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An Infrared Study of Nitric Oxide Adsorbed on Rhodium–Alumina Catalyst

HIROMICHI ARAI AND HIROO TOMINAGA

Engineering Research Institute, Faculty of Engineering, University of Tokyo,
Hongo, Bunkyo-ku, Tokyo, 113, Japan

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Infrared spectroscopic study was made of NO and CO and their mixture adsorbed on rhodium metals supported on γ-alumina. When NO is adsorbed on rhodium, two surface species are identified: cationic one (M–NO$^+$) produced by donation of an electron antibonding ($\pi_{2pz}{}^*$) of NO to d orbital of the metal to strengthen the NO bond, and anionic one (M–NO$^-$) produced by transfer of a d electron of the metal to an antibonding $\pi_{2pz}{}^*$ orbital of NO to weaken the NO bond. *Cis*-type coordination of NO and CO to one rhodium atom was found. When NO is first adsorbed and CO is introduced to react with the adsorbed NO, M–NCO (isocyanate) is formed which is stable up to 400°C under vacuum.

INTRODUCTION

Increasing social demands to clean polluted air environments have stimulated the research and development of technologies for the abatement of nitrogen oxides in fossil fuel combustion and their effluent. Research is extensively being carried out on the related subjects of catalysis, including some spectroscopic studies on nitrogen oxide adsorbed on some specific solid catalysts.

A first attempt was made by Terenin and Roev (*1*) to determine by use of infrared spectroscopy the structure of NO adsorbed on Fe, Ni, Cr—their metals, sulfates, and oxides. They have assigned the vibration spectra observed to a wide variety of the valence states of the NO molecule when it interacts with different kinds of adsorption site on the surface.

Subsequent applications of the spectroscopic method have been made to NO on silica-supported Pt and Pd by Dunkel and Hobert (*2*), and to NO on Ni and Fe by Blyholder and Allen (*3*). The latter study indicated that on both Ni and Fe some of NO dissociated to form a surface oxide, and that on neither metal did the admission of H_2 or O_2 to the adsorbed NO interact to produce any new surface species at 25°C.

More recently, an infrared study was made by Peri (*4*) of NO and CO adsorbed on chromia/γ-alumina to elucidate the nature and distribution of exposed Cr ions. Preadsorption of NH_3 and simultaneous adsorption of CO and NO were also explored to show that the valence state of Cr ion plays a key role in the catalysis. In the interaction of NO and CO on Pt/Al_2O_3, Unland (*5*) observed the formation of intermediates which gave the strong bands at 2267 and 2148 cm^{-1}. These were respectively assigned to Pt–NCO and (NCO)$^-$ anion, and were supposed to provide a new mechanistic pathway of NH_3 formation in the catalysis of automobile exhaust treatment. The kinetics of the reduction of NO by CO over a silica-supported Cu oxide was studied by London and Bell (*6*). The mechanism was elucidated from the infrared spectroscopic observations of CO, CO_2, NO, NO_2, and N_2O (*7*) together with that of the reaction intermediates including Cu^+NCO^-, 2200 cm^{-1}. Their presence suggested the dissociation of NO upon adsorption giving rise to N_2O which was presumed to be the precursor of N_2.

The present work is a part of the authors' investigation into the catalytic reactions of NO, and deals especially with the infrared spectroscopic observations on not only the adsorptions, but also the reactions of NO, CO, and O_2 over the alumina-supported Rh catalyst.

It is hoped that this study will afford additional insights into the complex reactions carried out on the catalyst surface.

EXPERIMENTAL METHODS

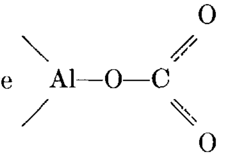
The Rh/Al_2O_3 catalysts were prepared by impregnation followed by reduction. In more detail, alumina powder, obtained by hydrolysis of aluminum isopropoxide, was slurried with an aqueous solution of rhodium trichloride. After being stirred vigorously to assure a good dispersion, it was evaporated to dryness and calcined at 500°C for 5 hr in air. On the calcination the chloride was decomposed to leave a brown powder of Rh/Al_2O_3. This was reduced at 450°C for 4 hr in hydrogen stream. For the inspection in an infrared cell, the catalyst powder was pressed into a disc which weighed 70 mg and was 20 mm in diameter and 0.1 mm in thickness.

The catalyst disc was placed in the cell, essentially similar to that used by Peri and Hannan (*8*). Before the experiment, *in situ* cleaning of the catalyst surface was performed at 400°C in the following way: (a) evacuation to 10^{-6} Torr, (b) oxidation in the presence of oxygen of 50 Torr for 30 min, (c) evacuation to 10^{-6} Torr for 10 min, (d) reduction in hydrogen of 50 Torr for 10 min, and (e) evacuation to 10^{-6} Torr for 10 min. Processing of the catalyst at high temperatures, including the above-mentioned cleaning, was accomplished in the heating section located in the upper half of the cell, and the catalyst was moved down into an infrared beam. The infrared spectra were recorded at 25°C on IRA-1 spectrometer, Japan Spectroscopic Co., equipped with an ordinate scale expansion attachment.

Nitric oxide hydrogen, oxygen, and carbon monoxide were supplied by Japan Unique Gas Co., and used without further purification.

RESULTS

I. NO and CO Adsorption on Alumina

Some blank experiments were made of NO and CO adsorption on alumina—the carrier of the catalysts. Nitric oxide was found to react with alumina surface when adsorbed at 25°C to give weak absorption bands at 1635, 1455, and 1230 cm^{-1}, which were ascribed to the presence of $\underset{/}{\overset{\diagdown}{\text{Al}}}\text{—}NO_2$ (*9*). On the other hand, carbon monoxide reacted with alumina at the temperatures above 200°C to give the absorption bands at 1590 and 1395 cm^{-1}, which suggested the carbonate structure  $\underset{/}{\overset{\diagdown}{\text{Al}}}\text{—O—C}\genfrac{}{}{0pt}{}{\nearrow\!\!\!\!/ \;O}{\searrow\!\!\!\!\backslash\; O}$ (*9*).

After the adsorption of CO on alumina at 300°C, the gas phase was pumped off at 25°C, and NO was introduced into the cell. When the alumina was heated up to 300°C, $\underset{/}{\overset{\diagdown}{\text{Al}}}\text{—}NO_2$ appeared while $\underset{/}{\overset{\diagdown}{\text{Al}}}\text{—}CO_3$ disappeared. During the reverse procedure, namely, after NO adsorbed and pumped off at 25°C, CO introduction gave rise to formation of $\underset{/}{\overset{\diagdown}{\text{Al}}}\text{—}CO_3$ at 25°C. This means that alumina is easily oxidized by NO, and the oxidized alumina gives $\underset{/}{\overset{\diagdown}{\text{Al}}}\text{—}CO_3$ at room temperature when CO is admitted.

II. NO Adsorption on Rh/Al_2O_3 Catalyst and Reaction with O_2

Figure 1 shows the spectra of NO molecules adsorbed on Rh/Al_2O_3 catalyst. At 25°C two intense absorption bands were observed at 1830 and 1740 cm^{-1}, together with a feeble one at 1910 cm^{-1}. The weak absorptions due to the adsorption of NO on the support, Al_2O_3 were intangible possibly because of overlaps with the strong absorption at 1740 cm^{-1}. In accordance with the rise in temperature of NO adsorption, the former two decreased (at 200°C) and almost disappeared (at 400°C) while the latter one increased. It is thus suggested that there are three kinds of NO species which differ from one another in thermal stability.

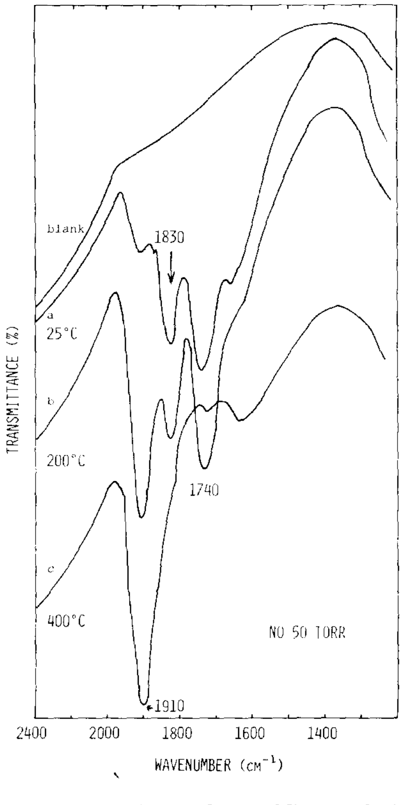


FIG. 1. Spectra observed at 25°C after dosing the $Rh-Al_2O_3$ catalyst with 50 Torr of NO at various temperatures for 15 min: (a) 25°C, (b) 200°C, (c) 400°C.

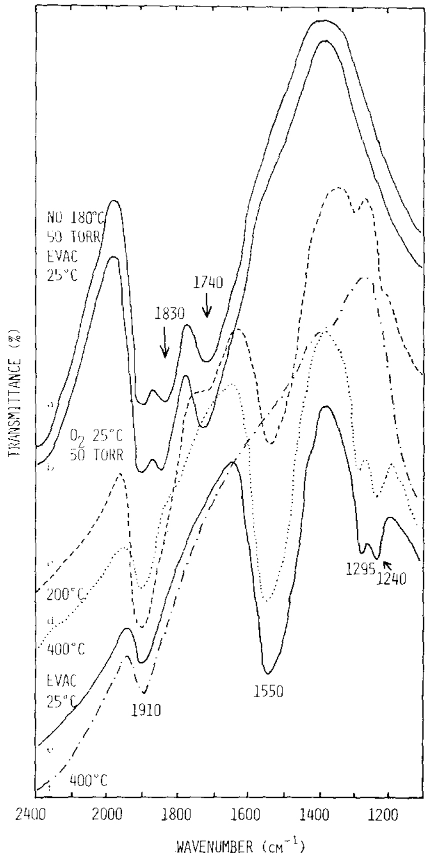


FIG. 2. The effect of oxygen on the spectrum of NO chemisorbed on Rh catalyst (50 Torr of NO at 180°C). (a) Evacuation at 25°C prior to adding O_2. The remaining spectra after adding O_2 (50 Torr) at 25°C (b), heating at 200°C (c), 400°C (d), after evacuation at 25°C (e), 400°C (f).

After a complete chemisorption of NO on Rh/Al_2O_3 at 180°C, the cell was evacuated at 25°C, and filled with O_2 to 50 Torr. Then the cell was heated up to 400°C and changes in the absorption spectra were recorded as shown in Fig. 2. Although no appreciable change was observed at 25°C, when heated to 200°C, the bands at 1830 and 1740 cm^{-1} disappeared and the band at 1910 cm^{-1} decreased a little. In addition, there, respectively, appeared three new bands at 1550, 1295, and 1240 cm^{-1}. With the rise in temperature up to 400°C, these three absorption bands increased, but the bands at 1910 cm^{-1} decreased. Evacuation at 400°C

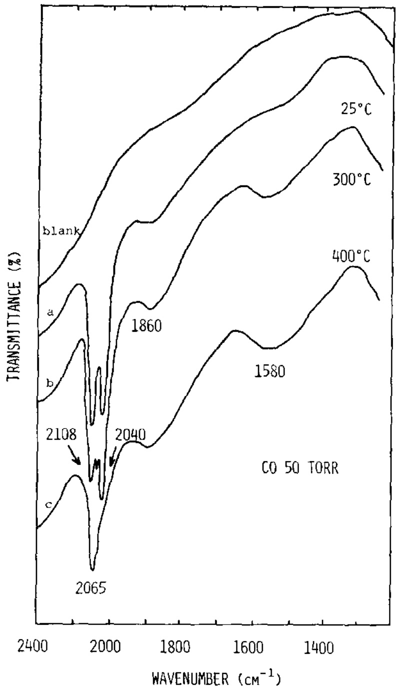


FIG. 3. Spectra of adsorbed CO on Rh catalyst: 50 Torr CO at 25°C (a), 300°C (b), and 400°C (c).

gave rise to the disappearance of all of the bands except 1910 cm^{-1}. It is noteworthy that the spectra obtained by this evacuation procedure are similar to those of Fig. 1c which were obtained by introduction of NO over the NO chemisorbed catalyst.

III. CO Adsorption on Rh/Al$_2$O$_3$

Results for CO adsorption on Rh catalyst at several temperature are shown in Fig. 3. The feature of the spectrum at 25°C is the presence of a broad band at 1860 cm^{-1} and two strong twin bands at 2108 and 2040 cm^{-1} with nearly equal intensities. A new band at 2065 cm^{-1} appeared between twin peaks when NO was adsorbed at 300°C. On adsorption at 400°C, the twin bands disappeared but the bands at 2065 and 1860 cm^{-1} did not disappear.

IV. Introduction of CO on NO Adsorbed Rh/Al$_2$O$_3$

After NO (50 Torr) was adsorbed on Rh/Al$_2$O$_3$ at 300°C and evacuated at the same temperature, CO (50 Torr) was admitted into the cell containing the catalyst. As shown in Fig. 4, the large band at 1910 cm^{-1} decreased in its intensity, and new bands appeared at 2101, 1755, 1580, and 1385 cm^{-1}. There was no detectable change when the cell was heated to 200°C except the appearance of small absorption band at 2040 cm^{-1}. During the heating, there was no shift in frequency of these bands. With further heating to 300°C, the bands at 1910 and 1755 cm^{-1} decreased while the twin sharp bands at 2108 and 2040 cm^{-1} increased. The most remarkable change was the appearance of a new band at 2235 cm^{-1}, which disappeared when water was introduced at 25°C. No change in the intensity of this band was observed by evacuation at 400°C.

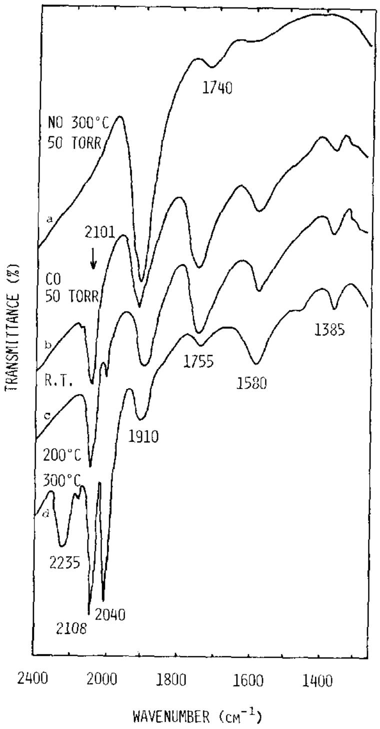


FIG. 4. The effect of CO on the spectrum of NO chemisorbed on Rh cata'yst (50 Torr of NO at 300°C). (a) Evacuation at 25°C prior to adding CO. The remaining spectra after adding CO at 25°C (b), heating at 200°C (c), and 300°C (d).

V. *Introduction of NO on CO Adsorbed Rh/Al_2O_3*

CO was first chemisorbed on rhodium catalyst at 50 Torr at 300°C, and the spectrum was recorded. Next, the cell was filled with NO gas at 50 Torr, and then heated. The changes in spectra by heating temperature are shown in Fig. 5. CO adsorption gave four bands at 2108, 2040, 1860, and 1580 cm^{-1} and the 2065 cm^{-1} band appeared as a shoulder on the strong band at 2040 cm^{-1}. By introduction of NO at 25°C, the 2065 and 1860 cm^{-1} bands disappeared, but there was no change in intensity of the twin bands at 2108 and 2040 cm^{-1}. The new bands at 1830, 1755 and 1660 cm^{-1} appeared at the same time.

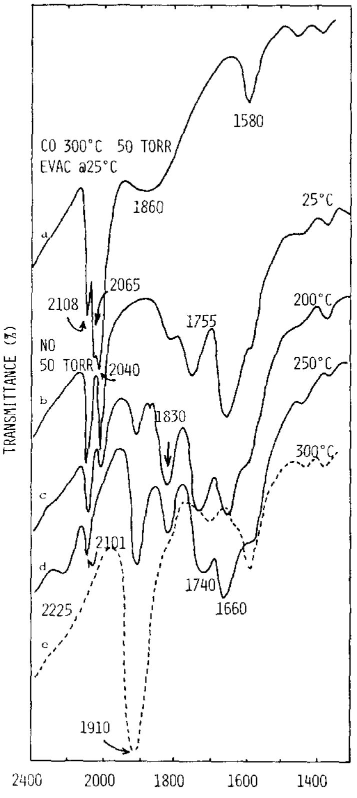


FIG. 5. The effect of NO on the spectrum of CO chemisorbed on Rh catalyst (50 Torr of CO at 300°C). (a) Evacuation at 25°C prior to adding CO. The remaining spectra after adding NO at 25°C (b), heating at 200°C (c), 250°C (d), and 300°C (e).

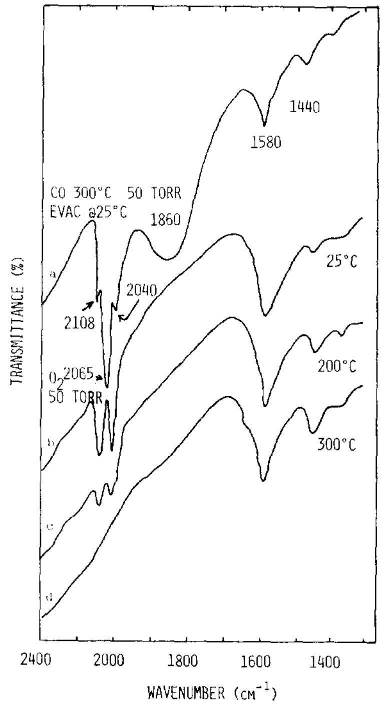


FIG. 6. The effect of O_2 on the spectrum of CO chemisorbed on Rh catalyst (50 Torr of CO at 250°C). (a) Evacuation at 25°C prior to adding CO. The remaining spectra after adding O_2 at 25°C (b), heating at 200°C (c), and 300°C (d).

On heating in the presence of NO at 200°C, the 1910 cm^{-1} band increased and the new bands at 2101, 1910 and 1755 cm^{-1} appeared. The 2040 cm^{-1} band decreased, the 2108 and 2101 cm^{-1} bands overlapped and the weak 2108 cm^{-1} band could not be detected. With further heating in NO at 250°C, the band at 2040 cm^{-1} disappeared completely and the band at 1910 cm^{-1} increased strongly. At 300°C the band at 1910 cm^{-1} increased in its intensity.

As shown in Fig. 6, CO was firstly adsorbed on rhodium surface at 50 Torr at 25°C and evacuated at 25°C. Then the cell was filled with O_2 at 50 Torr for 15 min at 25°C, another spectrum was recorded, and then the cell was heated to 200 and 300°C. On contact with O_2 at 25°C, the bands at 2065 and 1860 cm^{-1} disappeared rapidly, but there was no change in the intensity of the bands at 2108 and 2040 cm^{-1}. The

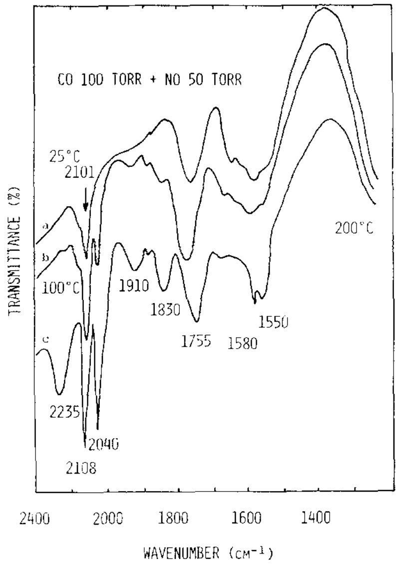


FIG. 7. Spectra observed at 25°C after dosing the Rh/Al_2O_3 catalyst with a mixture of CO (100 Torr) and NO (50 Torr) for 15 min at 25°C (a), 100°C (b), and 200°C (c).

bands at 1580 and 1440 cm^{-1} somewhat increased but no more at the higher temperatures. On heating, the bands at 2065 and 2040 cm^{-1} decreased with increasing temperature and disappeared completely at 300°C.

VI. Mixture of NO and CO Adsorbed on Rh Catalyst

Using a mixed gas consisting of CO (100 Torr) and NO (50 Torr), a series of ir spectra were observed as a function of temperature, giving some insights on the catalytic reactions over Rh/Al_2O_3 as shown in Fig. 7. The strong bands at 2101 and 1755 cm^{-1} and a broad band in the vicinity of 1580 cm^{-1} appeared at 25°C. New weak bands at 2040, 1910, and 1830 cm^{-1} appeared at 100°C. At 200°C the band at 2235 cm^{-1} appeared. The bands at 2108, 2040, 1910, and 1820 cm^{-1} increased with increasing temperature. Although the band at 2235 cm^{-1} did not disappear by evacuation at 400°C, it disappeared by addition of H_2O (5 Torr) at 25°C. This spectrum seemed identical to that of Fig. 4d. It should be noted that the band at 2235 cm^{-1} did not appear under the same conditions except for the composition of gas which was lean in CO, namely CO (50 Torr) and NO (100 Torr).

DISCUSSION

Most of the ir bands observed in this study can be assigned to the adsorbed species shown in Table 1.

Adsorbed NO

This simple diatomic molecule shows a remarkable sensitivity in vibration frequency to the type of its bonding to different adsorption sites on the surface of catalysts. NO can easily be oxidized into a nitrosonium ion NO^+ by donation of one electron from its antibonding orbital to the metal, and a coordination bond of $M\text{-}NO^+$ is formed by an additional electron pair donation from NO^+. The NO^+ has a considerably higher vibration frequency than that of NO. When ν_{NO} is much lower than that of gaseous NO molecule (1876 cm^{-1}), the nitric oxide is assigned to the structure of NO^-. The frequency ν_{NO} is dependent on the extent of donation of an electron from $\pi_{NO}{}^*$ to the metal *d* orbital (*10*).

The band at 1910 cm^{-1}, appearing in the spectra shown in Figs. 1 and 2, was shifted upscale from that of gaseous NO. This absorption band could not be found when the catalyst was reduced by hydrogen prior to NO adsorption. The intensity of this band increased in the presence of oxygen or nitric oxide in proportion to the temperature. As shown in Figs. 1 and 2, four different kinds of adsorbed NO appeared, and, in the presence of oxygen at elevated temperature, the band at 1910 cm^{-1} increased and the other three bands decreased and finally disappeared. Figures 1 and 2 show that extended contact of O_2 with the catalyst surface led to the growth

TABLE 1

The Changes of Relative Intensities of Infrared Bands Due to Adsorption and Reaction of NO, CO, and O_2 on Rh-Al_2O_3 Catalysts[a]

Frequency (cm^{-1}):		2235	2225	2108	2101	2065	2040	1910	1860	1830	1755	1740	1660	1580	1550	1440	1385	1240 1295
Adsorbed species:		M-NCO	N_2O	$\mathrm{M}{<}^{\mathrm{CO}}_{\mathrm{CO}}$ asym.	$\mathrm{M}{<}^{\mathrm{NO}}_{\mathrm{CO}}$ ν_{CO}	M-CO	$\mathrm{M}{<}^{\mathrm{CO}}_{\mathrm{CO}}$ sym.	M-NO^+	$^{\mathrm{M}}_{\mathrm{M}}{>}\mathrm{CO}$	M-NO	$\mathrm{M}{<}^{\mathrm{NO}}_{\mathrm{CO}}$ ν_{NO}	M-NO^-	M-NO^-	CO_3^{2-}	NO_2^- or NO_3^-	CO_3^{2-}	CO_3^{2-}	NO_2^- or NO_3^-
Treatment	(°C)																	
1 NO[b] ad. @	25 (a)							w		s		vs	sh					
Heat to	200 (b)							m		m		vs	sh					
	400 (c)							vs		d		vw	w					
2 NO[b] ad. @	180																	
and evac. @	25 (a)							s		s		s						
O_2[b] intro. @	25 (b)							s		s		s						
Heat to	200 (c)							vs		d		vw			s			w
	400 (d)							m				d			vs			vs
Evac. @	25 (e)							m							vs			vs
Heat to	400 (f)							m							d			d
3 CO[b] ad. @	25 (a)			s		ov	s		m									
Heat to	300 (b)			s		m	s		m					w				
	400 (c)			d		s	d		m					m				
4 NO[b] ad. @	300																	
and evac. @	25 (a)							vs				w						
CO[b] intro. @	25 (b)				m			m			m	d		m			w	
Heat to	200 (c)			ov	m		vw	m			m			m			w	
	300 (d)	m		s	ov		s	w			vw			m			w	
5 CO[b] ad. @	300																	
and evac. @	25 (a)			s		m	s		m					m		w		
NO[b] intro. @	25 (b)			s	ov	d	s		d	w	m		s	sh		w		
Heat to	200 (c)			ov	m		w	w		m	ov	m	s	sh		w		
	250 (d)		w	ov	d		w	m		w	ov	m	s	sh				
	300 (e)		d	d	d		d	vs		sh	d	w	d	m		w		
6 CO[b] ad. @	300																	
and evac. @	25 (a)			m		s	m		m					m		w		
O_2[b] intro. @	25 (b)			m		d	m		d					s		w		
Heat to	200 (c)			w			w							s		m		
	300 (d)			d			d							s		m		
7 (CO + NO)[c] @	25 (a)				s						s		w	m	m			
Heat to	100 (b)			sh	s		w	vw		w	s		w	m	m			
	200 (c)	s		s	ov		s	m		m	s			m	m			

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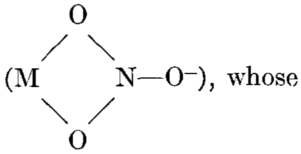
[a] Abbreviations vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, ov: overlap, d: disappear, completely.
[b] 50 Torr.
[c] CO: 100 Torr; NO: 50 Torr.

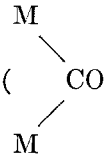
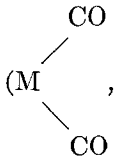
of the band at 1910 cm^{-1} at the expense of the bands at 1830 and 1740 cm^{-1}. This suggests that the adsorbed species, which produces these two bands, changed into that of 1910 cm^{-1}, the most stable one under evacuation at elevated temperature. The X-ray study of nitrosyl compounds showed that both M–N and N–O bonds of M–NO$^+$ were stronger than those of M–NO$^-$, respectively. From this it is concluded that the band at 1910 cm^{-1} is assigned to M–NO$^+$.

The behavior of another band in the spectrum of adsorbed NO, namely at 1740 cm^{-1}, makes a sharp contrast to that of the band at 1910 cm^{-1} in the presence of oxygen or nitric oxide, and in pretreatment of the catalyst by hydrogen. The band at 1740 cm^{-1} is very strong on the catalyst pretreated by hydrogen at 400°C, yet decreases rapidly in the presence of oxygen at 180°C. The band at 1830 cm^{-1}, shifted slightly from that of gaseous NO, disappeared easily by thermal desorption. In this case, the N–O bond is not significantly perturbed by adsorption and thus the M–N bond is weak. The band at 1660 cm^{-1} was very weak and its behavior to the change in various treatment was similar to that of the band at 1740 cm^{-1}.

These observations are summarized in Table 2 in comparison with the information on metal NO complexes found in literature (*11*). Nitric oxide is particularly interesting as a probe molecule because of the possible variety of adsorbed forms, ranging from NO$^+$ to NO$^-$, readily distinguishable spectroscopically. This may provide information about the reduction–oxidation state of catalyst surfaces.

As shown in Fig. 2, the bands in the region below 1600 cm^{-1} are due to an interaction of adsorbed NO with oxygen on the catalyst that forms the bidentate nitrato structure  $\left(\mathrm{M}\begin{array}{c}\mathrm{O}\\ \diagup\ \diagdown\\ \\ \diagdown\ \diagup\\ \mathrm{O}\end{array}\mathrm{N{-}O^-}\right)$, whose structure is identified in this laboratory in the spectrum of adsorbed NO_2 on the Rh/Al_2O_3 catalyst.

Adsorbed CO

A number of studies have been made of the infrared spectrum of carbon monoxide on metals or oxides. By analogy with the known metal carbonyl complexes, Eischens and Pliskin (*17*) interpreted the spectra of carbon monoxide adsorbed on Ni or Pd in terms of two types of structures: a linear CO occupying a single atom (2050 cm^{-1}) and a bridged CO between two adjacent metal atoms (1900 cm^{-1}). Yang and Garland (*12*) have studied in detail the case of CO adsorbed on rhodium, and proposed three types of surface species: a single linear (M–CO, 2040 ~ 2060 cm^{-1}), a bridged CO ( $\begin{array}{l}\mathrm{M}\\ \ \diagdown\\ \quad\mathrm{CO}\\ \ \diagup\\ \mathrm{M}\end{array}$, 1905 ~ 1925 cm^{-1}) and two CO's bonded to a single metal atom  $\left(\mathrm{M}\begin{array}{l}\ \ \mathrm{CO}\\ \diagup\\ \\ \diagdown\\ \ \ \mathrm{CO}\end{array}\right.$, symmetrical and asymmetrical modes, 2027 ~ 2040 cm^{-1}, 2055 ~ 2108 cm^{-1}) by analogy with rhodium metal carbonyls (*13*).

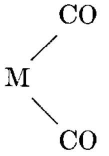
In the present study, the behavior of the twin bands at 2108 and 2040 cm^{-1} is always the same towards various treatments and is, respectively, assigned to asymmetric and symmetric modes for *cis* form of  $\mathrm{M}\begin{array}{l}\ \ \mathrm{CO}\\ \diagup\\ \\ \diagdown\\ \ \ \mathrm{CO}\end{array}$ (twin type). The band at 2065 cm^{-1} can be attributed to a linear CO, and the band at 1800 cm^{-1} is assigned to a bridged CO. On desorption of CO from rhodium catalyst at elevated temperature, the bands at 2108 and 2040 cm^{-1} dis-

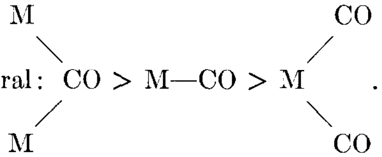
TABLE 2

The Coordination States of Metal NO Complexes and NO Adsorbed on Rh–Al_2O_3 Catalysts[a]

	NO^+	NO^-
A. Rh–Al_2O_3 Catalyst		
Stretching frequency of adsorbed species (cm^{-1})	1910	1755–1655
After the introduction of		
O_2	Increase	Decrease
CO or H_2	Decrease	Increase
B. Metal NO Complexes		
Structure	Linear	Bent
(M–N–O angle)	180°	120°
Stretching frequency of NO bond (cm^{-1})	Higher (1900–1700)	Lower (1720–1520)
Orbital type	*sp*	sp^2
Electronic structure	M–NO^+ The anti-bonding electron (π_{2p}^*) of NO transfers to the *d*-orbital of metal	M–NO^- The *d* electron of metal transfers to the orbital (π_{2p}^*) of NO
N–O bond	Strong	Weak
Bond distance		
N–O (Å)	1.10–1.20	1.15–1.25
M–N (Å)	1.60–1.80	1.80–2.00

[a] The electronic structure of NO molecule is $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{sp_0})^2(\sigma_{sp})^2(\pi_{2p_{xy}})^4(\sigma_{sp_N})^2(\pi_{2p_{xy}}^*)^1$. The stretching vibration of NO bond gives ir spectrum at 1876 cm^{-1}.

appeared most easily, followed by the band at 2065 cm^{-1}, and the band at 1860 cm^{-1} very slowly. The strength of metal–carbon bond order is thus in the order which seems natural:



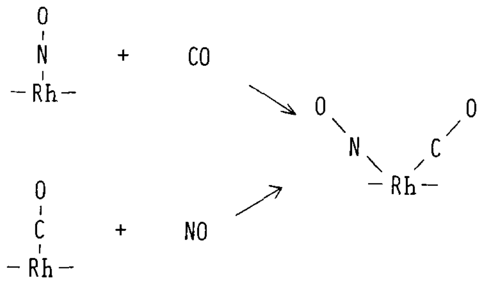
$$\begin{array}{c} M \\ \quad\diagdown \\ \quad\diagup \\ M \end{array} CO > M\text{—}CO > M \begin{array}{c} CO \\ \diagup\quad \\ \diagdown\quad \\ CO \end{array}.$$

There is no shift in the 2108 and 2040 cm^{-1} bands during oxidation. The twin type CO reacts with oxygen only at elevated temperature. On the other hand, the linear CO and the bridged CO react easily with oxygen at 25°C, probably because a coordination site for adsorption of O_2 remains at the metal atom. The two bands at 1580 and 1440 cm^{-1} are attributed to carbonate species.

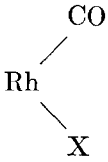
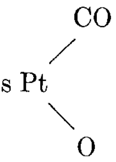
Reactions of NO and CO on Rh/Al_2O_3 Catalyst

Figure 4 shows the results of adding 50 Torr CO to the rhodium catalyst which had been exposed to NO at 300°C and then evacuated for 5 min at 25°C. The addition of CO gave the bands at 2101, 1755, 1580, and 1385 cm^{-1}, and lowered the intensity of 1910 cm^{-1} band. The bands at 1580 and 1385 cm^{-1} were assigned to carbonate species. Comparison with spectra obtained in the absence of preadsorbed NO reveals that carbonate species appeared at 25°C This indicates that CO reacted with oxygen of NO to form carbonate species at low temperature.

Adsorption of CO or NO separately gave no absorption at 2101 and 1755 cm^{-1}. These two bands appeared when NO and CO were adsorbed in stepwise and also when a mixture of NO and CO was introduced to rhodium catalyst. The behavior (appearance, disappearance, increase, and decrease) of these bands is always alike and they are associated together under various conditions. Consequently these two can be attributed to a single structure, namely a pair of CO and NO adsorbed to a Rh atom which is shown by



The band at 2101 cm^{-1} is ascribed to ν_{CO} of the above structure, which is significantly higher than that of linear species on Rh (2065 cm^{-}). This is in harmony with the fact that π^* orbital energy of NO is lower than that of CO (*14*), and thus the back donation of *d* electrons from Rh to CO decreases by adsorption of NO so that the ν_{CO} frequency increase (*12*, *15*, *16*). The band at 1755 cm^{-1} is ascribed to ν_{NO} of the above structure. Figure 4 shows that admission of CO to the NO preadsorbed surface produced the band at 1755 cm^{-1}, which grew at the expense of the band at 1910 cm^{-1} (M–NO^+). This indicates that some of NO^+ changed into NO^- by coadsorption of CO to Rh–NO which is of electron releasing property. This large shift suggests strongly a very localized interaction of CO for adsorbed NO species. In this connection, the spectra of transition metal complexes such as $\text{Rh(CO)(NO)(PPh}_3)_2$, $[\text{IrCl(NO)(CO)(PPh}_3)_2]^+$, $[\text{IrI(NO)(CO)(PPh}_3)_2]^+$ and $[\text{Os(NO)(CO)}_2(\text{PPh}_3)_2]^+$ show the bands of NO vibrational frequency respectively at 1670, 1680, 1720, and 1750 cm^{-1} (*11*).

The NO frequency might not be appreciably modified if the CO atom were adsorbed on a rhodium atom, which is next to the one adsorbed by NO. These facts indicate that the NO molecule is bonded to the same rhodium atom as CO. Moreover, similar structures have already been postulated for rhodium and other ligand species  $\mathrm{Rh}\begin{array}{l}/\,\mathrm{CO}\\ \backslash\,\mathrm{X}\end{array}$ (X: O, H, CH_2CH_2) by Yang and Garland (*12*), and for platinum and oxygen species  $\mathrm{Pt}\begin{array}{l}/\,\mathrm{CO}\\ \backslash\,\mathrm{O}\end{array}$ by Primet *et al.* (*15*).

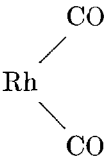
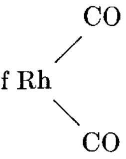
Addition of O_2 to rhodium catalyst which had been previously adsorbed by NO and CO (ν_{CO} 2101 cm^{-1}, ν_{NO} 1755 cm^{-1}) gave no change in spectrum below 100°C. Above 100°C, the bands at 2101 cm^{-1} and 1755 cm^{-1} disappeared and new band at 1910 cm^{-1} (ν_{NO^+}) appeared. In this connection,  $\mathrm{Rh}\begin{array}{l}/\,\mathrm{CO}\\ \backslash\,\mathrm{CO}\end{array}$ was also rather inactive when exposed to oxygen, and hence the reaction of oxygen molecule is suggested to be hindered because of steric and/or valency disadvantages.

Figure 5 shows the effects of adding 50 Torr NO to the rhodium catalyst that had been exposed to CO at 300°C and then evacuated for 5 min at 25°C. Although there is no change for the bands of  $\mathrm{Rh}\begin{array}{l}/\,\mathrm{CO}\\ \backslash\,\mathrm{CO}\end{array}$ species, the bands at 2065 and 1860 cm^{-1} disappeared completely at 25°C and the bands appeared at 1755 cm^{-1}. This is interpreted as follows. The linear CO and the bridged CO species, having an extra site for another molecule, can react with

NO to form $\mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{CO}}{\diagdown \mathrm{NO}}$, but twin CO per one rhodium leaves no site for NO molecule to chemisorb and thus remains unchanged.

In attempting to identify the adsorbed species responsible for the band at 2235 cm^{-1}, it is helpful to review the conditions under which this band appears. The species were found upon CO–NO mixture introduction to the catalyst above 200°C, but only when CO is largely in excess of NO. The species also appeared when CO was added to preadsorbed NO on rhodium catalyst at 300°C. The species was not desorbed by evacuation at 400°C but it disappeared by introducing 5 Torr of H_2O at 25°C.

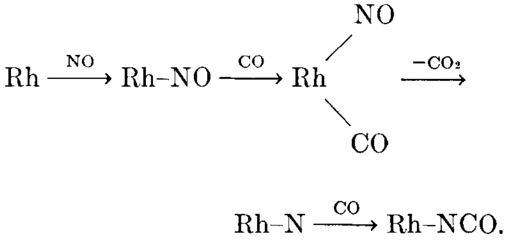
Unland (*5*) has observed isocyanate intermediates at 2260 cm^{-1} during the reaction of NO and CO over noble metal catalysts by the infrared method including labeling experiments, and London and Bell (*6, 7*) have proposed the mechanism of fission of N–O bond during the reaction of NO and CO over CuO/SiO_2 catalyst and postulated the formation of a copper nitride species (Cu–N) by infrared and kinetic studies. In view of these, the band at 2235 cm^{-1} is assigned to Rh–NCO.

It is noteworthy that when NO was added to CO preadsorbed catalyst, no Rh–NCO was found but N_2O adsorbed species appeared at 2225 cm^{-1}, which was identified as such by N_2O adsorption on rhodium catalyst. The formations of N_2O species support the idea that NO dissociates upon adsorption on rhodium atom having a CO ligand. It is supposed that the species ($\mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{NO}}{\diagdown \mathrm{CO}}$) are produced and that these decompose to give CO_2 and nitride (Rh–N), and that the latter can react with gaseous NO to produce the N_2O.

London and Bell (*6, 7*) have postulated the formation of a copper nitride species Cu–N, which was supposed to give N_2O by reaction with NO or to form Cu–NCO by reaction with CO. Accordingly the $\mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{NO}}{\diagdown \mathrm{CO}}$ species can be the precursor of NO dissociation. This conclusion is further supported by the observation that M–N_2O (*6*) and M–NCO formed at the expense of $\mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{NO}}{\diagdown \mathrm{CO}}$ species. The dissociation of the N–O bond should be preceded by a weakening of the bond through the transfer of an electron from carbon monoxide ligand, via rhodium atom, into the antibonding orbital of the N–O bond.

A reaction mechanism which is capable of explaining the formation of CO_2, NCO and N_2O can be shown by the following steps.

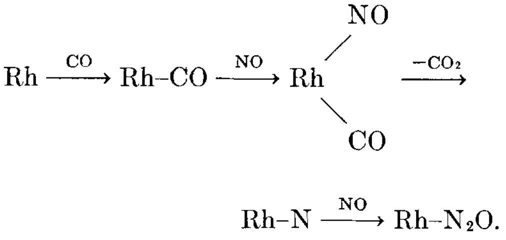
CO reaction with preadsorbed NO on catalyst:



$$\mathrm{Rh} \xrightarrow{\mathrm{NO}} \mathrm{Rh{-}NO} \xrightarrow{\mathrm{CO}} \mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{NO}}{\diagdown \mathrm{CO}} \xrightarrow{-\mathrm{CO_2}}$$

$$\mathrm{Rh{-}N} \xrightarrow{\mathrm{CO}} \mathrm{Rh{-}NCO}.$$

NO reaction with preadsorbed CO on catalyst:



$$\mathrm{Rh} \xrightarrow{\mathrm{CO}} \mathrm{Rh{-}CO} \xrightarrow{\mathrm{NO}} \mathrm{Rh}\genfrac{}{}{0pt}{}{\diagup \mathrm{NO}}{\diagdown \mathrm{CO}} \xrightarrow{-\mathrm{CO_2}}$$

$$\mathrm{Rh{-}N} \xrightarrow{\mathrm{NO}} \mathrm{Rh{-}N_2O}.$$

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