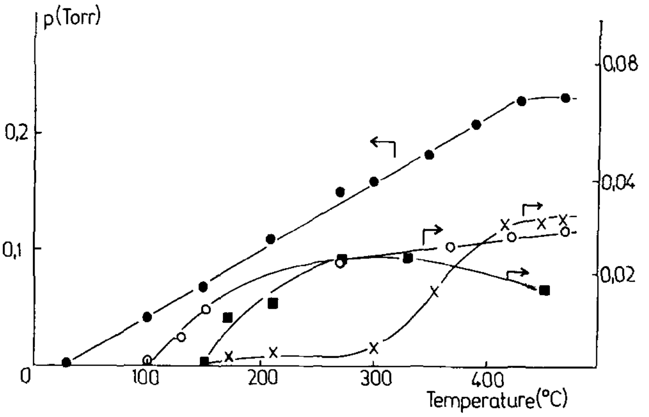


Fig. 5. Thermal desorption of gases after the adsorption of 10 Torr NO at 400°C for 30 min. (●) NO; (○) N_2; (■) N_2O; (X) O_2. The cooling of the sample was performed in NO atmosphere. The gases were pumped off at 25°C for 5 min. Heating rate was 10°C/min. The sample was cleaned at 400°C before the measurement.

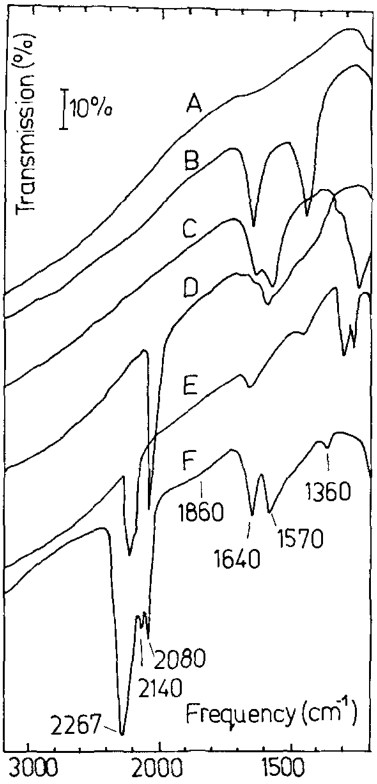


FIG. 6. Infrared spectra observed at room temperature after dosing the 5% Pt/Al_2O_3 sample with 50 Torr of different gases and with 45 Torr of a reacting mixture at 400°C. (A) cleaned sample; (B) CO_2; (C) NO; (D) CO; (E) N_2O (in the presence of gaseous N_2O); (F) 10% CO + 5% NO + 85% N_2. The adsorption time was 30 min. The sample was cleaned at 400°C before each measurement.

The formation of isocyanate complexes was followed in the present study as a function of time, temperature and partial pressure of reacting gases.

Figure 6 shows the spectrum obtained when the sample was treated with a reacting gas mixture at 400°C for 30 min. The infrared spectra of the individual reactants and products of the NO + CO reaction recorded on the same Pt/Al_2O_3 samples and under the same conditions are also shown.

The results obtained are in good agreement with those of Unland. An intense band appeared at 2267 cm^{-1} [–NCO], a medium intense one at 2140 cm^{-1} $[NCO]^-$, and a weaker one at 2080 cm^{-1} [–CO]. It is to be noted that the bands at 2267 and 2140 cm^{-1} appeared with reduced intensity when the gases were pumped off for 1 min before the sample was cooled down from the temperature of adsorption. Other bands in the spectra are the same as found by Unland.

On investigating the effect of the pressure of the reacting gas mixture at 400°C, it appeared that the band at 2267 cm^{-1} was formed with maximum intensity at 45 torr of reacting gases (Fig. 7). A further increase in the pressure had only a slight effect.

Figure 8 shows the effect of temperature on the formation of the bands. The band at 2267 cm^{-1}, [–NCO], appeared at a surprisingly low temperature, even 150°C. After the initial fast process, the intensity of the band increased almost linearly with time. This is illustrated in Fig. 9. Above 300°C the appearance of this band was very fast; at 400°C the intensity of the band showed a maximum with time. Figure 10 shows the effect of the adsorption temperature of reacting gas mixture on the intensity of the band at 2267 cm^{-1}.

The lowest temperature of appearance of the band at 2140 cm^{-1} was 350°C; its intensity increased in time even at 400°C.

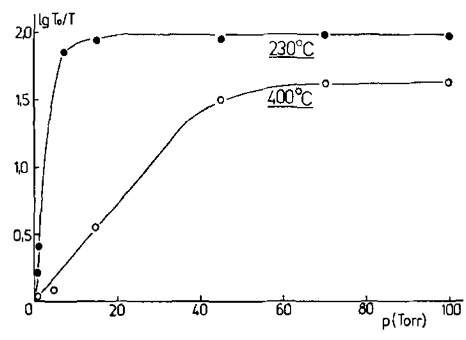


FIG. 7. Intensity of the band at 2267 cm^{-1} observed at room temperature after dosing the 5% Pt/Al_2O_3 sample with different amounts of reacting gas mixture at 230 and 400°C. The sample was cleaned at 400°C before each measurement.

The intensity of the band at 2080 cm^{-1} (linear CO) hardly changed with the temperature above 180°C or with the time of adsorption.

The band at 2267 cm^{-1} also appeared in the infrared spectrum when NO was first adsorbed at 400°C on the reduced surface and, after a short evacuation at 25°C, CO was admitted to the surface. The intensity of the band at 2267 cm^{-1} formed under such conditions depended on the pressure of NO, the temperature of NO adsorption and the subsequent temperature of CO adsorption. The lowest temperature of NO adsorption at which this band appeared was 230°C.

No bands appeared at 2267 and 2140 cm^{-1} at any temperature when the adsorption of the gases was made in the opposite sequence, i.e., when CO was adsorbed first.

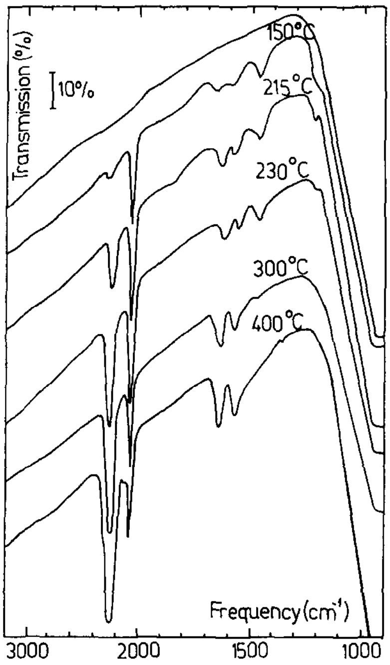


FIG. 8. Infrared spectra observed at room temperature after dosing 5% Pt/Al_2O_3 sample with 45 Torr of a 10% CO, 5% NO and 85% N_2 mixture at different temperatures for 1 min. The sample was cleaned at 400°C before each measurement.

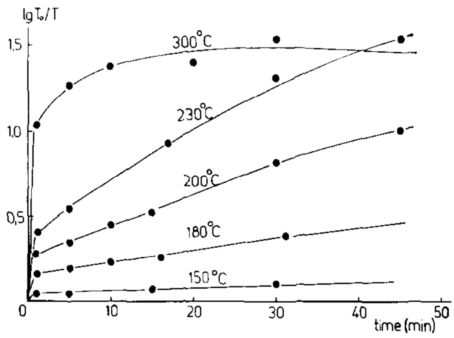


FIG. 9. Change of the intensity of the band at 2267 cm^{-1} with time observed at room temperature after dosing the sample with 45 Torr of a 10% CO, 5% NO and 85% N_2 mixture at different temperatures. The sample was cleaned at 400°C before each measurement.

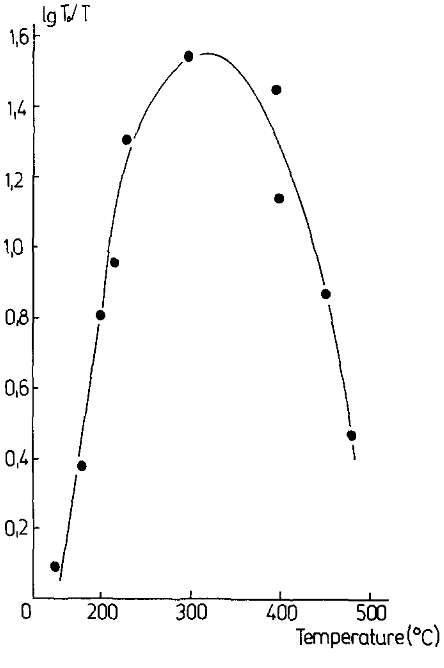


FIG. 10. Dependence of the intensities of the band at 2267 cm^{-1} (observed at room temperature) on the temperature of dosing 5% Pt/Al_2O_3 sample with 45 Torr of a 10% CO, 5% NO and 85% N_2 mixture. The adsorption time was 30 min. The sample was cleaned at 400°C before each measurement.

Detailed measurements were carried out with respect to the effect of the NO:CO ratio on the formation of surface isocyanates. Some results obtained at 230°C

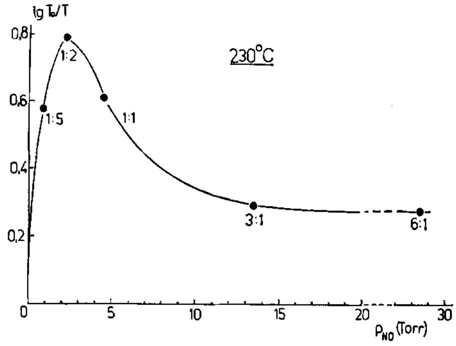


FIG. 11. Dependence of the intensity of the band at 2267 cm^{-1} on the partial pressure of NO in the reacting gas mixture. The 5% Pt/Al_2O_3 sample was dosed with 45 Torr of reacting gas mixture (NO + CO + N_2) at 230°C. The adsorption time was 30 min. The partial pressure of CO was always 5 Torr. The sample was cleaned at 400°C before each measurement.

are shown in Fig. 11. The isocyanate band at 2267 cm^{-1} appeared even in an excess of NO. The maximum intensity of this band was observed at an NO:CO ratio of 1:2. At 400°C, in an excess of NO, the band at 2267 cm^{-1} was significantly less than at 230°C. Whereas, at 230°C the intensity of this band increased with the time of adsorption, at 400°C the highest intensity was measured at the very beginning (1–5 min) of the adsorption, the intensity afterwards decreasing.

The fact that isocyanate was formed in an excess of NO initiated a study of the effect of surface pretreatment.

At 400°C with a 1:2 NO:CO mixture the band at 2267 cm^{-1} formed with almost maximum intensity *on an oxidized surface,* too (Fig. 12). The intensity of the band at 2140 cm^{-1} increased in time. Under these conditions, no band seems to appear at 2080 cm^{-1}. The lowest temperature of formation of the band at 2267 cm^{-1} was 200°C in this case (Fig. 13).

The band at 2267 cm^{-1} appeared even *in the presence of excess NO* (NO:CO, 2:1). At 400°C its intensity increased sharply in the first 3 min, and then markedly decreased (Fig. 12). Whereas, at a 1:2 NO:CO gas composition the intensity of the band at 2267 cm^{-1} increased with the temperature on either reduced or oxidized surfaces up to 320–350°C, in the presence of an NO excess the intensity exhibited a maximum at 230°C (Fig. 13).

DISCUSSION

As regards the adsorption of NO on different surfaces it is a general experience now that the adsorption of NO is much faster and stronger, and occurs to a larger extent, on a reduced than on an oxidized surface (*10*). It is assumed that the reduced centers play a decisive role in activating the NO molecule and promoting its dissociation in the catalytic reduction of NO.

There are many data strongly suggesting that most of the chemisorbed NO is bound via only one end (nitrogen end) of

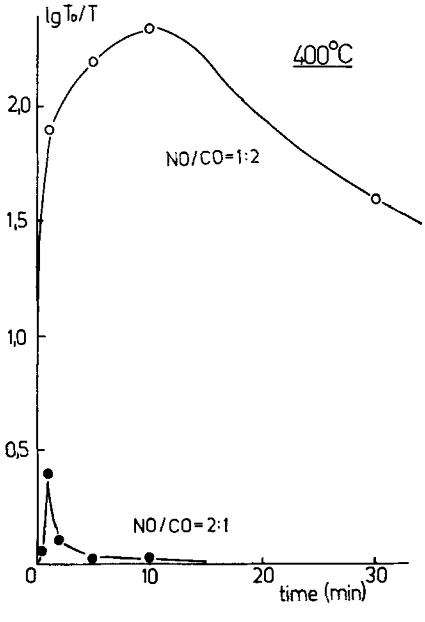


FIG. 12. The change of intensity of the band at 2267 cm^{-1} with time on an *oxidized* surface. The 5% Pt/Al_2O_3 sample was dosed with 45 Torr of a CO, NO, N_2 gas mixture of different composition at 400°C. Spectra were taken at room temperature. The oxidation of the cleaned Pt/Al_2O_3 sample was performed with 100 Torr O_2 at 400°C for 30 min.

the molecule, i.e., that it is linearly bonded to the surface. In accordance with this, at saturation coverage approximately one NO molecule adsorbs per surface metal atom, as was shown by Otto and Shelef (*11*) in the case of platinum black. Recent flash desorption studies (*12*) and Auger and uv photoemission spectroscopy (*13*) have indicated that the adsorption of NO on Pt is nondissociative, and that NO is present in the molecular form. This finding, however, refers mostly to room temperature adsorption. At elevated temperatures, as was observed on W surfaces by Yates and Madey (*14*) using field electron microscopy, the adsorbed molecular NO may undergo a configurational change by an activated process and become bound to two surface sites via both ends of the molecule. This may promote the dissociation of adsorbed NO.

Our present thermal desorption measurements actually showed that the dissociation of adsorbed NO occurs at elevated temperatures, adsorbed N and O being formed. The latter is very strongly bound to the surface platinum, and cannot be completely desorbed merely by heating the sample to 450°C during constant evacuation. The presence of adsorbed O on Pt could be the reason that the thermal desorption and decomposition of surface isocyanate resulted in the formation mainly of N_2 and CO_2 (*15*).

An important result of our adsorption studies is the detection of a surface interaction between NO and CO. The extent of adsorption of a CO + NO mixture was significantly larger than the sum of the adsorptions of the separately adsorbed gases. This became apparent only at higher temperatures (300–400°C) where a reaction occurs between CO and NO. The observed increase in the gas uptake cannot be ascribed to the adsorption of product gases (N_2, CO_2, N_2O), as the adsorption of these gases by themselves above 300°C is relatively slight. Taking into account the results of infrared spectroscopic measurements it is more probable that the enhanced adsorption is the result of the formation of surface complexes.

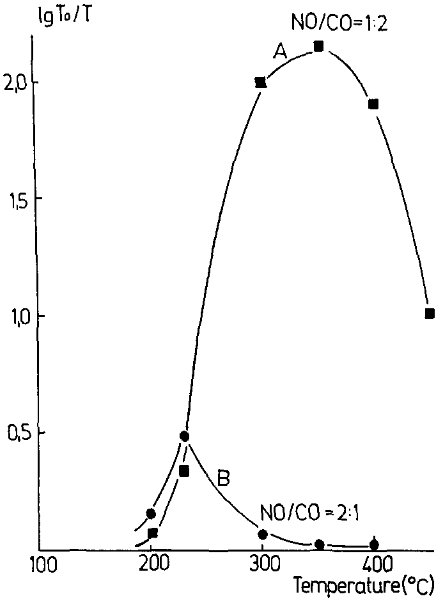


FIG. 13. Dependence of the intensities of the band at 2267 cm^{-1} on the temperature of dosing an *oxidized* 5% Pt/Al_2O_3 sample with 45 Torr of a CO, NO, N_2 gas mixture of different compositions. NO/CO ratio: (A) 1:2; (B) 2:1. Adsorption time 10 min. Spectra were taken at room temperature. The oxidation of the cleaned Pt/Al_2O_3 sample was performed with 100 Torr O_2 at 400°C for 30 min.

One of the reasons that the coadsorption became apparent only at 300–400°C is possibly that the dissociation of adsorbed NO and the formation of adsorbed N are enhanced in this temperature range. Accordingly, the great increase in the gas uptake could be attributed to the reaction between adsorbed N and gaseous CO:

$$\text{Pt–N} + \text{CO} = \text{Pt–NCO}, \qquad (1)$$

i.e., to the formation of a surface isocyanate complex.

The reaction between adsorbed oxygen and carbon monoxide cannot play an important role in the enhanced gas uptake, as surface carbon dioxide and carbonate on Pt are more unstable than surface isocyanate. The important roles of NO dissociation and of adsorbed N in the surface complex formation are supported by the observation that NO adsorbed at 300–400°C promoted the adsorption of CO at lower temperatures. However, this was experienced only when the sample was cooled down to lower temperatures in the presence of gaseous NO. It is very likely that in this case NO was combined with adsorbed N formed in the dissociation process at higher temperatures by the reaction:

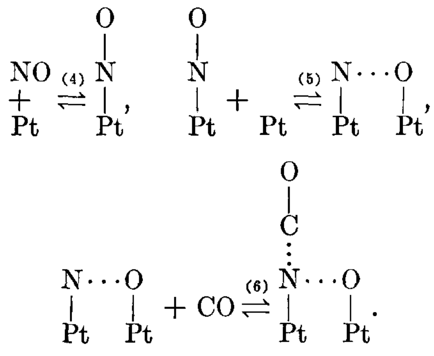
$$\mathrm{Pt{-}N + NO \rightleftharpoons Pt{-}N{-}NO}. \qquad (2)$$

At 200°C, due to the effect of evacuation and to the introduction of CO, NO was replaced by CO:

$$\mathrm{Pt{-}N{-}NO + CO \rightleftharpoons Pt{-}N{-}CO + NO}, \qquad (3)$$

and isocyanate was formed.

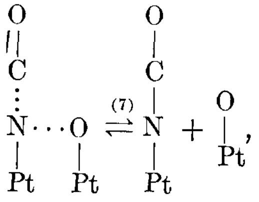
Although infrared spectroscopic measurements suggest the most probable explanation for the significant coadsorption to be the formation of surface isocyanate species, one cannot completely rule out that the intermolecular interaction between NO and CO may also contribute to the enhanced adsorption. This molecular interaction may precede the formation of isocyanate complexes. As the molecular interaction became apparent only at elevated temperature, it can be correlated with the configurational change of the adsorbed NO discussed above in the following way:



$$\begin{array}{c}\mathrm{NO}\\+\\\mathrm{Pt}\end{array} \overset{(4)}{\rightleftharpoons} \begin{array}{c}\mathrm{O}\\|\\\mathrm{N}\\|\\\mathrm{Pt}\end{array}, \qquad \begin{array}{c}\mathrm{O}\\|\\\mathrm{N}\\|\\\mathrm{Pt}\end{array} + \mathrm{Pt} \overset{(5)}{\rightleftharpoons} \begin{array}{cc}\mathrm{N}\cdots & \mathrm{O}\\|&|\\\mathrm{Pt}&\mathrm{Pt}\end{array},$$

$$\begin{array}{cc}\mathrm{N}\cdots & \mathrm{O}\\|&|\\\mathrm{Pt}&\mathrm{Pt}\end{array} + \mathrm{CO} \overset{(6)}{\rightleftharpoons} \begin{array}{cc}\mathrm{O}&\\|&\\\mathrm{C}&\\\vdots&\\\mathrm{N}\cdots & \mathrm{O}\\|&|\\\mathrm{Pt}&\mathrm{Pt}\end{array}.$$

This surface complex may be transformed to surface isocyanate



$$\begin{array}{cc}\mathrm{O}&\\\|&\\\mathrm{C}&\\\vdots&\\\mathrm{N}\cdots & \mathrm{O}\\|&|\\\mathrm{Pt}&\mathrm{Pt}\end{array} \overset{(7)}{\rightleftharpoons} \begin{array}{c}\mathrm{O}\\|\\\mathrm{C}\\|\\\mathrm{N}\\|\\\mathrm{Pt}\end{array} + \begin{array}{c}\mathrm{O}\\|\\\mathrm{Pt}\end{array},$$

or may also be present on the surface simultaneously with the isocyanate species. [It might be argued that the band observed at 2140 $\mathrm{cm^{-1}}$ is due to the former surface species. This is not likely, however, as this band appeared only at higher temperatures and was more resistant to heating than the band at 2267 $\mathrm{cm^{-1}}$ (*15*)].

The band at 2267 $\mathrm{cm^{-1}}$ ascribed to covalently bonded –NCO appeared at relatively low temperature, even 150°C. It must be mentioned that Unland (*5–7*) observed the formation of this band only above 300°C. Control measurements showed that this band cannot be attributed to the chemisorption of any of the reactants (CO, NO) or product gases (N_2O, N_2, CO_2). Of these gases only N_2O produced a band very near to 2267 $\mathrm{cm^{-1}}$. This band, however, was very weak and disappeared completely after evacuation for 10 min at 25°C. Its stability and position did not change even in the presence of excess CO; *this also shows that the band* at 2267 $\mathrm{cm^{-1}}$ cannot be produced by adsorbing an $N_2O + CO$ mixture on a reduced Pt/Al_2O_3 surface. It should be noted that Egerton and Sheppard (*16*) found an infrared adsorption band of considerable intensity near 2230 $\mathrm{cm^{-1}}$ from N_2 adsorbed on Pt/SiO_2. This band, however, is even weaker than that due to adsorbed N_2O; it was completely removed by pumping for only 6 min at −140°C.

As the dissociation of NO at low temperatures is a slow process on platinum, it can be assumed that the presence of CO promotes the rupture of the N–O bond by the formation of a surface complex between NO and CO (reactions 4–6), which will be converted to surface isocyanate.

However, a recent theoretical work which appeared just before the completion of the writing of this paper confirms that the dominant route of formation of isocyanate complexes is probably the reaction between adsorbed N and gaseous carbon monoxide (*17*). Using the crystal field surface orbital-bond energy bond order (CFSO–BEBO) model, a value of 12 kcal/mole was obtained for the dissociation of NO on Pt (111) surfaces. As the calculated activation energies for the NO + CO reaction according to other mechanisms are much higher [37 kcal/mole (Rideal–Eley mechanism) and 40 kcal/mole (Langmuir–Hinshelwood mechanism)], it was proposed that the first step of the NO + CO reaction is the dissociation of the NO molecule on the Pt (111) surface.

Unland reported that when NO was in excess over CO the 2267 and 2148 cm^{-1} bands did not appear at 400°C. On our sample, however, we were able to detect isocyanate complexes in well-measurable intensities in an excess of NO and even on oxidized samples (Figs. 11–13). In our opinion this is not surprising, as the reduction of oxidized surfaces by CO is obviously a faster process than the reoxidation step by NO. The probable reason that Unland could not find bands due to isocyanate complexes in an excess of NO is that he used a longer reaction time before taking a spectrum, during which the excess NO oxidized the surface NCO species formed. This explanation seems to be supported by the change of the intensity of the NCO band in time at 400°C (Fig. 12) and by the observation that the reaction of isocyanates with NO at 400°C is very fast (*15*).

In contrast, at lower temperatures, e.g., 230°C, in the presence of an NO excess the intensity of the –NCO band increased with time; this is in agreement with our finding that the reaction of isocyanate complexes with NO at 230°C is very slow (*15*).

It should be mentioned that in a study of the competitive coadsorption of CO and NO on Pt (111) and Pt (100) surfaces Lambert and Comrie (*12*) found no evidence for the formation of adsorbed isocyanate species. This indicates that the adsorption and interaction of reacting gases on a highly dispersed catalyst can differ in many respects from those which occur on the surface of single crystals.

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